Earth abundant metals for circular economy: New avenues for renewables and polymer valorization

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Abstract

Earth abundant metals for circular economy: New avenues for renewables and polymer valorization

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The pervasiveness of nitrogen containing motifs in pharmaceuticals, agrochemicals and advanced materials highlights the constant demand for sustainable and practical synthetic methodologies for C-N bond formation reactions. This thesis delineates the development of innovative stategies for the selective synthesis of nitrogen containing compounds by replacing conventional, petroleum-derived feedstocks with more abundant and renewable resources. Leveraging the catalytic potential of earth-abundant base metals and *end-of-use* materials, different N-containing compounds including amines, amino alcohols, nitriles and amides have been synthesized aligning with circular economy approach. A homogenous cobalt-triphos catalytic system is developed for the synthesis of amines derivatives using hydrogenative amination of polyesters, including post-consumer plastics and used cooking oils. This methodology enables the direct conversion of waste-derived polyesters into a diverse array of functionalized amines with high selectivity, demonstrating the feasibility of transforming *end-of-use* materials into high-value chemicals. The selective formation of primary amines from carboxylic acids and esters using base metal catalysts is a prolonged adversity and the developed cobalt catalytic system is extended to carboxylic acids, esters, and vegetable oils to afford primary amines including industrially pertinent fatty amines with excellent primary amine selectivity. In addition, a green, copper-based heterogeneous catalytic protocol was established for the aerobic oxidative transformation of alcohols and ammonia into nitriles and primary amides. Utilizing air as the sole oxidant, this method achieves high conversions and excellent selectivities, underscoring its potential for scalable and environmentally benign synthesis. All works are accompanied by comprehensive mechanistic investigations and are expected to inspire future developments of base metal catalysis in C–N bond formation.

Häufig vorkommende Metalle für die Kreislaufwirtschaft: Neue Ansätze zur Aufwertung von erneuerbaren Rohstoffen und Polymeren

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Die Allgegenwärtigkeit stickstoffhaltiger Strukturen in Pharmazeutika, Agrochemikalien und Hochleistungsmaterialien unterstreicht den stetigen Bedarf an nachhaltigen und praxisnahen Synthesemethoden für C-N-Bindungsknüpfungsreaktionen. Diese Dissertation beschreibt die Entwicklung innovativer Strategien zur selektiven Synthese stickstoffhaltiger Verbindungen durch den Ersatz konventioneller, erdölbasierter Ausgangsstoffe durch einfacher zugängliche und erneuerbare Ressourcen. Durch die Nutzung des Potenzials von basismetallhaltigen Katalysatoren und *End-of-Use*-Materialien wurden verschiedene stickstoffhaltige Verbindungen, darunter Amine, Aminoalkohole, Nitrile und Amide, im Einklang mit dem Ansatz der Kreislaufwirtschaft synthetisiert. Ein homogenes Cobalt-Triphos-Katalysatorsystem wurde für die Synthese von Aminoderivaten mittels hydrierender Aminierung von Polyestern, einschließlich Post-Consumer-Kunststoffen und gebrauchten Speiseölen, entwickelt. Diese Methodik ermöglicht die direkte Umwandlung von abfallbasierten Polyestern in eine Vielzahl funktionalisierter Amine mit hoher Selektivität und demonstriert so die Machbarkeit der Transformation von *End-of-Use*-Materialien in wertgesteigerte Chemikalien. Die selektive Bildung von primären Aminen aus Carbonsäuren und Estern unter Verwendung von Basismetallkatalysatoren stellt eine langanhaltende Herausforderung dar. Das entwickelte Cobalt-Katalysatorsystem wurde daher auf Carbonsäuren, Ester und pflanzliche Öle ausgeweitet, um primäre Amine, einschließlich industriell relevanter Fettsäureamine, mit exzellenter Selektivität für primäre Amine zu erhalten. Darüber hinaus wurde ein grünes, kupferbasiertes heterogenes Katalyseprotokoll für die aerobe oxidative Umwandlung von Alkoholen und Ammoniak in Nitrile und primäre Amide etabliert. Unter Verwendung von Luft als einzigem Oxidationsmittel erzielt diese Methode hohe Umsätze und ausgezeichnete Selektivitäten, was ihr Potenzial für eine skalierbare und umweltfreundliche Synthese unterstreicht. Sämtliche Arbeiten werden durch umfassende mechanistische Untersuchungen begleitet und sollen zukünftige Entwicklungen der Basismetallkatalyse in der C–N-Bindungsbildung inspirieren.

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List of abbreviations

acac	Acetylacetonate
AI	Artificial intelligence
$Al(O\text{-}iPr)_3$	Aluminium isopropoxide
API	Active pharmaceutical ingredient
BET	Brunauer-Emmett-Teller
BDM	1,4-benzenedimethanol
CE	Circular economy
Co	Cobalt
CPME	Cyclopentyl methyl ether
Cu	Copper
DFT	Density-functional theory
EELS	Electron energy-loss spectroscopy
EDX	Energy-dispersive X-ray spectroscopy
EG	Ethylene glycol
equiv.	Equivalent
et al	Et alii
etc.	Et cetera
Fe	Iron
GHG	Green house gas
H_2	Hydrogen
h	Hour
HDO	Hydrodeoxygenation
HFIP	Hexafluoroisopropanol
HPLC	High performance liquid chromatography
IL	Ionic liquid
i-	*Iso*-
IPPD	N-isopropyl-N′-phenyl-1,4-phenylenediamine
L	Ligand
LCA	Life cycle analysis
Me	Methyl
MFCA	Material flow cost accounting
Mn	Manganese
mmol	Millimole
NHC	N-heterocyclic carbene
NMR	Nuclear magnetic resonance
O_2	Oxygen
OTf	Triflate, trifluoromethanesulfonate
P3HB	Poly(3-hydroxypropionic acid)
PBT	Polybutylene terephthalate

Pd	Palladium
PECHD	Polyethylene-1,4-cyclohexanedicarboxylate
PEN	Polyethylene naphthalate
PET	Polyethylene terephthalate
PHB	Polyhydroxybutyrate
PLA	Polylactic acid
Pt	Platinum
R	(organic) rest
Rh	Rhodium
rt.	Room temperature
Ru	Ruthenium
THF	Tetrahydrofuran
TON	Turn over number
TPA	Terephthalic acid
UCO	Used cooking oil
V	Vanadium
VCO	Volatile organic compounds
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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1. Introduction

1.1 Circular economy paradigm in chemical synthesis

Serving as the basis of significant scientific endeavors, chemical synthesis exerts an enormous impact on human life and has become an indispensable part in numerous translational applications including pharmaceuticals, material science and technology fields. With the inclusion of diverse innovative strategies and enhanced selectivity as well as efficiency, modern chemical synthesis has progressed considerably beyond traditional stepwise approaches. However, the rising costs of chemicals, driven by substantial resource depletion and environmental hazards arising from chemical waste have been constantly raising sustainability concerns.[1] With continues execution of high-CO_2-emitting processes, such as ammonia, methanol and other primary chemical syntheses, the chemical industry accounts for significant amount of CO_2 emissions among the whole industrial sector.[2] Global market share for industrial chemicals is valued over $6.3 billion in 2025 and these products and allied compounds are now pervasive not only in the waste streams but also in the environment.[3]

To foster a sustainable future, chemical synthesis must align with the principles of circular economy (CE), “an economy that is restorative and regenerative by design”.[4-6] CE emphasizes waste elimination, product recycling (to their at most value) and resource conservation along with economic viability. Being an efficient alternative to the traditional linear (take-make-dispose) model CE not only promotes renewables and waste as feedstock but also effectively contributes to the CO_2 neutrality mission.[7-10] While CE and decarbonization have been central to numerous climate summits and interdisciplinary research studies, integrating this into product design at atomic and molecular levels is highly crucial.[11-15] To implement CE principles effectively, multiple approaches such as mass balance,[16] life cycle analysis (LCA),[17-19] material flow cost accounting (MFCA)[20] etc. are being executed in the chemical sector. Additionally, the realm of artificial intelligence (AI), machine learning (ML), and automation have made monitoring CE protocols more effective and hence substantial escalation in the research domain focusing on CE principles has been seen in the past decade.

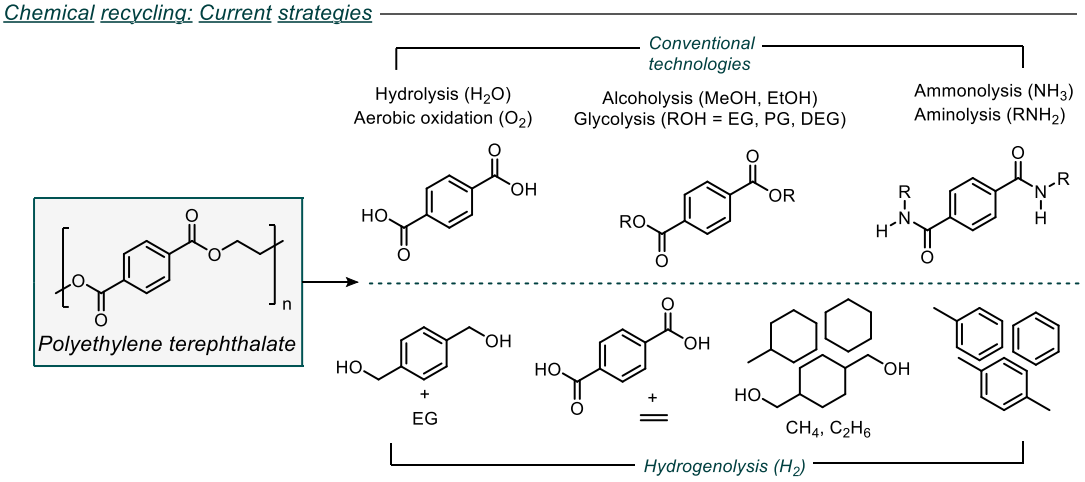
Catalysis, a pivotal discipline in chemical synthesis, facilitates the efficient and selective construction of molecules, thereby contributing to enhanced sustainability.[21-26] By lowering activation energy and facilitating reactant molecules to surmount the kinetic impediment, catalysis not only enhances the reaction rate but also curtails waste formation (caused by stoichiometric reactants) and elevates yield and purity of the desired molecules.[27] The field of catalysis has undergone significant advancements in recent years, particularly in the realm of active pharmaceutical ingredient (API) manufacturing. These advancements, including groundbreaking transformations such as asymmetric synthesis and cross-coupling reactions, have had a substantial impact on the pharmaceutical industry. As a result of these developments, catalytic transformations have become an effective method for synthesizing several essential drugs.[28-30] Currently, more than 85% of commercialized chemical manufacturing processes rely on at least one catalytic conversion pathway and integration of machine learning techniques and computational quantum mechanics has led to significant advancement in catalyst design field.[31-32] Although catalysis is very much in line with CE principles, it often relies on the use of expensive and rare noble metals. Implementation of earth abundant metals for chemical transformations contribute

significantly to CE and reduces the environmental impact associated with mining and extraction. Being less expensive than noble counterparts, the use of earth-abundant metals is also more economically viable and accessible for a broader range of industries.

1.2 **Plastics - challenges and opportunities**

Since the very first commercialization of synthetic plastic in 1907, their convenience has entrenched them severely into human routines, thereby fostering an escalation in global plastic production. From a global share of 376 million metric tons in 2020 it is expected that global plastic production might increase to overwhelming 500 million metric tons by the year 2050.[33-34] Unfortunately, the pace of waste management significantly lags behind these projections, with a mere 9% of plastic waste being successfully recycled. Of the total plastic production of 8.3 billion metric tons, approximately 12% is incinerated, while the remaining accumulates in designated landfills or is discarded in uncontrolled aquatic and terrestrial environments. The total annual lifecycle emissions from plastic account for 4.5% of global greenhouse gas (GHG) emissions. Overcoming the inherent challenges posed by plastic pollution through the implementation of a circular economy approach is of paramount importance.[35-37]

Favorably, a prominent shift of research focus towards polymer recycling has been seen recently and currently, four distinct plastics recycling technologies exist: primary (close loop), secondary, tertiary, and quaternary recycling.[38] Primary recycling involves the automated or manual sorting of wastes to separate uncontaminated plastics and employing them as new products.[39-40] Secondary recycling focuses on mechanical recycling and quaternary recycling involves incineration of plastic waste.[41-43] Tertiary recycling, also known as chemical recycling, offers recovery of value-added products, by breaking down plastics into monomers or converting them into high-value products which can be further used for chemical processes.[43,44-46] Among various recycling technologies established, chemical recycling allows depolymerization without compromising polymer functionality and has been broadly studied by researchers recently.



Scheme 1: Current strategies for PET chemical recycling

Chemical recycling demonstrates clear advantages over existing recycling technologies by simultaneously addressing two major challenges: minimizing the negative environmental effects of

plastic wastes and opening new avenues for the access of valuable chemicals.[47-53] As an example, polyethylene terephthalate (PET), a widely used polyester derived from petroleum, represents approximately 12% of the total global plastic waste.[54] Its chemically inert nature contributes to slow natural degradation, resulting in significant environmental challenges.[55-59] Common chemical recycling methods for PET include, glycolysis, alcoholysis, hydrolysis, aminolysis, hydrogenolysis and aerobic oxidation.[60-64] Furthermore, research focusing on PET depolymerization using biocatalysis are expanding and also have been commercialized recently(**Scheme 1**).[65-66]

1.3 **Renewables as chemical resources**

The enhanced dependence on depleted fossil oil reserves and their reckless consumption for chemical synthesis has led to gradual exhaustion of these resources along with severe environmental harm. Global warming and climate change caused via unchecked extraction of these feedstocks have driven researchers to explore and develop new approaches to sustainable chemical synthesis.[67] Usage of renewable resources such as biomass which is continuously generated by photosynthesis (170 billion metric tons per year) unlike fossil fuels, which require millions of years to form, can be a viable alternative for petroleum based resources.[68] The major classes of renewable resource are carbohydrates (75% of total contribution), lignin, terpenes and vegetable oil (plant oil).[68] Among renewable feedstocks, vegetable oils are considered as one of the most significant raw materials for the chemical industry and >200 million metric tons of vegetable oils are produced every year.[69-70] They have a plethora of applications for the production of surfactants, cosmetic products, lubricants, flooring materials and for resin.[71] Moreover, several organic transformation using vegetable oils as chemical feedstock have been reported.[72] Vegetable oils are triglycerides with long chain fatty acids, with varying composition with respect to the plant, crop, and the growing conditions.[73] The significant parameters affecting the chemical properties of these oils include length of the carbon chain, stereochemistry of the double bonds of the fatty acid chains and their degree of unsaturation. Most of the oils vary from C8 to C24 in carbon chain length with C16 and C18 being common. Vegetable oils such as coconut typically have shorter chains of C12 and C14 as well. Among industrial uses of oleochemicals, breaking of triglycerides via hydrolysis or transfer esterification is commonly the first step. So formed fatty acids or esters along with glycerol are used widely with derivatization.[74] For example, while fatty acids (or methyl esters) are broadly applied in lubricants, surfactants and polymers, glycerol is used in cosmetics, pharmaceuticals, sweeteners, and wetting agents.[75,76]

1.4 **Biogenic waste for chemical synthesis**

The utilization of bio-waste feedstocks in the synthesis of value-added chemicals can be regarded as a "double green" approach, as it addresses both resource and waste concerns concurrently.[73] Thus, turning biogenic waste into energy and high-value chemicals, has been extensively encouraged towards implementing a successful circular bioeconomy and so far, numerous high-value chemicals have been synthesized. Common biomass waste includes agricultural waste, food processing waste, municipal solid waste, used cooking oil (UCO) and sewage sludge.[77] Used cooking oil belongs to the family of municipal wastes that pose high end environmental problems. UCO is generated in large quantities from households, restaurants, and the food industry. Its valorization as a chemical feedstock offers both

sustainability and waste management benefits. The total annual production of UCO exceeds 190 million metric tons and are used as major raw materials in many industrial processes. [79-81]

Used cooking oil consists mainly of long-chain triglycerides and free fatty acids, with a composition similar to fresh vegetable oil but often containing impurities and breakdown products from the cooking process. They can also undergo reactions such as oxidation, hydrolysis as well as polymerization and loose its nutrition value. In chemical synthesis, UCO can be used as feedstock for synthesizing several value-added compounds. Their specific composition can also be exploited as sources of chemicals to produce fuels, bio-plasticizers, surfactants, absorbents for volatile organic compounds (VOCs) etc.[82-83] Recently, UCO were chemically modified (e.g., through epoxidation and ring-opening reactions) to produce polyols, which are then used to make rigid polyurethane foams.[84]

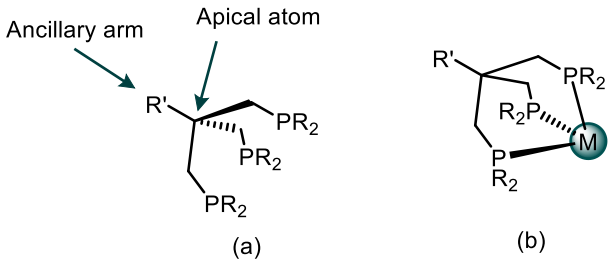
As mentioned in the above sections, the development of sustainable methods to convert waste and renewable feedstocks into value-added chemicals is of paramount importance. This thesis focuses on the synthesis of nitrogen containing chemicals, a class of compounds with widespread relevance, from circular feedstocks such as carboxylic acids, esters, alcohols, polymer waste, and vegetable (used) oils.

2. Development of hydrogenation reactions

Distinguished by its cost-effectiveness and environmental benignity hydrogenation represents one of the most fundamental transformations in organic chemistry.[85] The inertness of hydrogen (H_2) molecule under ambient conditions necessitates the use of a catalyst for its activation and numerous heterogeneous as well as homogeneous catalysts have been developed for the hydrogenation reactions. In homogeneous hydrogenation catalysis, transition metal complexes are predominantly employed as catalysts and upon activation of H_2, these complexes generate metal hydride species, which subsequently deliver hydrogen atoms to the substrate.[86] The beginning of the hydrogenation field can be traced back to 1897, when the French chemist Paul Sabatier (Nobel laureate, 1912), in collaboration with Jean-Baptiste Senderens, elucidated that finely divided nickel could serve as a catalyst for the hydrogenation of unsaturated organic molecules.[87] A seminal advancement in homogeneous hydrogenation catalysis was marked by the discovery of the Wilkinson's catalyst (chlorido-tris(triphenylphosphine)-rhodium), named after Geoffrey Wilkinson, who, alongside Ernst Otto Fischer, was awarded the Nobel Prize in Chemistry in the year 1973.[88] Although homogeneous hydrogenation catalysts had previously been reported, Wilkinson's catalyst was the first to achieve reaction rates which are comparable to heterogeneous catalyst systems. An improvement of Wilkinson's catalyst was developed in the following years by Schröck and Osborn.[89] Further progress in the field was characterized by the pursuit of enantio- and diastereoselective hydrogenation, leading to the development of the Monsanto process for the industrial synthesis of L-DOPA, a pharmaceutical agent for Parkinson's disease.[90] Subsequent breakthroughs include the advent of Crabtree's catalyst - an iridium-based complex that significantly broadened the applicability of homogeneous hydrogenation to include sterically hindered and functionally diverse alkenes and pioneering contributions of Noyori, whose ruthenium-based complexes enabled highly enantioselective hydrogenation of a wide array of functional groups.[91-92]

2.1 **Development of cobalt-triphos system for hydrogenation reactions**

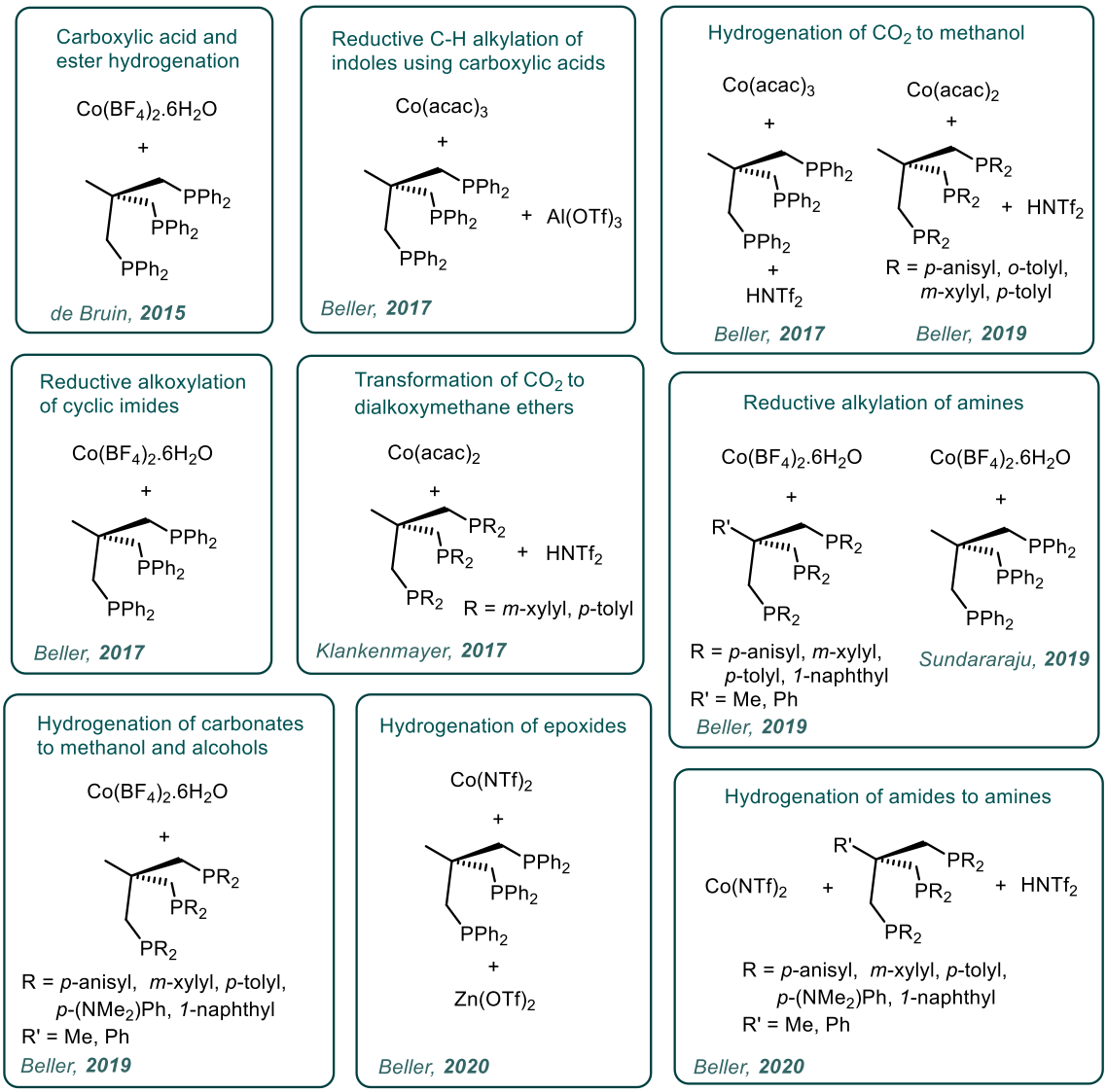
Cobalt, derived from the German word Kobold (“goblin”), falls into the category of electron-rich base metal among the transition elements and was first isolated by Swedish chemist Georg Brandt in 1735.[93] Functioning as an indispensable trace element within the human physiology, cobalt’s principal biological significance derives from its integral role as the central atom in cobalamin (vitamin B12), a molecule of paramount importance for the ontogenesis and regeneration of erythrocytes. Furthermore, owing to its prevalent occurrence as a secondary product in the metallurgical extraction of copper and nickel, cobalt is characterized by both its relative economic accessibility and its substantial abundance in global mineral reserves (20-30 ppm).[94-95]



Scheme 2: a) General structure b) fac coordination mode to metal center**.**

The significance of cobalt in catalysis dates back to the first half of the twentieth century, when Otto Roelen discovered the “oxo synthesis” (hydroformylation reaction) and introduced $HCo(CO)_4$ as a catalyst for this transformation in 1938. Moreover, at the same time, cobalt emerged as a principal catalyst in the Fischer–Tropsch process for the synthesis of hydrocarbons from syngas (mixture of H_2 and carbon monoxide), which remains reliant on this metal to this day.[93]

Within the domain of homogeneous transition metal catalysis, substrate activation generally takes place within the coordination sphere of a transition metal complex. Such complexes feature a central metal atom or ion surrounded by various organic or inorganic ligands. These ligands not only stabilize and solubilize the metal center but also modulate its steric and electronic properties, thereby allowing for precise tuning of the catalyst's reactivity.[96] Ligands can also play active roles in catalysis, such as serving as proton or electron shuttles, or acting as labile placeholders that dissociate to allow substrate binding. As metal centers and ligands can be endlessly varied, homogeneous catalysts offer highly diverse and tunable structures and numerous ligand classes have been so far reported.[97] Among the various phosphine ligands reported, triphosphine based ligands remain attractive for coordination chemistry as well as applications in catalysis. Tridentate ligands can often provide greater thermal and kinetic stability than more kinetically labile mono- and di-phosphine ligands due to enhanced chelation effect and provide well-defined coordination modes to transition metal centres.[93] In the year 1962, W. Hewertson and H. R. Watson synthesized tripodal triphos ligand comprising scaffold $R'C(CH_2PR_2)_3$, and since then they are amongst the most studied facially coordinating triphosphine ligands.[98] This facially capping ligand framework consists of an apical atom where three arms of the coordinating phosphine originate,



Scheme 3: Development of cobalt triphos system for hydrogenation reactions

and a fourth auxiliary arm that does not generally coordinate (**Scheme 2**). For instance, tripodal triphos ligand 1,1,1-tris(diphenylphosphinomethyl)ethane has an apical carbon atom with three diphenylphosphino coordinating groups plus an ancillary methyl group. Characteristic fac coordination of triphos to a transition metal center offers considerable flexibility and enhances the stability of the metal complex. Remarkably, facile tuning of the chemical reactivity of these ligands can be achieved via further functionalization of the aryl groups (electron-donating, electron-withdrawing groups etc.) present providing more possibilities in catalyst development.[99]

Earlier work in the field of cobalt triphos system was reported by groups of Mealli and Sacconi including the synthesis of cobalt triphos complexes as well as their structural characterization.[100-101] In the year 2015, the group of Bas de Bruin reported cobalt triphos catalyst system for the hydrogenation of carboxylic acids and esters for the formation of alcohols.[102] The combination of $Co(BF_4)_2 \cdot 6H_2O$ and triphos ligand at 100° C in the presence of 80 bar H_2 was able to reduce a range of esters and carboxylic acids with turnover numbers of up to 8000. The cobalt system outperformed previously reported

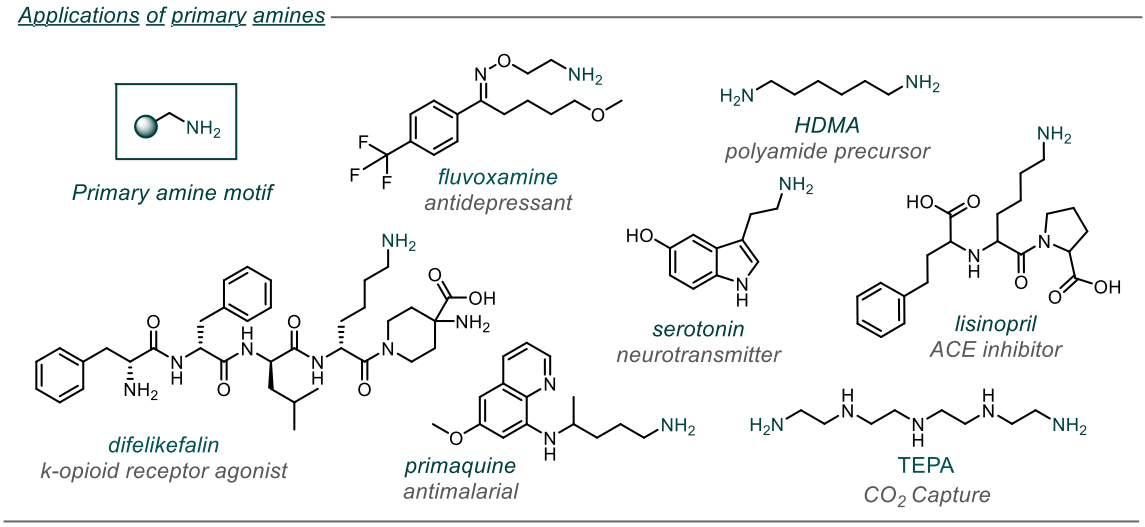
ruthenium and iridium-based system which required harsh reaction conditions and higher noble metal loading. In addition, the combination of other multidentate ligands such as tetraphos was inactive for the reactions confirming the crucial role of triphos ligand in the hydrogenation reaction. After the seminal work of Bas de Bruin and co-workers, many groups including Beller, Klankenmayer, and Sundararaju have studied cobalt triphos complexes for diverse hydrogenation reactions (**Scheme 3**).[103-112] The presence of acidic co-catalysts can work synergistically with transition metal complexes to promote hydrogen activation, substrate binding, or facilitate key steps such as hydride transfer or protonation.[113] Among various reactions reported using cobalt triphos system, presence of co-catalysts such as triflimide ($HNTf_2$), aluminium triflate ($Al(OTf)_3$), zinc triflate ($Zn(OTf)_2$) etc were used. $HNTf_2$ has been widely studied as acidic catalyst for numerous organic transformations which is mainly attributed to its advantages such as good solubility in organic solvents, noncoordinating property (conjugate base (Tf_2N-)) and low nucleophilicity.[114]

2.2 **Amines as valuable building blocks**

The pervasiveness of amine derivatives in pharmaceuticals, agrochemicals, biological probes, and natural products has encouraged researchers to their broad synthesis.[115-120] Nucleophilic characteristics of this functional group which confers high reactivity make them highly beneficial in numerous transformations. Ammonia is the simplest of all amines with central nitrogen atom bonded to three chemically equivalent hydrogen atoms. As mentioned above ammonia synthesis falls under the category of large-scale chemical production and has been widely employed in the preparation of fertilizers, amine derivatives, polymers, rocket fuels (hydrazine), inorganic acids, and ammonium salts.[121] Based on the number of carbon-containing groups attached to the nitrogen atom amines are classified as primary, secondary, or tertiary amines and differ notably in their chemical as well as physical properties. The unique ability of amines to engage in hydrogen bonding, solubility modulation and participation in key biochemical interactions has made amines an important part in modern therapeutics.[122-126] Owing to wide applications of amine derivatives in various domains, sustainable approaches to amine synthesis remain a key focus since many years among researchers.

2.3 **Primary amines**

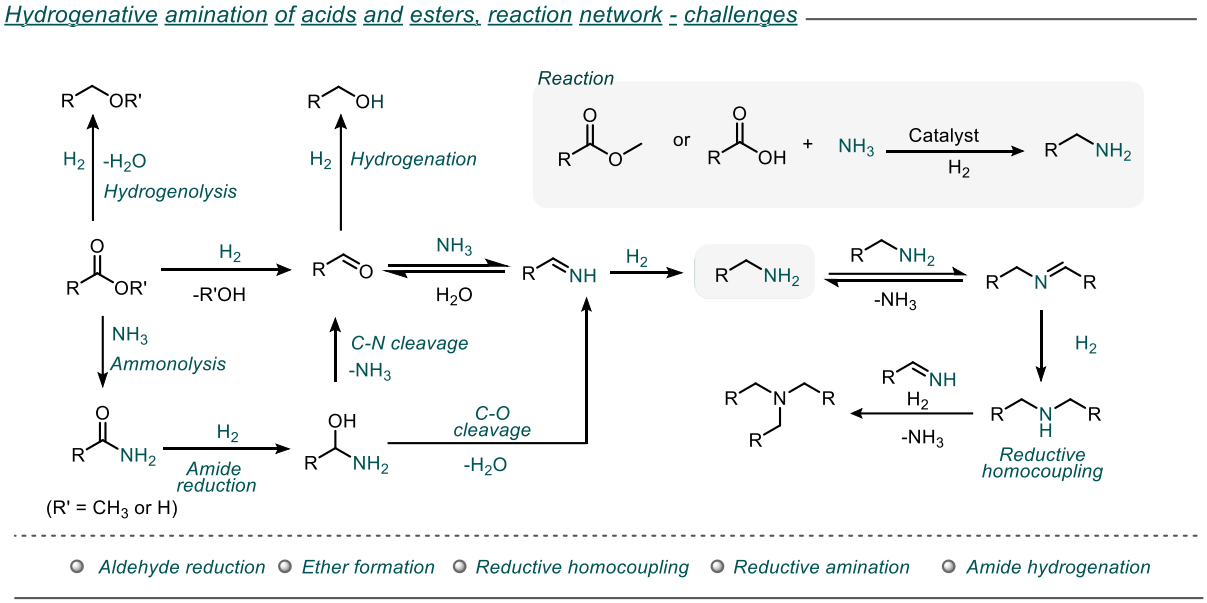
Primary amines are derivatives of ammonia in which one hydrogen atom is replaced by an aryl or alkyl group. They are significant class of chemicals with a multitude of applications in diverse sectors. Primary amines are ubiquitous in a wide range of bioactive compounds, agrochemicals and materials (**Scheme 4**).[127-130] Remarkably, they are also among the most versatile intermediates in the atom-economical synthesis of secondary and tertiary amines, as well as heterocycles. Apart from traditional stoichiometric methods such as Gabriel synthesis and Curtius rearrangement various catalytic protocols to synthesize primary amines such as hydroamination, reductive amination, alcohol amination, allylic amination, C-H amination, amination of halides, nitro and nitrile reduction etc. have been developed.[131]



Scheme 4: Selected examples of applications of primary amines

2.4 State of the art – Primary amines from carboxylic acid and ester derivatives

The formation of carbon–nitrogen bonds in the chemical industry is primarily achieved by catalytic reductive amination.[122] This synthetic methodology uses aldehydes or ketones as starting materials and has been widely used for synthesis of primary amines including pharmaceutical moieties. Nevertheless, obstacles such as sensitivity, high reactivity, and limited availability of some aldehydes restrict their utility in chemical synthesis. Being cost-effective, structurally diverse and shelf stable, carboxylic acids and esters represent an ideal genesis for numerous synthetic transformations among diverse oxygenous feedstock chemicals.[132]

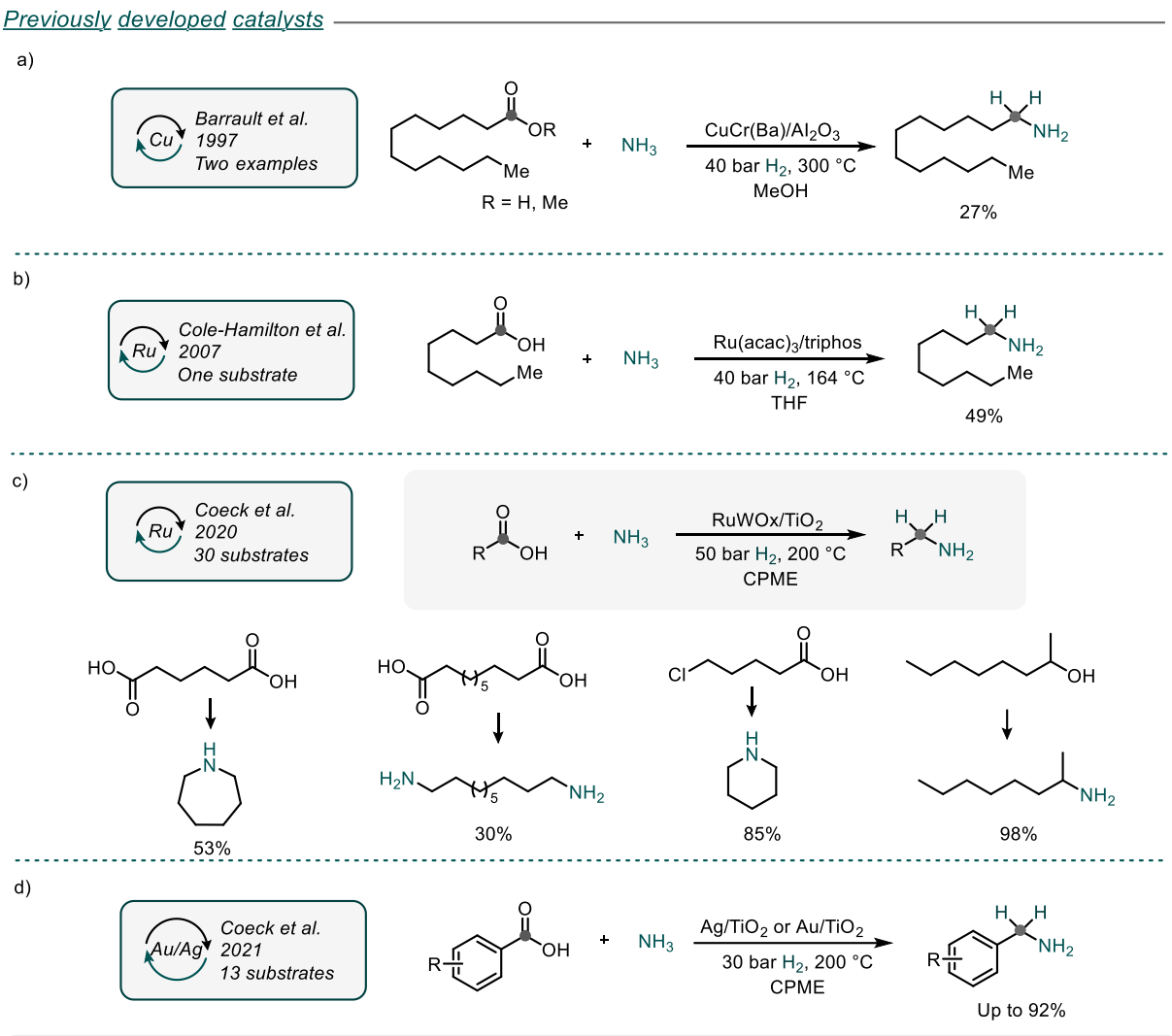


Scheme 5: Hydrogenative amination of acids and esters - reaction network and challenges

The carbon atom in carboxylic acids and esters is surrounded by three groups (C-R, C−O and C=O), making it sp^2 hybridized and trigonal planar.[132d] The presence of electronic lone pair in the oxygen atom, result in the formation of a resonant form between neutral and zwitterionic configurations. Structural peculiarities (H-bonding (in acids), steric effects (esters) and leaving group ability) and resonance

stabilisation makes the carbonyl group in carboxylic acids and esters often thermodynamically and kinetically less reactive, and poses certain synthetic challenges compared other carbonyl derivatives such as aldehydes and ketones. The control of chemoselectivity while using carboxylic acids or esters in reductive aminations is significantly challenging due to the formation of several intermediates and the side reactions resulting from the reactivity of so formed intermediates (**Scheme 5**).[133]

The partial reduction of esters or carboxylic acids to aldehydes is challenging, as the generated aldehydes are more prone to reduction than the original substrate. In addition, possible etherification and amide formation reactions complicate the selectivity. Furthermore, reductive homocouplings, which lead to the formation of secondary or tertiary amines is an added obstacle in the reaction network.[134]



Scheme 6: Catalysts developed for primary amine synthesis from acids and esters

In 1994, Barrault *et al*. reported a $CuCrO_2$-based heterogeneous catalyst for the reductive amination of carboxylic acids and esters (**Scheme 6**a).[183] Reactions performed using methyl dodecanoate in the presence of ammonia and hydrogen gave 27% of primary amines along with mixtures of corresponding amines. Methylation of primary amines was observed in some cases and relatively severe reaction conditions (300 °C) were required.

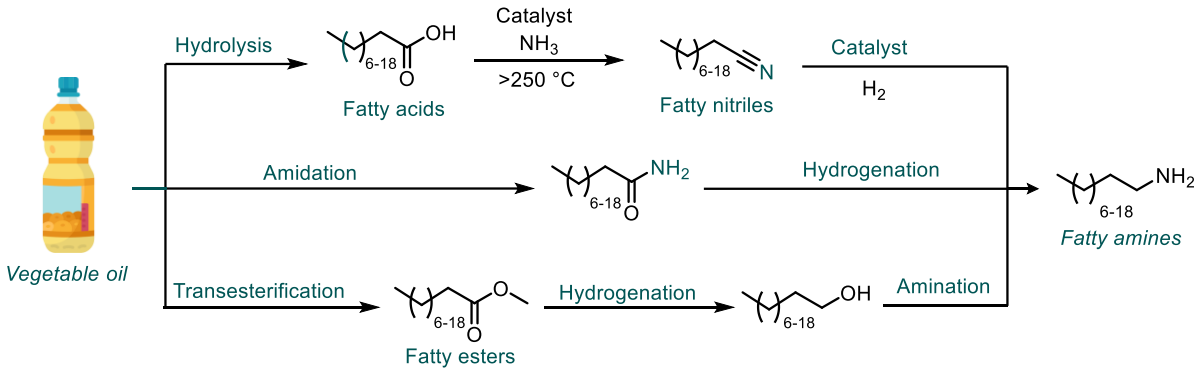
The first and only homogeneous catalyst developed for the conversion of carboxylic acids to primary amines until today was disclosed by Cole-Hamilton and co-workers (**Scheme 6**b).[184] The work primarily focused on the hydrogenation of amides for the production of amines using ruthenium-1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) catalyst system. In this study, an example of carboxylic acid, nonanoic acid was also employed in the presence of ammonia. Initial testing of liquid ammonia gave a mixture of primary amine (15%), secondary amine (47%), alcohol (3%) and secondary amide (35%). However, excess of aqueous ammonia gave 41% of the desired primary amine. This seminal work established the groundwork for future development of metal-catalyzed reductive amination reactions.

A heterogeneous catalytic system for the one-pot reductive amination of carboxylic acids to amines in the presence of hydrogen and ammonia was reported by Coeck et al. in 2020 (**Scheme 6**c).[185] The ruthenium–tungsten bimetallic catalyzed reaction using cyclopentyl methyl ether (CPME) as solvent gave primary amines in yields up to 96% along with secondary amines as side products. The reaction proceeded via dehydration of the ammonium carboxylate to the corresponding amide, and it was observed that proper tuning of catalyst support resulted in high selectivity of primary amines. Among different aliphatic and aromatic substrate tested, higher reaction temperature (200 °C) lead to the hydrogenation of aromatic rings. In case of dicarboxylic acids, cyclic molecules were formed as the major product. For example, reaction of adipic acid produced mixture of azepane and caprolactam. However, longer dicarboxylic acids, such as sebacic acid gave 30% of linear product, 1,10-diaminodecane. While aliphatic C–Cl bonds were liable to nucleophilic substitution with NH_3, aromatic halogen bonds were degraded upon hydrogenation of the aromatic ring. Moreover, the catalyst was also tested for alcohol amination reactions. The same group reported another heterogeneous catalytic system for reductive amination of benzylamines in the presence of Ag/TiO_2 or Au/TiO_2 catalysts with a noble metal loading of 0.025 mol% Au (**Scheme 6**d).[186] Unlike the above mentioned report, the Ag/Au based catalyst tolerated functional groups such as methoxy, N,N-dimethyl, trifluoromethyl groups etc and no hydrogenation of aromatic rings was observed. Mechanistic analysis by periodic DFT calculations indicated that the synergistic action of the multisite reaction environment at the metal-support interface plays a crucial role in the heterolytic cleavage of hydrogen and selective polarization and reduction of the CN moiety.

2.5 **Primary fatty amines**

Among primary amines, primary fatty amines (aliphatic amines with more than six carbons per alkyl chain) are highly significant class of chemicals due to their wide applications in numerous sectors.[139-145] The well-established and general fatty amine synthesis also called “nitrile process” is a multistep approach: the first step is the conversion of triglycerides to fatty acids through hydrolysis. Subsequently, fatty nitriles are produced through the reaction of fatty acids with ammonia in the presence of metal oxide catalysts such as alumina or zinc oxide to obtain the corresponding nitriles, which are further reduced to the desired amines. This hydrogenation is typically conducted in the presence of a nickel catalyst (**Scheme 7**).[146-149] Additionally fatty amine synthesis via amidation followed by amide hydrogenation and alcohol amination pathways are explored these days (**Scheme 7**).[150] The hydrolysis step in the "nitrile route" is highly energy-intensive, requiring high temperatures, pressures, and excess

ammonia, while water removal is needed to drive the reaction and contribute to a high carbon footprint.[146]. Hydrogenation of fatty nitriles (using nickel catalysts) often leads to side reactions and



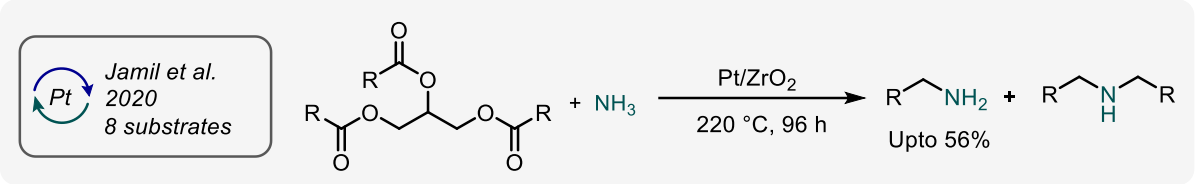
Scheme 7: Conventional primary fatty amine synthesis

byproducts, resulting in low fatty amine yields and complex purification. Each step also demands additional purification and catalyst recovery, increasing environmental and economic costs. Streamlining this multistep process into a selective one-pot synthesis using waste feedstocks could effectively reduce these challenges.

2.6 **State of the art - Primary amine from triglycerides**

First report of hydrogenative amination of triglycerides were shown in a patent application by Henkel, using ZnO-Al_2O_3.[151] The seminal work showed excellent selectivity towards amines however significantly harder reaction conditions (250 bar H_2 and 310 °C) were required. In the year 2016 a homogeneous catalytic method for the direct synthesis of N-alkylated amines from triglycerides under hydrogen was reported by our group using the [$Ru(acac)_3$]/triphos/$HNTf_2$ catalytic system (acac – acetylacetonate).[152] Recently Mizugaki and co-workers presented a general direct reductive amination of triglycerides to fatty amines using a titanium oxide-supported platinum–molybdenum (Pt–Mo/TiO_2) catalyst. However, in this work employing ammonia for reductive amination yielded 74% of secondary amine instead of primary fatty amine.[153] The first catalytic system for the synthesis of primary amines from triglycerides with good primary amine selectivity was reported by Shimizu et al. (**Scheme 8**).[154] The platinum based heterogenous catalyst (Pt/ZrO_2) transformed triglycerides into the corresponding amines, amides, and nitriles under various reaction conditions. In case of transformation of triglyceride to primary fatty amines, up to 56% of primary fatty amine was obtained along with secondary amines via reductive homocoupling. A series of triglycerides with different chain lengths (C4–C18) were converted into the corresponding primary and secondary fatty amines. The formation of primary fatty amides observed during reaction suggested the possibility of an amidation-hydrogenation reaction pathway. Nevertheless, the long reaction time (96 hours) as well as high temperature (220 °C) restrains the broad applicability of this protocol.

Reductive amination of triglycerides



Scheme 8: Pt/ZrO_2 catalyzed primary fatty amine synthesis for triglycerides

Thus, the development of a highly selective catalyst for one-pot transformations of carboxylic acid derivatives and vegetable oils towards primary amines continues to be of high interest and recently our group developed a cobalt triphos catalytic system for the synthesis of amines from mentioned resources. Details of this work will be discussed in section 5.

3. Hydrogenolysis of polyesters

Hydrogenative catalysis is a sustainable approach towards organic synthesis as it implies less waste generation (less stoichiometric waste as compared to conventional reductants), high atom-economy and most importantly molecular hydrogen can be produced from renewable sources.[155-156] Compared to conventional approaches, hydrogenolysis of polymers is an efficient depolymerization approach for polymer degradation, and this methodology allows upcycling of polymers into value-added chemicals which have substantially higher chemical value than monomers.[157-158] For this reason, several heterogeneous as well as homogeneous catalyzed hydrogenative depolymerizations have been reported.

3.1 Homogeneous catalysts for hydrogenolysis of polyesters

The most established and widely adopted method for classifying catalysts is based on the physical state (phase) of the catalyst in relation to the reactants.[159] Homogeneous and heterogeneous catalytic systems represent the most extensively explored technologies in chemical synthesis. In homogeneous catalysis, both the catalyst and the substrate(s) coexist within the same phase, typically as liquid solutions. In contrast, heterogeneous catalysis involves the catalyst and substrate(s) residing in different phases - most commonly, a solid catalyst interacting with liquid or gaseous reactants - where the catalytic process occurs at the surface of the catalyst.

In the year 2013, Milstein reported the first example of homogeneous catalytic hydrogenation of polyesters in a patent which made influential contributions to the hydrogenation field.[160] In the next year this Milstein's Ru(II) PNN complexes were tested for hydrogenative depolymerization of polyesters into diols by Robertson and co-workers (**Scheme 9**a).[161] Polyesters were efficiently depolymerized to the corresponding diols with up to 80% yield in the presence of hydrogen at 120 °C for 48 hours. Diverse polymers including PET, polylactic acid (PLA), polyhydroxybutyrate (PHB), poly(3-hydroxypropionic acid) (P3HP) and PET based water bottle were tested for the reaction. Among two ruthenium catalyst tested. RuPNNbipy (**Scheme 9**a (i)) showed higher activity in depolymerization reactions and the high activity of this catalyst is attributed to its less sterically bulky dipyridyl backbone compared to the diethylaminomethyl arm on the second catalyst (**Scheme 9**a (ii)).

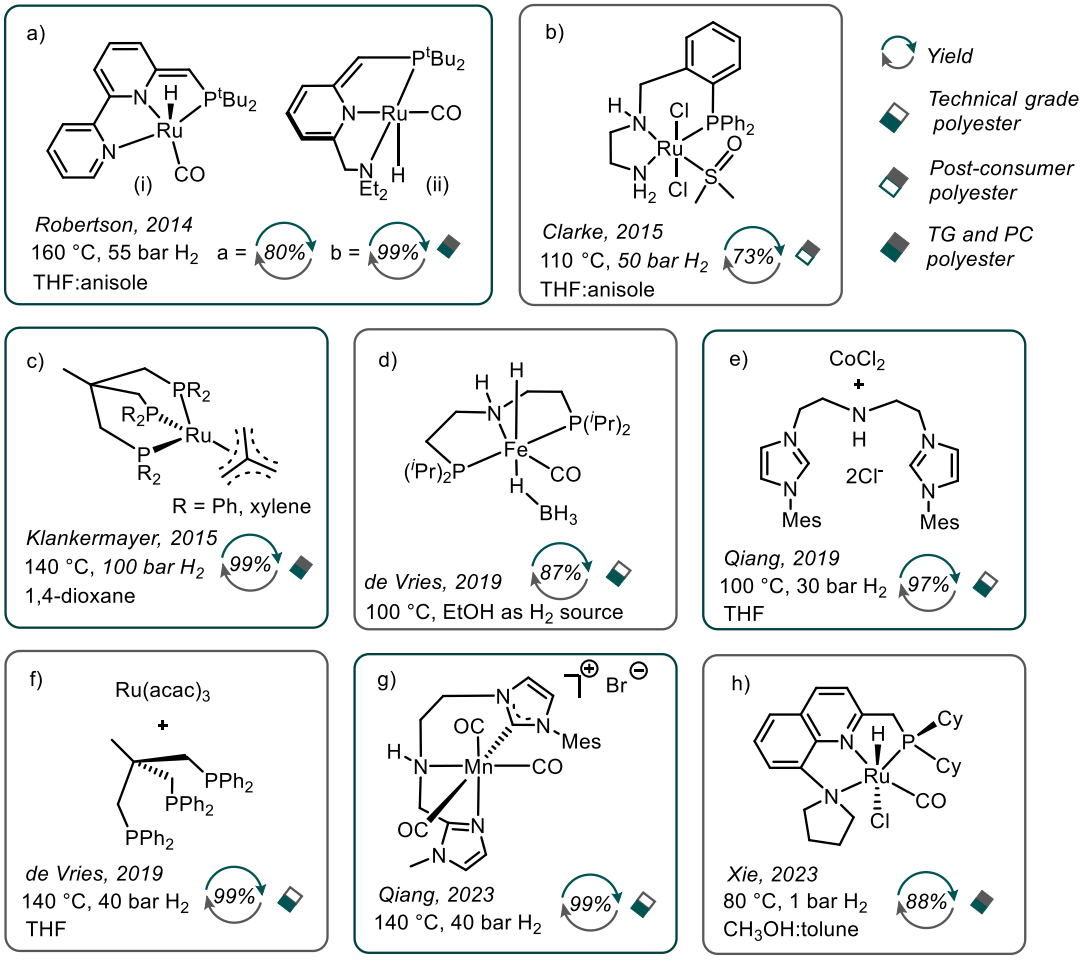
After these seminal reports by Robertson, hydrogenative depolymerization of PET was demonstrated by Clarke using a range of tridentate aminophosphine ruthenium complexes (**Scheme 9**b).[162] Two model diesters were used for the catalyst development and seven ruthenium based precatalysts were tested. Technical-grade (TC) PET was depolymerized with up to 73% conversion and 53% of 1,4-benzenedimethanol (BDM) was obtained. The reaction was performed in the presence of 50 bar hydrogen at 110 °C in a solvent mixture of anisole-toluene with a lower catalyst loading (1 mol%) compared to the previous work. Interestingly, all reaction were performed using real samples of waste PET.

In 2018, Klankermayer reported hydrogenative depolymerization of a wide range of polyesters to diols using the [Ru(triphos)tmm)] and [Ru(triphos-xyl)tmm)] catalysts (**Scheme 9**c).[163] Depolymerization reactions performed in the presence of $HNTf_2$ as co-catalyst at 140 °C in 1,4-dioxane solvent gave corresponding diols upto 99% selectivity with full conversion. During the initial screening it was observed that the hydrogenative depolymerization of PET was more challenging when the [Ru(Triphos)tmm)] was used as the catalyst and only 64% of selectivity was observed towards corresponding diols. Possible etherification in the presence of acid-activated catalyst led to less diol selectivity and further reactions were performed in the presence of modified [Ru(triphos-xyl)tmm)] system. PET flakes from several post-consumer (PC) PET-based products including water bottle, dyed soda bottle, synthetic pillow filling, sports jersey and yoghurt pots were tested for reaction and excellent yields of BDM were obtained.

The first base metal catalyst for depolymerization of polyesters was developed by de Vries and co-workers in 2019 (**Scheme 9**d).[164] The polyester Dynacol 7360 (a polymer made from adipic acid and 1,6-hexanediol) was tested for the depolymerization reaction and 1,6-hexanediol was obtained in 87 % isolated yield in the presence of the Fe-MACHO-BH catalyst. Unlike the previous reports the system used a transfer hydrogenative protocol (using EtOH as solvent and hydrogen source) instead of employing molecular hydrogen for hydrogenolysis.

In the same year the group of Liu developed phosphine free cobalt-based catalytic system for the hydrogenation of unactivated esters (**Scheme 9**e).[165] The developed *in-situ* formed cobalt-NHC catalytic system was successfully employed for the depolymerization of polycaprolactone (PCL) and 97% corresponding diol was obtained in the presence of 30 bar hydrogen at 100 °C. The same group reported NHC-based NNC-pincer manganese catalyst for wide range of hydrogenation reactions.[166] The hydrogenolysis ability of the developed Mn system was tested for polyesters such as PET and PCL and corresponding diols were obtained in very good yield (**Scheme 9**g). Non-noble metal-based catalysts developed for hydrogenolysis have not been studied for a larger variety of polyesters (only up to 2 examples) and to the best of our knowledge post-consumer products have not yet been tested.

An alternative strategy for polyester recycling via a tandem hydrogenation etherification pathway was reported by de Vries and co-workers (**Scheme 9**f).[167] The ruthenium-triphos system and a Lewis acid as cocatalyst were selected as the catalyst and several linear aliphatic polyesters were successfully converted to polyols which could be further employed for the synthesis of polyurethanes.



Scheme 9: Homogeneous catalyst systems for polyester hydrogenolysis

Recently, Xie and coworkers reported a very mild protocol for polyester depolymerization in the presence of a quinaldine-based ruthenium complex (**Scheme 9**h).[168] Initial transesterification of the polyester into oligomeric fragments in the presence of methanol facilitated the hydrogenolysis at 80 °C in the presence of 1 bar hydrogen. Preliminary mechanistic studies conducted, suggested that quinaldine-based catalysts are likely hydrogenated for the generation of the active species. The catalyst system was studied for a wide range of technical-grade and post-consumer polyesters including water, beverage, mouthwash, handwash bottles and soundproof boards and upto 89% of corresponding diols were obtained.

3.2 **Heterogeneous catalysts for hydrogenolysis of polyesters**

The development of heterogeneous catalyst systems for the hydrogenolysis of polyesters started many years later compared to homogeneous systems. Heterogeneous catalysts offer several advantages over homogeneous system including easy separation, thermal, air and moisture stability, recyclability etc.[169] A heterogenous catalyst also comprises of support which serves as a carrier or medium for the active catalytic species, facilitating their delivery to the reaction environment and enhancing several parameters including dispersion of metal particles, catalyst longevity, recovery and overall efficiency in

chemical transformations.[170-173] During the development of optimal hydrogenolysis catalyst, certain challenges such as hydrogen adsorption, C-O bond saturation, and hydrogen spillover have to be addressed. The majority of hydrogenolysis reported for polyesters using heterogeneous catalyst, focus mainly on depolymerization of PET based polymers. Moreover, while most of the homogeneous catalyst systems afforded the corresponding diols, heterogeneous systems yielded variety of depolymerisation products including terephthalic acid (TPA), aromatics (p-xylene, m-xylene, ethylbenzene, benzene), ethylene, cyclohexanes (gasoline and jet fuel range), 1,4-cyclohexanedimethanol (CHDM) etc.[158]

In the year 2020, Yan and co-workers reported a Ru/Nb_2O_5 catalyst for the hydrogenolysis of PET towards arenes using water as reaction medium (**Scheme 10**a).[174] The catalyst enabled the precise cleavage of interunit C-O and C-C linkages of aromatic polymers and corresponding monocyclic arenes were obtained in up to 85% yield. Among various catalysts tested (Pd/Nb_2O_5, Pt/Nb_2O_5, Ru/TiO_2, Ru/ZrO_2 and Ru/HZSM-5) Ru on Nb_2O_5 provided the best results. Ultra-small particle sizes present on the ruthenium catalyst, prevented the hydrogenation of aromatic rings and enhanced the activity. Additionally, C-O bond activation as well as a Bronsted acid sites for C-C bond cleavage offered by NbOx species made this support optimal for the reaction. Several measurements including adsorption-desorption DRIFTS experiments, X-ray absorption near edge structure spectroscopy, DFT calculations, etc. were conducted in detail to investigate the catalyst characteristics.

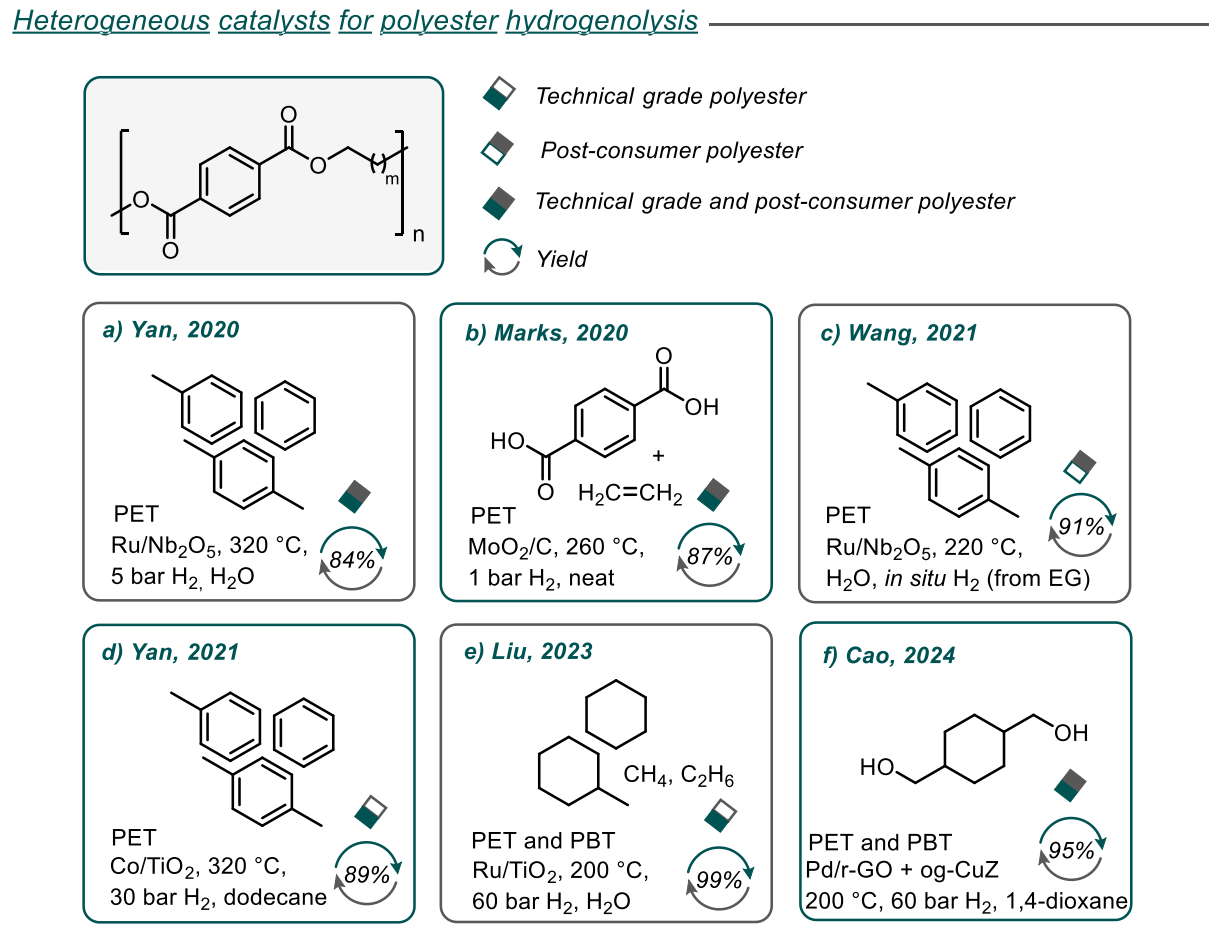
In the same year, the Marks group developed a carbon-supported single-site molybdenum-dioxo (C/MoO_2) catalyst for the selective depolymerization of PET to TPA and ethylene under neat conditions (**Scheme 10**b).[175] The reaction was performed under 1 bar of hydrogen at 260 °C and several control experiments suggested the formation of a vinyl benzoate intermediate during hydrogenolysis. Performing the reaction under argon atmosphere resulted in a lower yield of TPA and small quantities of ethylene suggesting a two-step reaction pathway, a β-scission pathway as well as hydrogenolysis of the intermediate vinyl benzoate for the formation of desired acid and ethylene products.

In 2021, Wang and colleagues successfully converted PET based plastics into arenes using *in-situ* formed hydrogen from ethylene glycol (EG) (**Scheme 10**c).[176] The authors reported direct conversion of PET from sources such as polyester clothes, Coca-Cola bottles and polyester film using Ru-based Nb_2O_5 catalyst at 220 °C. Reforming experiments for ethylene glycol generated hydrogen as well as CO_2 and *in-situ* generated hydrogen was chosen for hydrogenolysis. Mechanistic experiments suggested that the interaction between ruthenium and Nb_xO offered a high concentration of $Ru^{\delta+}$ species which enhanced the hydrogenolysis capability of the developed system and prevented an undesired decarboxylation reaction during hydrogenolysis.

In the same year, Yan and his group successfully converted PET into aromatics using a Co/TiO_2 catalyst in the presence of 30 bar hydrogen at 340 °C using octane as the solvent (**Scheme 10**d).[177] The main reaction pathway for the conversion of PET to aromatics included hydrogenation as well as hydrodeoxygenation (HDO) reaction. Decarboxylation or decarbonylation reaction towards toluene were also observed as side reactions during the process. Catalyst characterization revealed that the Co/TiO_2 catalyst exhibited a low Brunauer-Emmett-Teller (BET) surface area, with cobalt particles situated

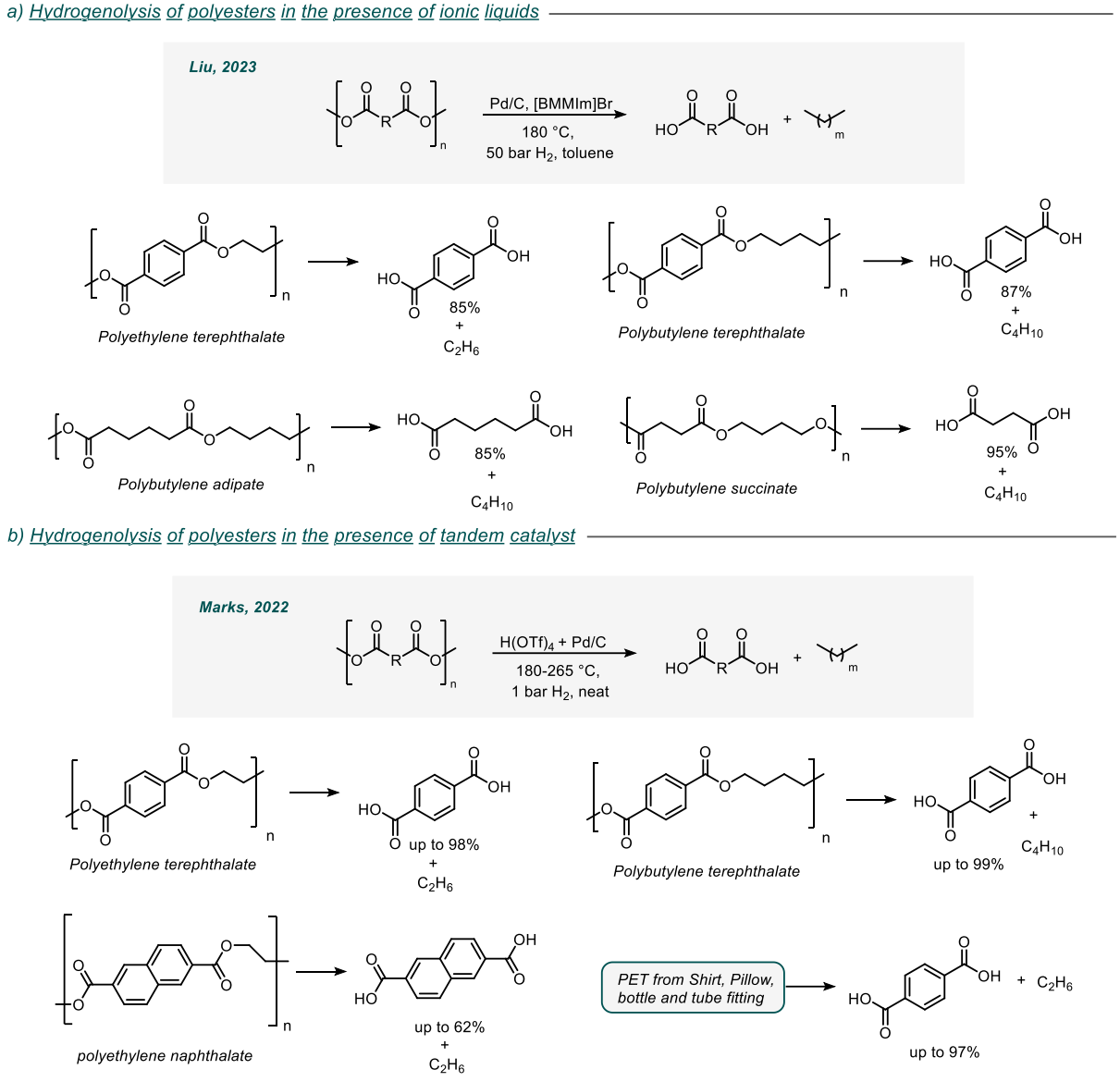
outside the pores. The catalyst also works as a bifunctional system with both metal and acid sites, which can catalyze hydrodeoxygenation (HDO) reactions.

In a separate study, Liu and his group utilized a Ru/TiO_2 heterogeneous catalyst for the hydrogenolysis of PET and polybutylene terephthalate (PBT) into alkanes at 200 °C and 60 bar hydrogen (**Scheme 10**e).[178] Under optimized conditions, PET was converted into alkanes specifically cyclohexane and methane while PBT yielded cyclohexane, methane, and ethane under the same reaction parameters. Model reactions using ethylene glycol dibenzoate demonstrated that the strong interaction between ruthenium nanoparticles and the TiO_2 support facilitates electron transfer from TiO_2 to ruthenium which allows the developed Ru/TiO_2 catalyst to perform polymer hydrolysis as well as hydrogenation simultaneously.



Scheme 10: Heterogeneous catalyst systems for polyester hydrogenolysis

Recently, trans-isomer-enriched 1,4-cyclohexanedimethanol (CHDM), was synthesized from PET leveraging a dual-catalyst system consisting of palladium on reduced graphene oxide (Pd/r-GO) and oxalate-gel-derived copper-zinc oxide (og-CuZn) (**Scheme 10**f).[179] The hydrogenation/hydrogenolysis relay catalysis developed in the study converted PET into polyethylene-1,4-cyclohexanedicarboxylate (PECHD), which is then converted into CHDM with an overall yield of 95 % in a two-stage process. This method transformed post-consumer products including dyed beverage bottles, a polyester strapping band, and PET fabrics to cyclohexanedimethanol in good yield.



Scheme 11: Tandem catalyst for polyester hydrogenolysis

A general strategy for recycling polyesters including aromatic and aliphatic polyesters, copolyesters, and polyester mixtures into carboxylic acids and hydrocarbons via C_{alkoxy}–O bond breakage using ionic liquids (ILs) was developed by the Liu group (**Scheme 11**a).[180] DFT calculations found that the hydrogen-bonding interaction between the ionic liquid and the ester group in the polyester enhances the nucleophilicity of the halide anion and activates the C–O bond. Among various ionic liquids tested, [BMMIm]Br showed the best results when combined with hydrogenation catalyst Pd/C, and various polyesters were converted into the corresponding carboxylic acids and alkanes.

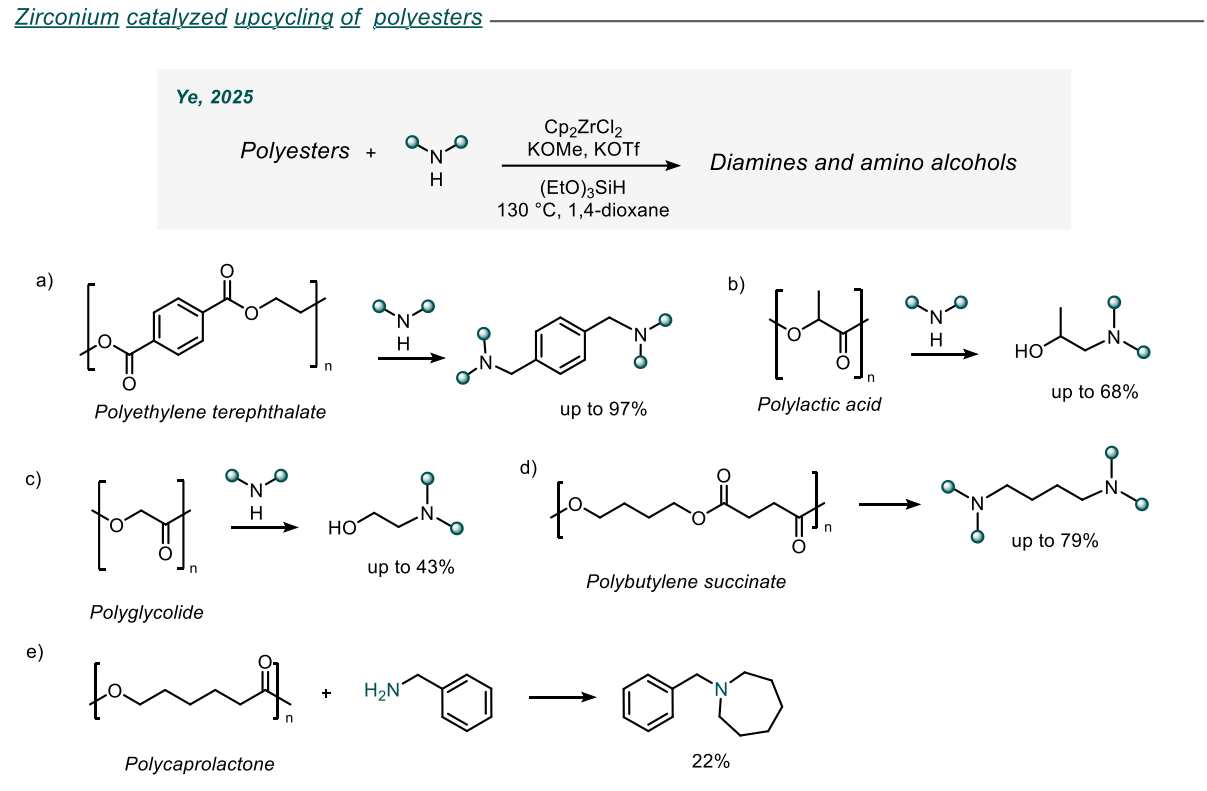
Similarly, the Marks group developed a tandem catalyst which is a combination of an electrophilic homogeneous catalyst $Hf(OTf)_4$ and a heterogeneous hydrogenation catalyst (Pd/C) for the depolymerisation of polyesters towards dicarboxylic acid (TPA) and ethane under 1 bar hydrogen pressure (**Scheme 11**b).[181] The reaction was perfomed using polyesters including PET, PBT, polyethylene naphthalate (PEN) and post-consumer PET products such as water bottles, shirts, and pillow stuffing at 265 °C in the presence of DMSO:mesitylene as solvent mixture. Reaction optimization

as well as mechanistic studies were performed using the PET model substrate, ethylene glycol bis(dimethylterephthalate). Combined experimental and DFT mechanistic analysis indicated that the reaction pathway involves the C=O bond cleavage of the alkoxy group assisted by $Hf(OTf)_4$ forming carboxylic acid and alkene, followed by alkene hydrogenation to obtain the final products.

3.3 **Hydrogenative amination of polyesters**

Among different amine compounds, diamines are significant precursors for the preparation of various pharmaceuticals, polymers, agrochemicals, ligands, ionic liquids, and other organic materials.[182-183] Synthesis of diamines via depolymerization of polyesters is a sustainable upcycling approach towards waste minimization.

The first report of conversion of PET waste to valuable diamine monomer *para*-xylylenediamine, was described in a patent application in the year 1988.[184] The process of poly(ethylene terephthalate) to diamine monomers was achieved via a three-step process involving (a) ammonolysis of the PET to produce terephthalamide and ethylene glycol (b) pyrolytic dehydration of the terephthalamide to produce terephthalonitrile (c) hydrogenation of the terephthalonitrile to produce the *para*-xylylenediamine. The multistep process gave an excellent yield of the desired *para*-xylylenediamine, however, harsh reaction conditions as well as separate purification processes in each step constrains the applicability of the process.



Scheme 12: Zirconium catalyzed upcycling of polyesters

Very recently, Ye and coworkers introduced a $(EtO)_3SiH$-mediated, Zr-catalyzed reductive amination for the conversion of polyester waste into amines, amino alcohols, and pyrroles (**Scheme 12**).[185] The process described the valorization of polyesters such as PET, PBS, PCL, and PLA as well as some biomass derived molecules. Mechanistic experiments performed using dimethyl terephthalate showed that, Zr catalysis proceeds through the aminolysis of esters, facilitated by the Lewis acidity of the zirconocene species, followed by Zr−H mediated amide reduction. The described protocol is an effective work compared to previous patent however, a more sustainable approach such as replacing silane using molecular hydrogen is highly essential for sustainability enhancements. Our group developed a cobalt based homogeneous catalyst for the valorization of polyesters towards valuable amines and aminoalcohols using molecular hydrogen and ammonia which will be discussed in detail in the coming sections.

3.4. **Synthesis of N-containing compounds from alcohol and ammonia in the presence of air**

The utilization of air as an oxidizing agent in chemical reactions offers a multitude of advantages from economical, industrial, and sustainability aspects.[186-188] Due to its ubiquity, enhanced safety, and cost efficiency (relative to molecular oxygen), air serves as an oxidant of choice for diverse oxidation processes including large-scale applications. The use of air for chemical reactions overcomes the necessity of expensive infrastructure required for the generation as well as storage of molecular oxygen, thereby yielding substantial reductions in both capital expenditures and ongoing operational costs. Furthermore, the intrinsic dilution of oxygen within air (comprising approximately 21% by volume) also mitigates the risk of forming explosive gas mixtures, a significant hazard associated with the use of concentrated oxygen. The synthesis of nitriles and amides from alcohols using base metal catalyst in the presence of ammonia, and air as an oxidant is a sustainable and green approach. Nitriles as well as amides represent valuable fine and bulk chemicals and serve as central intermediate in organic synthesis, drug discovery and materials science. Our group has developed Cu-oxide nanoparticles for the preparation of nitriles and amides from alcohols in the presence of ammonia via an aerobic oxidation process and this work will be discussed in detail in section 5.3.

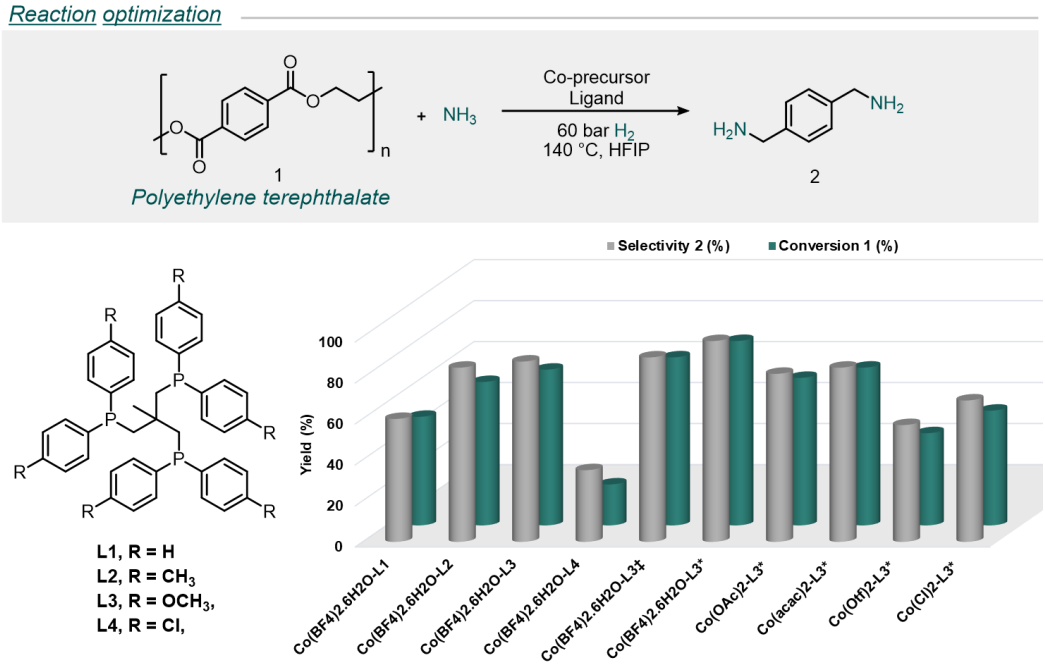
4. Objectives of this work

The development of new methodologies for the preparation of C-N bond formation reactions is of significant importance due to their crucial role in various domains, including pharmaceuticals, life sciences, agrochemicals, and polymers. First and foremost, the replacement of petrochemical feedstocks with more abundant renewable or waste materials has the potential to address sustainability concerns to a greater extent. The primary objective of the present work is the utilization of more abundant feedstocks for chemical transformations, with the aim of enhancing circularity and sustainability within the domain of chemical synthesis. The initial segment of the research focuses on the synthesis of amines and amino alcohols from polyesters and used cooking oil, employing a homogeneous cobalt-based catalyst. A variety of technical-grade and post-consumer products were successfully converted to amines and amino alcohols, exhibiting high selectivity. The second part of the text is primarily concerned with the selective preparation of primary amines from carboxylic acids and esters using ammonia and molecular hydrogen in the presence of a cobalt catalyst. Moreover, the work encompasses the efficient conversion of seven distinct commercial vegetable oils to fatty amines, exhibiting high primary amine selectivity despite the homocoupling potential of fatty amines under reductive conditions. The final work presented herein explores the development of a copper-oxide nanoparticle catalyst for the synthesis of nitriles and primary amides. This catalyst is utilized in the presence of alcohols, ammonia, and air as the oxidant. The work is characterized by meticulous optimization studies, extensive substrate scope, and mechanistic investigations. The objective of the present work is to motivate chemists to adopt more eco-friendly approaches to chemical synthesis and contribute more to circularity as well as sustainability.

5. Summary of Published Articles

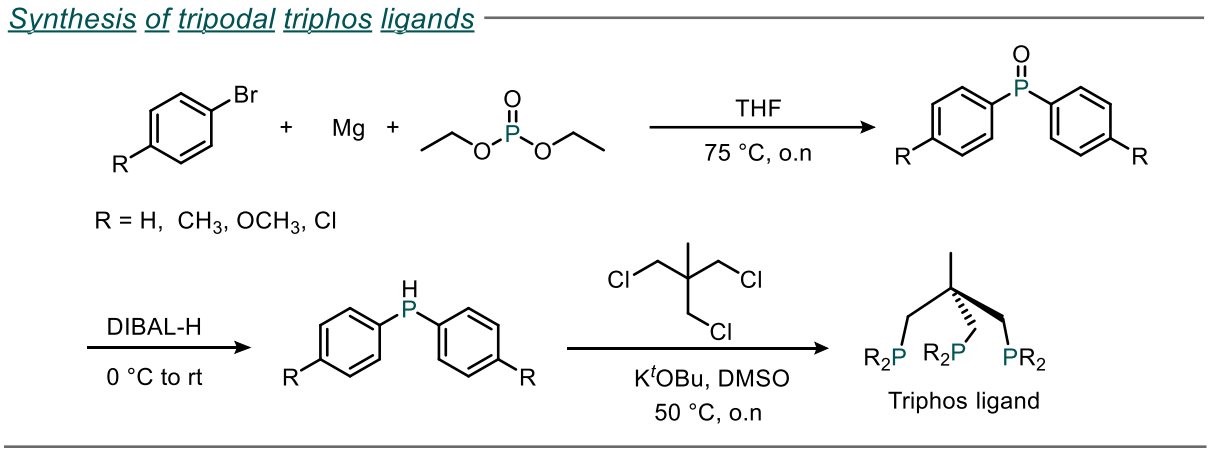
5.1. A catalytic approach to the valorization of polyesters and biogenic waste for the production of amines

Excessive consumption of synthetic polymers due to their widespread utility in daily life has lead to severe environmental concerns. Development of novel recycling technologies to minimize waste accumutions from plastics are always of high interest.[189] Among the various recycling strategies, chemical recycling, specifically polymer upcycling approach enables the efficient conversion of waste materials into valuable feedstock chemicals. Hydrogenolysis - a process that uses hydrogen to cleave chemical bonds has been widely studied as an efficient sustainable approach for depolymerization reactions.[190] Notably, several transformations including mild reaction conditions were achieved in the past years. However, these reactions have primarily focused on noble metal catalysts.[191] Among various class of polymers, polyesters hold a significant position and account for synthesis of wide range of consumer products. As an application of circularity principles in polymer recycling recently we developed a cobalt based catalyst for the synthesis of amines from polyesters. As mentioned in the introductory part of this thesis amines are significant class of compounds with plethora of applications in diverse fields including life science, materials and pharmaceuticals. Upcycling of polyesters to form structurally diverse amines will minimizes waste accumulation problems along with using polymers as efficient chemical feedstocks. The developed system was also studied for the transformation of used cooking oil (UCO) to synthesise primary fatty amines from ammonia and molecular hydrogen. UCO belongs to important class of municipal wastes and contribute significantly in waste accumulation concerns. Analysis of key components in UCO was performed prior to the reaction and studies were performed without further purification of UCO obtained after cooking.



Scheme 13: Reaction optimization. ‡isolated complex. *Reaction in the presence of Al(O-*i*Pr)$_3$

To develop an optimal catalyst for the depolymerization reactions, initial optimization reactions were performed by using PET as the model compound in the presence of gaseous ammonia and hydrogen (**Scheme 13**). Initial screening conducted using cobalt tetrafluoroborate and triphos (1,1,1-tris(diphenylphosphinomethyl)ethane; tripodal-triphos; **L1**) ligand gave 60% conversion of PET with 53% selectivity towards *para*-xylenediamine and ethylene glycol. The reaction was performed at 140 °C in the presence of 5 bar ammonia and 60 bar hydrogen for 24 hours. Inspired by the critical role of triphos ligands in ester hydrogenations as well as reductive amination reactions, we synthesized three electronically different triphos ligands (**L2**–**L4**) (**Scheme 14**).[192] Next, the *in-situ* generated cobalt-phosphine complexes from newly synthesized ligands were tested for the depolymerization reaction, and triphos ligands consisting electron-donating groups (methyl, methoxy, **L2** and **L3**) displayed high activity and selectivity for the formation of the *para*-xylenediamine with high conversion. In contrast, the chloro-substituted ligand **L4** showed lower conversion and lower selectivity. Testing the isolated Co-(**L3**)$_2$ (**C1**) complex for the model reaction, increased the yield of *para*-xylenediamine up to 82%. Furthermore, several acidic and basic co-catalysts were tested and in the presence of aluminium isopropoxide (Al(O-*i*Pr)$_3$) 90% of *para*-xylylenediamine was obtained.



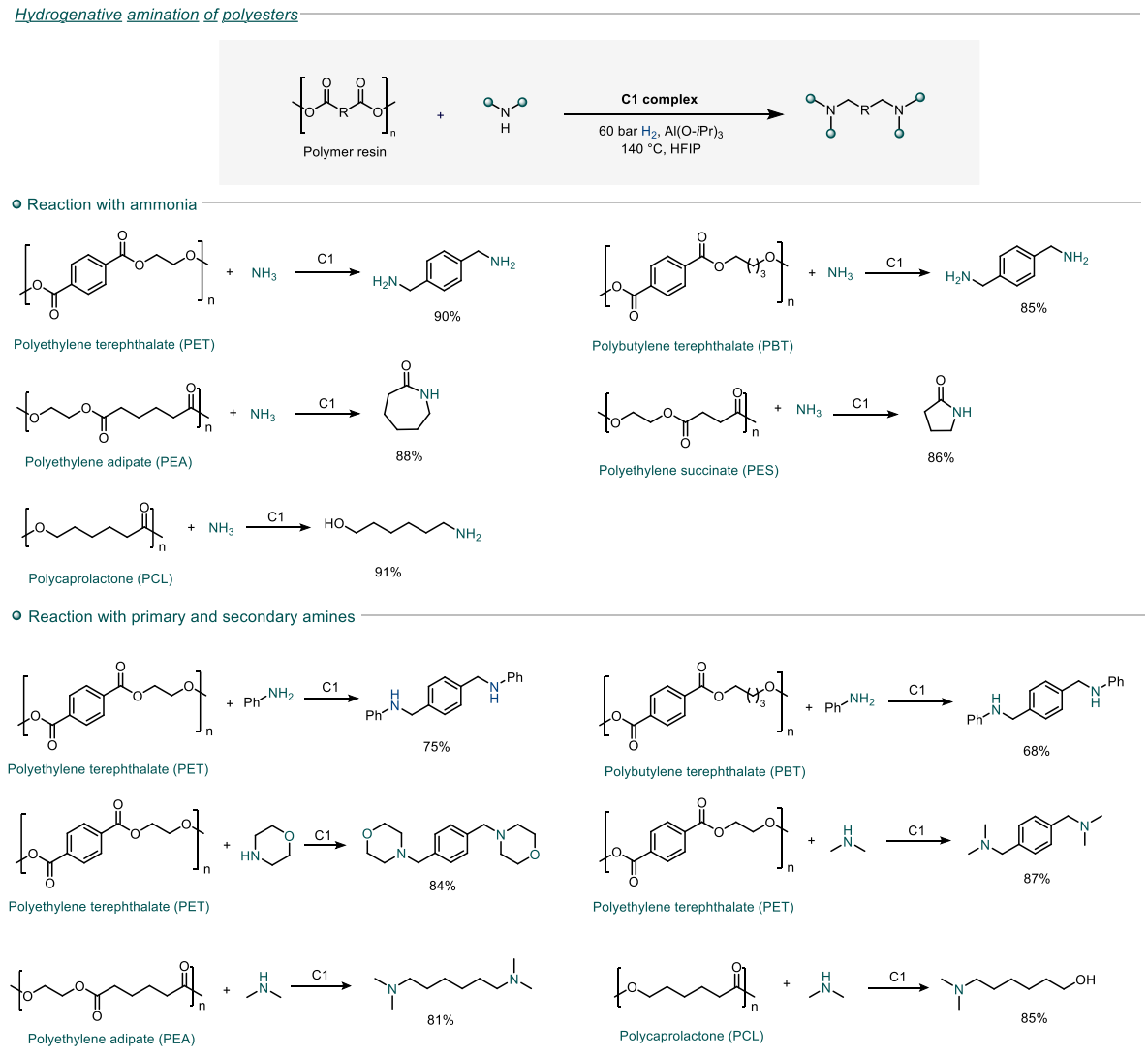
Scheme 14: General procedure for triphos ligand synthesis

Other cobalt (II) metal precursors tested for the reactions showed no improvement in the catalysis. Testing of different solvents confirmed that fluorinated solvents specifically hexafluoroisopropanol (HFIP) worked best for the selective formation of *para*-xylylenediamine. HFIP has several unique properties and dissolves PET at very mild temperature.[193] The hydrogen bond donating ability of HFIP is known for enhancing chemical reactivity.[194] We also assume the substrate activation via enhanced acidity due to the presence of two trifluoro methyl groups makes HFIP suitable for the depolymerization.[195] The lower boiling point (58.2 °C) makes this solvent easy for distillation and the used HFIP was conveniently recycled and reused for several cycles.[196]

After optimization of the depolymerization of PET, amination of other polyesters was performed under the standard conditions using various amine sources (**Scheme 15**). With respect to secondary or tertiary

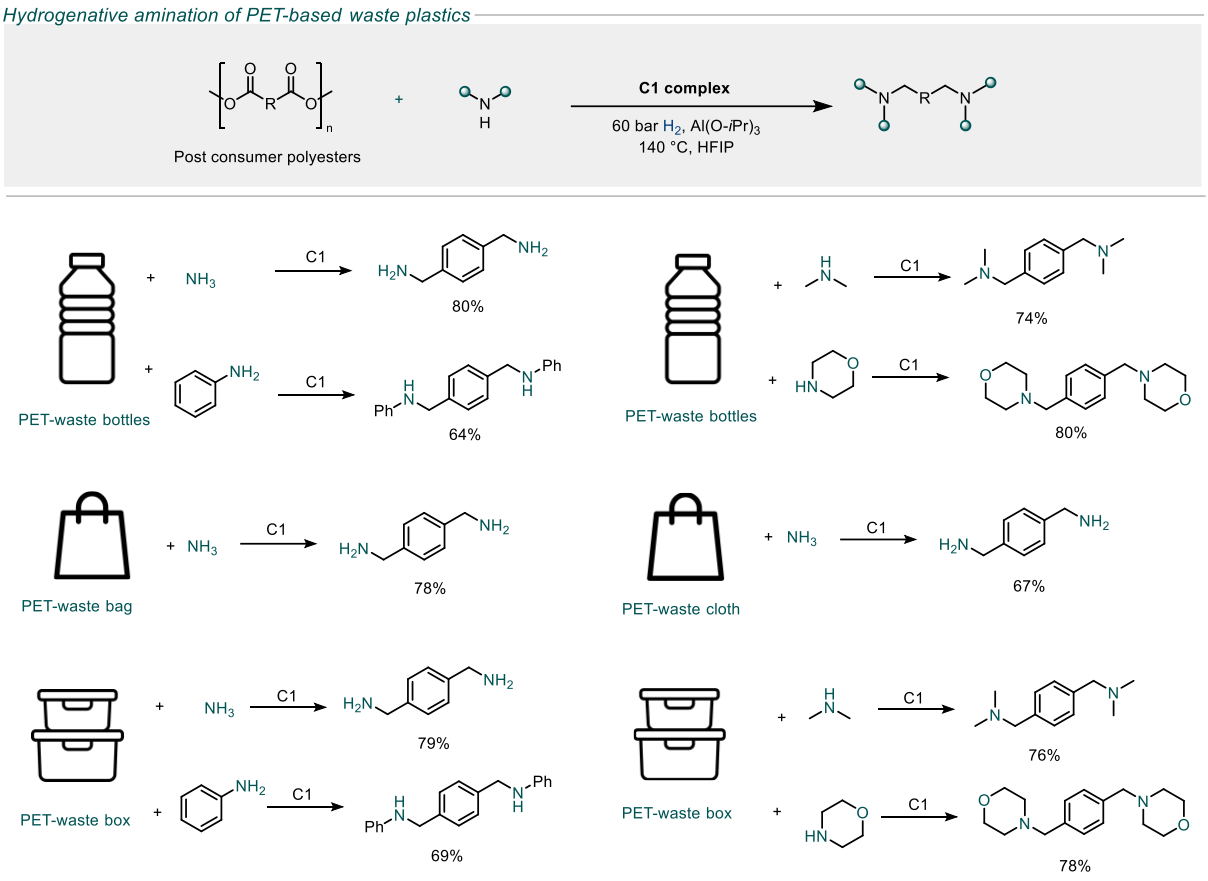
counterparts, synthesis of primary amines from carboxylic acids or esters is more challenging. Therefore, we examined depolymerization of polyesters in the presence of ammonia and 85% of *para*-xylylenediamine was obtained when PBT was employed in the reaction. Next, we studied the catalyst for depolymerization of challenging aliphatic polyesters such as polyethylene adipate (PEA), PES and PCL. Interestingly, reaction of PEA as well as PES in the presence of ammonia gave the caprolactam and butyrolactam products in 88% and 86% yield respectively. Hydrogenation of PCL in the presence of ammonia gave excellent yield of 6-aminohexan-1-ol with a extended reaction time of 36 hours.

To synthesise diverse amine containing products different amine derivatives were tested for depolymerization reactions. When aniline was employed as an amine source, PET and PBT polymers gave corresponding N,N'-(1,4-phenylenebis(methylene))dianiline up to 75% isolated yield. Due to the high importance of the morpholine functional group in pharmaceuticals and allied industries, we performed the depolymerization of PET in the presence of morpholine and corresponding diamine was



Scheme 15: Hydrogenative amination of polyesters

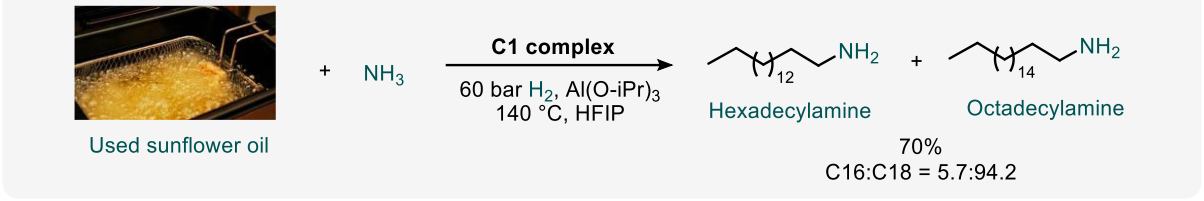
obtained in very good, isolated yield. In the next steps we used N,N-dimethyl amine for depolymerization of PET and PEA and 1,4-phenylene)bis(N,N-dimethylmethanamine) and tetramethylhexane-1,6-diamine were obtained in good yield. Notably, testing N,N-dimethyl amine for the depolymerization of PCL gave 6-dimethylamino-1-hexanol in very good yield. Subsequently to further expand the scope of the catalyst's application, depolymerization of PET based post-consumer products were tested. For this purpose PET-based waste products like water bottles, polyester cloth, PET-bags and parcel boxes were collected, sorted and cut into small pieces (ca. 5-8 mm) before reaction (**Scheme 16**). All mentioned waste materials were treated with ammonia and *para*-xylylenediamine was obtained up to 80% yield. Similarly, water bottles and plastic boxes were also transformed with aniline, morpholine and dimethylamine and corresponding diamines were obtained up to 70% isolated yields. Moreover, the scalability of the current system was tested and 5 gram PET bottle pieces were used in the reaction and 67% of *para*-xylylenediamine was isolated.



Scheme 16: Hydrogenative amination of PET based post-consumer products

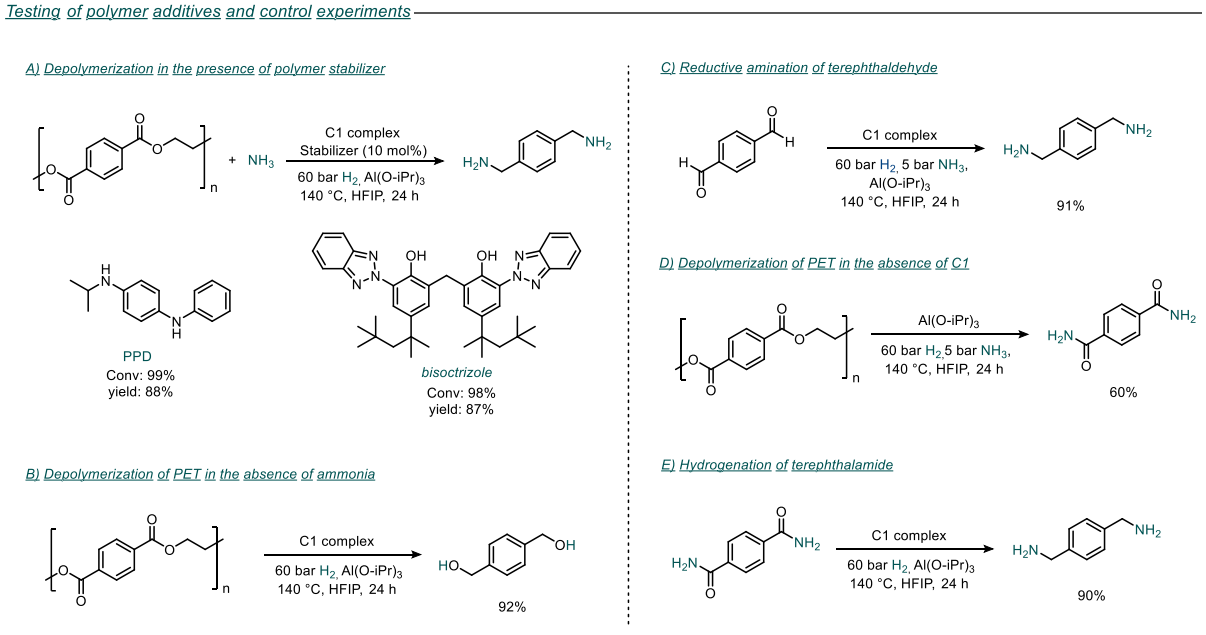
To utilize more *end-of-use* materials as chemical feedstocks, we investigated Co-triphos(p-anisole) system for the synthesis of fatty amines from used cooking oil. Accordingly, sunflower oil used for cooking purpose was collected, filtered and fatty acid composition was analysed. It was found that used sunflower oil contains 6.3% of C16 fatty acid (6.2% saturated, 0.1% unsaturated) and 91.55% C18 fatty acid (3.2% saturated, 88.35% unsaturated) composition along with 2.15% of other components. Interestingly, after the reaction of treating UCO with ammonia in the presence of cobalt catalyst and molecular hydrogen 70% of total fatty amine yield was obtained (**Scheme 17**).

Co-catalyzed one-pot synthesis of fatty amines



Scheme 17: Hydrogenative amination of used cooking oil

Chemicals which are added to the polymer to enhance their life span, processability, desired physical or chemical properties are called polymer additives.[197] Even though their content in polymers is mostly few percent, they have significant impact on polymer stability as well as properties. We performed model reaction in the presence of polymer stabilizers to evaluate the tolerance of developed cobalt system in the presence of different polymer additives (**Scheme 18** a). Interestingly, employing N-isopropyl-N′-phenyl-1,4-phenylenediamine (IPPD; anti-ozonant) and methylene bis-benzotriazolyl tetramethylbutylphenol (bisoctrizole; light stabilizer) for the reductive depolymerization gave desired diamines in excellent yields and no catalyst inhibition was observed. Moreover, several control experiments were performed to get more insight into reaction pathways and we assume that current depolymerization technique involve domino hydrogenolysis-ammonolysis pathway in which hydrogenolysis-reductive amination strategy can be the major route (**Scheme 18** b-e).



Scheme 18: Testing of polymer additives and control experiments

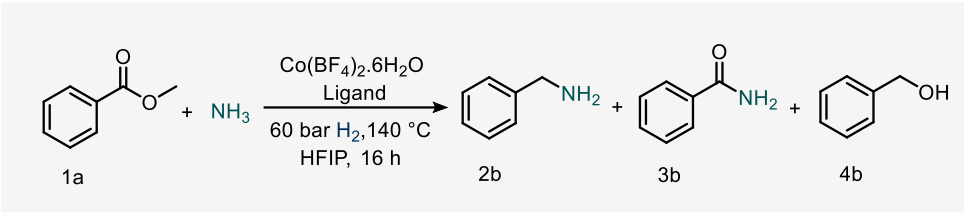
5.2 A highly selective cobalt catalyst for primary amine synthesis from carboxylic acids, esters and vegetable oils

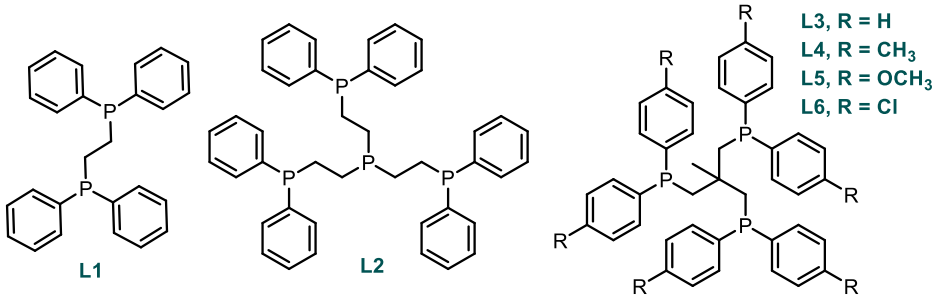
Over the past ten years, transition metal catalysis using ammonia as a nitrogen source for amine synthesis has advanced exponentially.[121a] However, achieving high primary amine selectivity under mild reaction conditions continues to be a significant challenge. Problems such as catalyst deactivation due to the formation of stable transition metal-ammonia complexes, which can result in less reactive metal-amine species and chemoselectivity issues arising due to the primary amines reactivity compared to ammonia which can lead to undesired side reactions and the formation of secondary or tertiary amines are key issues in this field.[121b] Development of non-noble metal catalyst which can efficiently synthesise primary amines employing employing abundantly available feedstock such as ammonia and molecular hydrogen from renewable resources is highly significant. Carboxylic acids and esters are both classes of easily available building blocks for chemical transformations and are available in nature making them feedstocks of choice for numerous synthetic applications. In this regard, non-noble metal based transformations for primary amine synthesis utilizing carboxylic acid derivatives is an attractive synthetic approach which contributes significantly towards sustainability. As mentioned in the introduction part, compared to other carbonyl counterparts synthesis of primary amines from carboxylic acid derivatives under hydrogenative conditions rises several chemoselectivity issues. Possibility of numerous side reactions including aldehyde reduction to alcohols, ammonolysis, etherification reactions as well as formation of secondary and tertiary amines are highly challenging to control during the reaction progress. Hence, the development of an efficient catalyst which can selectively form primary amine from carboxylic acids and esters is still highly desirable.

As mentioned in the last section, recently our group developed cobalt-triphos catalyst system for hydrogenative amination of polyesters and used cooking oil to synthesise various amines. Motivated by this results we explored further possibilities of base metal catalyst systems for the amination of carboxylic acids and esters for the selective synthesis of primary amines. The work also extended towards the selective formation of fatty amines from seven diverse vegetable oils such as palm oil, sunflower oil , rapeseed oil, olive oil, walnut oil, pumpkin seed oil, and coconut oil. Fatty amines are significant class of oleo-chemicals which are widely used as renewable and sustainable alternatives to petrochemicals in various industries and their syntheisis via vegetable oil valorization is an effective and sustainable approach. The analysis of vegetable oil composition was performed before the reaction and it was found that most of the vegetable oils comprise of C16 and C18 fatty acids in high amount. Notably, in case of coconut oil, C12 and C14 fatty acids were also present in high amount.

For the initial optimization reactions, direct amination of methyl benzoate with ammonia in the presence of molecular hydrogen was choosen as the model reaction. Initially, *in-situ* generated complexes of cationic Fe, Mn, Co, Ni, and Cu salts and various bi-, tri-, and tetradentate ligands, specifically dppe; (1,2-bis(diphenylphosphino)ethane; **L1**) tetraphos (tris[2-(diphenylphosphino)ethyl]phosphine; **L2**), and

Catalyst optimization





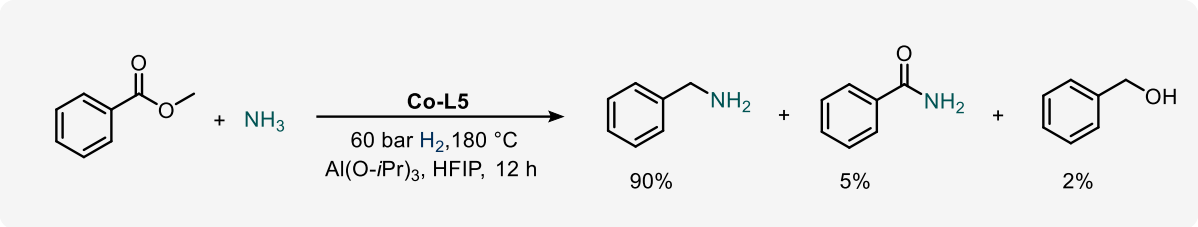
Entry	Catalyst	Conv. (%)	2b (%)	3b(%)	4b(%)
1	Co-**L1**	85	-	60	24
2	Co-**L2**	78	-	58	19
3	Co-**L3**	89	25	55	8
4	Co-**L4**	85	65	12	7
5	Co-**L5**	98	79	11	4
6	Co-**L6**	70	10	48	10
7	Co-**L5** (1:1.1)	54	11	39	2
8	Co-**L5** (1:2.1)	>99	82	10	5
9	Co-**L5** + Al(O-*i*Pr)$_3$	>99	92	5	2

Table 1: Amination of methyl benzoate with ammonia: Reaction optimization

tripodal triphos (tri-(1,1,1-tris(diphenylphosphinomethyl)ethane; **L3**) (**Table 1**) were tested. As shown in the **Table 1**, with the exception of the triphos-ligated Co catalyst (Co-**L3**), the tested complexes did not promote the formation of benzylamine 2b but provided only benzamaide 3b (47-85%) and benzyl alcohol 4b (8-24%). Reaction of using Co-**L3**, gave 25% of the desired product 2b along with formation of benzamide 3b and benzyl alcohol 4b. In order to enhance the selectivity of the process, three electronically distinct substituted triphos ligands (**L4**-**L6**) were prepared and the corresponding *in-situ* generated cobalt complexes were tested in the benchmark reaction. Similar to previous work, triphos-substituted ligands with electron-donating groups (methyl, methoxy, **L4**-**L5**) displayed high selectivity towards final desired product and the chloro-substituted ligand **L6** was comparatively less active.

Moreoever, using 1:2.1 Co-**L5** ratio, the yield of 2b was increased. Higher yields of the desired benzylamine 2b were obtained in the presence of acidic co-catalyst Al(O-*i*Pr)$_3$ and 92% of the desired product was achieved. Testing different solvents revealed that fluorinated ones, especially HFIP showed best activity and selectivity in the benchmark reaction. It is noteworthy that the majority of 3d-metal phosphine complexes exhibit sensitivity in comparison to their noble analogs, therefore, thermal stability of the cobalt system was studied. Nevertheless, the catalyst demonstrated no deactivation in the model reaction at 180 °C and exhibited excellent chemoselectivity (**Scheme 19**).

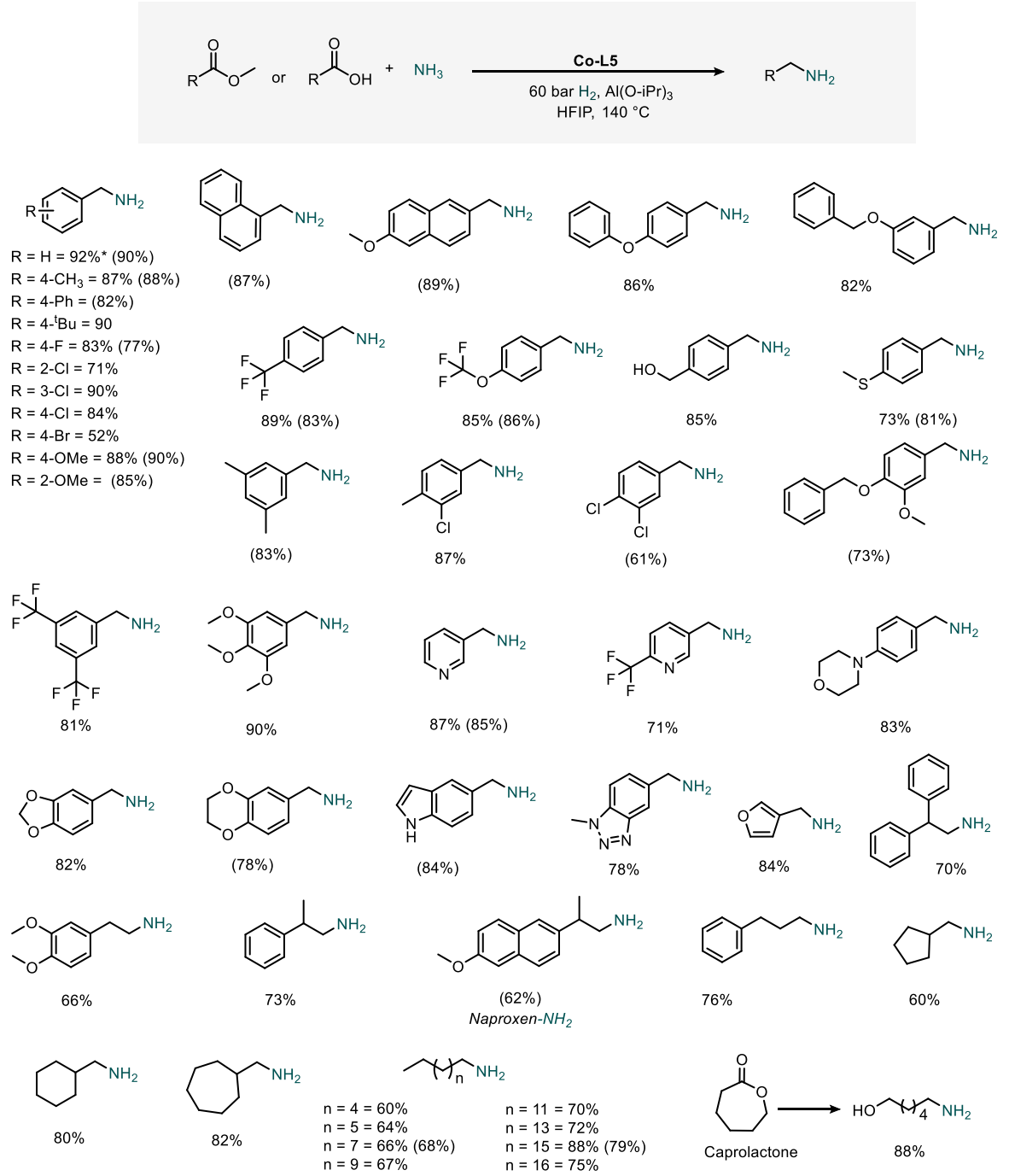
Co-catalyst stability experiments



Scheme 19: Co-triphos catalyst stability experiment

Next, the developed system was tested for a range of esters and carboxylic acids, and aromatic, heterocyclic, and aliphatic derivatives were subjected to amination reactions with ammonia (**Scheme 20**). Notably, amination of carboxylic acids and corresponding methyl esters the showcased similar activity and selectivity during the process. In addition to conventional substrates, a number of functionalized substrates such as halogenated benzylamines, methoxy-, benzyloxy-, trifluoromethoxy-, hydroxy-, and thioether groups substituted benzylamines were obtained up to 89%. Moreover, the amination of di- and tri-substituted methyl benzoates and acids were transformed to corresponding primary amines. A series of amines comprising significant heterocycles, including pyridine, furan, benzodioxole, benzodioxane, indole, benzotriazole, and morpholine were synthesized from the corresponding heterocyclic esters and acids. Aliphatic substrates which are comparatively challenging were succesfully transformed into corresponding primary amines upto 82% yield. In addition to methyl esters, various other esters—such as ethyl, butyl, and tert-butyl benzoates- were also successfully converted to the corresponding primary amines. Furthermore, ε-caprolactone as an example of lactone substrate could be transformed into the respective amino alcohol. Notably, in case of halogenated substrates reductive dehalogenation of chloro and bromo substituents were observed in varying amounts.

As an extension of the catalyst application, Co-**L5** system was utilized to synthesise different fatty amines from pure triglycerides as well as natural vegetable oils (**Scheme 21**). For the initial screening three diverse commercially available triglycerides were chosen (C7, C16, and C18) and desired fatty amines were obtained upto 86% yield.



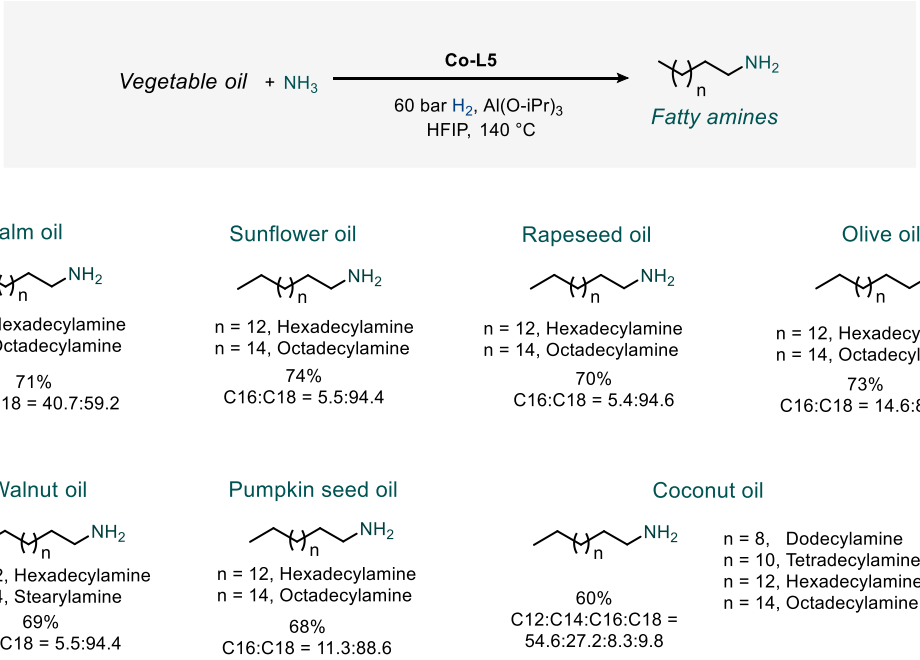
Scheme 20: Selected examples of primary amine synthesis from acids and esters. Yields are given in the paranthesis for acids

After triglyceride testing, seven distinct vegetable oils were chosen for hydrogenative amination. A fatty acid assay was generated after hydrolysis for each vegetable oil for the ease of analytics before reaction. As mentioned above for the majority of vegetable oils characteristic C16 and C18 fatty acids were prominent whereas, coconut oil had a high composition of C12 fatty acid and the presence of C14 fatty acid was also observed and varied in saturation of C-C bond (**Table 2**).

Entry	Vegetable oil	Fatty acid assay
1	Palm oil	39.4% C16 fatty acid (39.2% saturated, 0.2% unsaturated) 58% C18 fatty acid (5.4% saturated, 52.6% unsaturated)
2	Sunflower oil	5.9% C16 fatty acid (3.1% saturated, 2.8% unsaturated) 92.4% C18 fatty acid (3.1% saturated, 89.3% unsaturated)
3	Rapeseed oil	6.1% C16 fatty acid (6.0% saturated, 0.1% unsaturated) 91.9% C18 fatty acid (29.9% saturated, 58.9% unsaturated)
4	Olive oil	15.1% C16 fatty acid (14.3% saturated, 0.8% unsaturated) 83.4% C18 fatty acid (3.4% saturated, 80% unsaturated)
5	Coconut oil	47.7% C12 fatty acid 19.4% C14 fatty acid 7.7% C16 fatty acid 8.9% C18 fatty acid (3.1% saturated, 5.8% unsaturated)
6	Pumpkin seed oil	11.2% C16 fatty acid (11.1% saturated, 0.1% unsaturated) 87.8% C18 fatty acid (5.5% saturated, 82% unsaturated)
7	Walnut oil	6.7% C16 fatty acid (6% saturated, 0.1% unsaturated) 92.51% C18 fatty acid (2.6% saturated, 89.91% unsaturated)

Table 2: Fatty acid composition of different vegetable oils

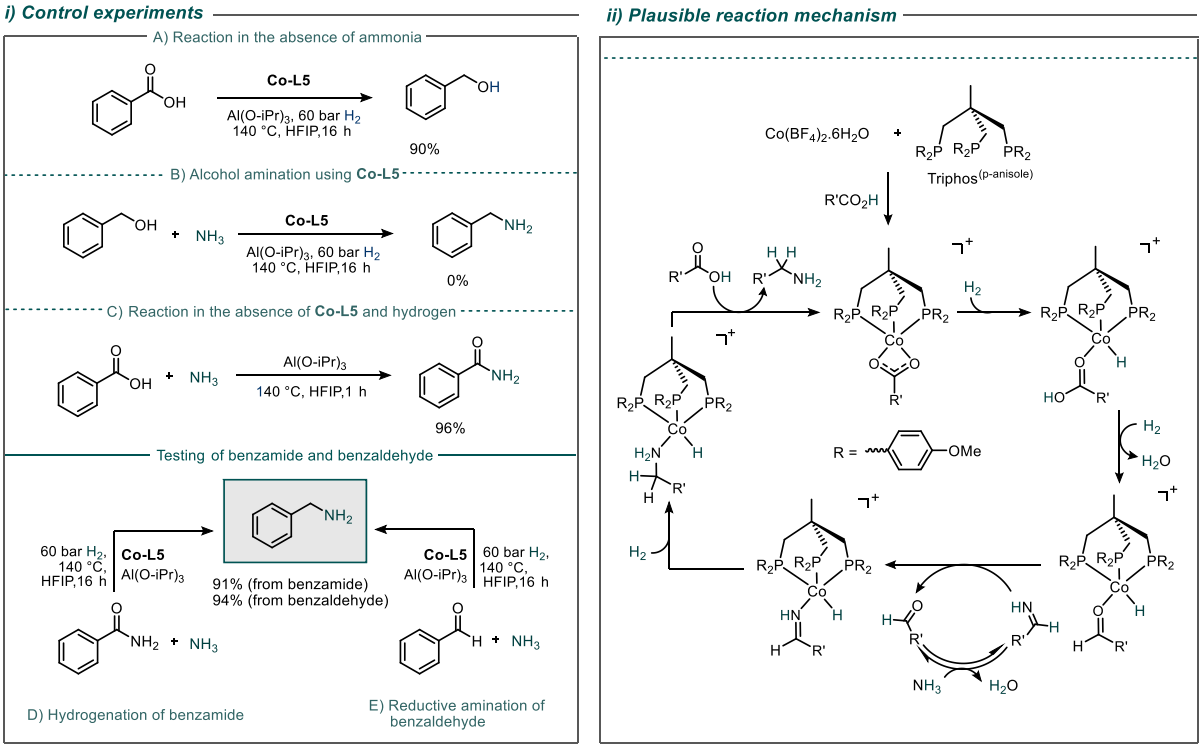
Hydrogenative amination of vegetable oils



Scheme 21: Hydrogenative amination of vegetable oils

Palm oil, sunflower oil , rapeseed oil, olive oil, walnut oil, pumpkin seed oil, and coconut oil underwent reductive amination with ammonia and molecular hydrogen to give primary fatty amines C12-C18 in up to 74% yield (**Scheme 21**). Notably, hydrogenation of the double bond was observed on all cases.

As mentioned above the reaction of acids and esters with ammonia and hydrogen can form multiple products and possibility of two general pathways exist for primary amine synthesis. a) The catalytic hydrogenation of carboxylic acid results in the formation of benzaldehyde, which reacts with ammonia to form an imine intermediate and subsequent hydrogenation of imine intermediate yields the primary amine. b) the primary amide formed from the carboxylic acid, can hydrogenate to give the desired amine. To differentiate between the reaction pathways, several control experiments were conducted (**Scheme 22** i). Under standard reaction conditions without ammonia, benzoic acid gave benzyl alcohol in 90% yield (**Scheme 22** a) and no formation of benzylamine was observed from benzyl alcohol under standard conditions confirming no possibility of an alcohol amination mechanism (**Scheme 22** b). Moreover, hydrogenation of benzamide and benzaldehyde also occurred under these conditions and benzylamine was obtained at 91% and 94% respectively (**Scheme 22** d and e). Notably, the Lewis acid-catalyzed formation of amide is also possible under standard reaction conditions (**Scheme 22** c). Therefore, we suggest a domino hydrogenation reductive amination pathway towards primary amine formation.



Scheme 22: Control experiments and proposed reaction mechanism[7.2]

To get more insight into developed catalysts several mechanistic experiments including high-pressure NMR, EPR measurements and ESI-MS analysis were performed. Based on all the experimental data obtained and the literature precedents,[102,198] we propose a plausible reaction mechanism (**Scheme 22** ii). Initially, the formation of Co(triphos(p-anisole))(alkanoate) species happens followed by heterolytic hydrogen splitting, forming a Co-H complex. After hydride addition to the carbonyl carbon, second heterolytic hydrogen splitting process takes place. After expelling one equivalent of water, a

[Co(triphos(p-anisole))(H)(aldehyde)]$^{+}$ species is formed. Subsequently, the Co-imine complex is formed from primary imine generated from the aldehyde in the presence of ammonia. Finally, after β-hydride addition and hydrogen coordination, followed by hydrogenolysis, the desired primary amine is released, and the catalytically active species is regenerated (**Scheme 22** ii).

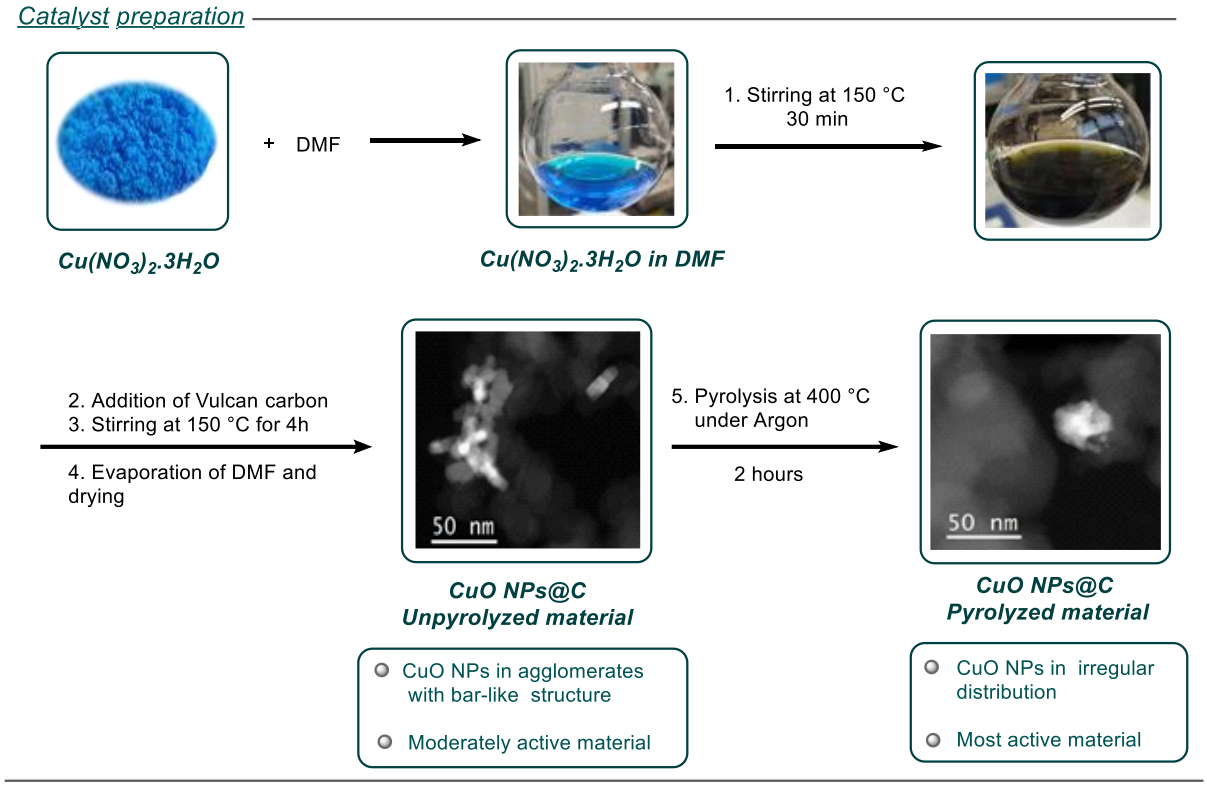
5.3. Cu-oxide nanoparticles catalyzed synthesis of nitriles and amides from alcohols and ammonia in presence of air

C–N coupling transformations are significant class of reactions for manufacturing various fine and bulk chemicals, including pharmaceuticals, synthetic fibres, fertilizers, pigments and agrochemicals.[199] The development of sustainable and cost-effective catalytic strategies for synthesizing nitrogen-containing compounds are of high significance due to the mentioned widespread applications of nitrogen containing compounds. Among these N-containg compounds, nitriles as well as amides are key precursors for numerous synthetic transformations and has crucial role in numerous applications.[200-201] The classical chemical synthesis of nitriles such as the Rosenmund–von Braun reactions and the Sandmeyer reactions require harsh reaction conditions, uses toxic reagents and result in huge amount of chemical waste.[202] Industrially, nitriles are typically produced by ammoxidation at high temperatures (>300 °C), however, this process is not efficient for the synthesis of complex nitriles.[203-205] Similarly, amide bond formation is equally significant in organic synthesis and life sciences including synthesis of polymers, pharmaceuticals, peptide, protein, perfume intensifiers, pigments, detergents and lubricants. However, traditional primary amides synthesis involve reacting activated carboxylic acids or acids derivatives with ammonia, often utilising stoichiometric activating agents which result in low atom efficiency and generation of significant amount of waste.[206]

To enhance sustainability in these approaches, it is highly crucial to develop alternate greener methods employing inexpensive and readily available starting materials for the synthesis of structurally distinct nitriles and amides. In this regard, using alcohols which are economical, easly availabile and has potential to be obtained from renewables are an attractive choice for the chemical synthesis of nitriles and amides.[207-208] Moreover, utilizing ammonia, green starting material which is produced on a large scale and enormously used in chemicals and fertilizers, is another abundant reagent which can be utilized for the C-N bond formation reactions.[121]

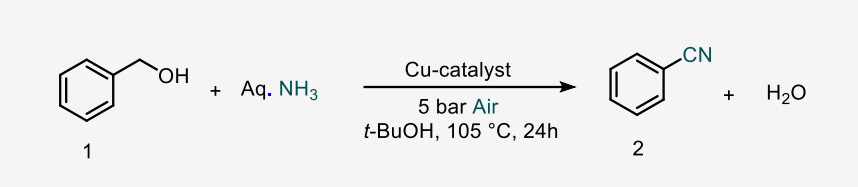
Previous works in this field of nitrile synthesis from alcohols and ammonia have been accomplished using Au, Ru, Fe, Co, and Mn based heterogeneous and homogeneous Fe and Cu based catalysts.[209] However, most of the reactions employed molecular oxygen as the oxidant. Compared to chemical oxidants or molecular oxygen, using air as oxidant is a viable approach as they are abundant, safer, inexpensive, eco-friendly and forms only water as a by-product. Catalytic synthesis of primary amides has been studied using Mn, Co, Fe and Au based catalysts. Several Co, Cu, Fe and V catalysts were developed for catalytic oxidative conversion of alcohols into nitriles or amides.[202,210] Despite these advances, highly selective and efficient catalysts for C-N bond formation using air as the oxidant is of high interest. In 2022, our group reported carbon-supported copper nanoparticles as effective catalysts for aerobic oxidation of alcohols with ammonia to synthesize wide range of nitriles and amides.

At first, Cu-based catalysts were prepared using general and commonly used impregnation and pyrolysis method (**Scheme 23**). For this purpose $Cu(NO_3)_2{\cdot}3H_2O$ was dissolved in DMF and stirred at 150 °C for 30 minutes. Vulcan XC-72R (as carbon powder) was added to the solution and stirred for 4 hours at 150 °C. Subsequently, after slow evaporation of DMF and drying immobilized solid materials were obtained. Finally, obtained material was pyrolyzed at different temperatures under argon to obtain carbon-supported copper oxide nanoparticles.



Scheme 23: Synthesis of Cu-oxide catalysts

After catalyst preparation, in order to select the optimal Cu-based catalyst, model reaction was performed using benzyl alcohol and aqueous ammonia in the presence of air for the synthesis of benzonitrile and all the freshly prepared catalysts were tested. Initial testing of $Cu(NO_3)_2.3H_2O$ and mixture of copper nitrate and Vulcan carbon gave no satisfactory results (**Table 3**. Entry 1 and 2). To our surprise, the impregnated, non-pyrolyzed material, CuO@C, produced 60% of the desired product (**Table 3**, entry 3). After pyrolysis of this CuO@C material, we observed a further increase in the activity. As a result, materials pyrolyzed at different temperatures (CuO@C-300-800; 300-800 indicates the applied pyrolysis condition in °C) were tested and the one pyrolyzed at 400 °C was found to be the most active and selective catalyst (**Table 3**, entries 4-7). From this material (CuO@C-400), complete conversion of benzyl alcohol took place and produced 98% of the desired product, benzonitrile (**Table 3**, entry 5). On the other hand, the materials pyrolyzed at 600 °C (CuO@C-600) and 800 °C (CuO@C-800) also exhibited good activities, but less compared to CuO@C-400.



Entry	Catalyst	Conv. (%)	Yield (%)
1	$Cu(NO_3)_2.3H_2O$	3	2
2	$Cu(NO_3)_2$-carbon	37	33
3	CuO@C unpyrolyzed	67	60
4	CuO@C-300	75	70
5	CuO@C-400	>99	98
6	CuO@C-600	85	83
7	CuO@C-800	83	79

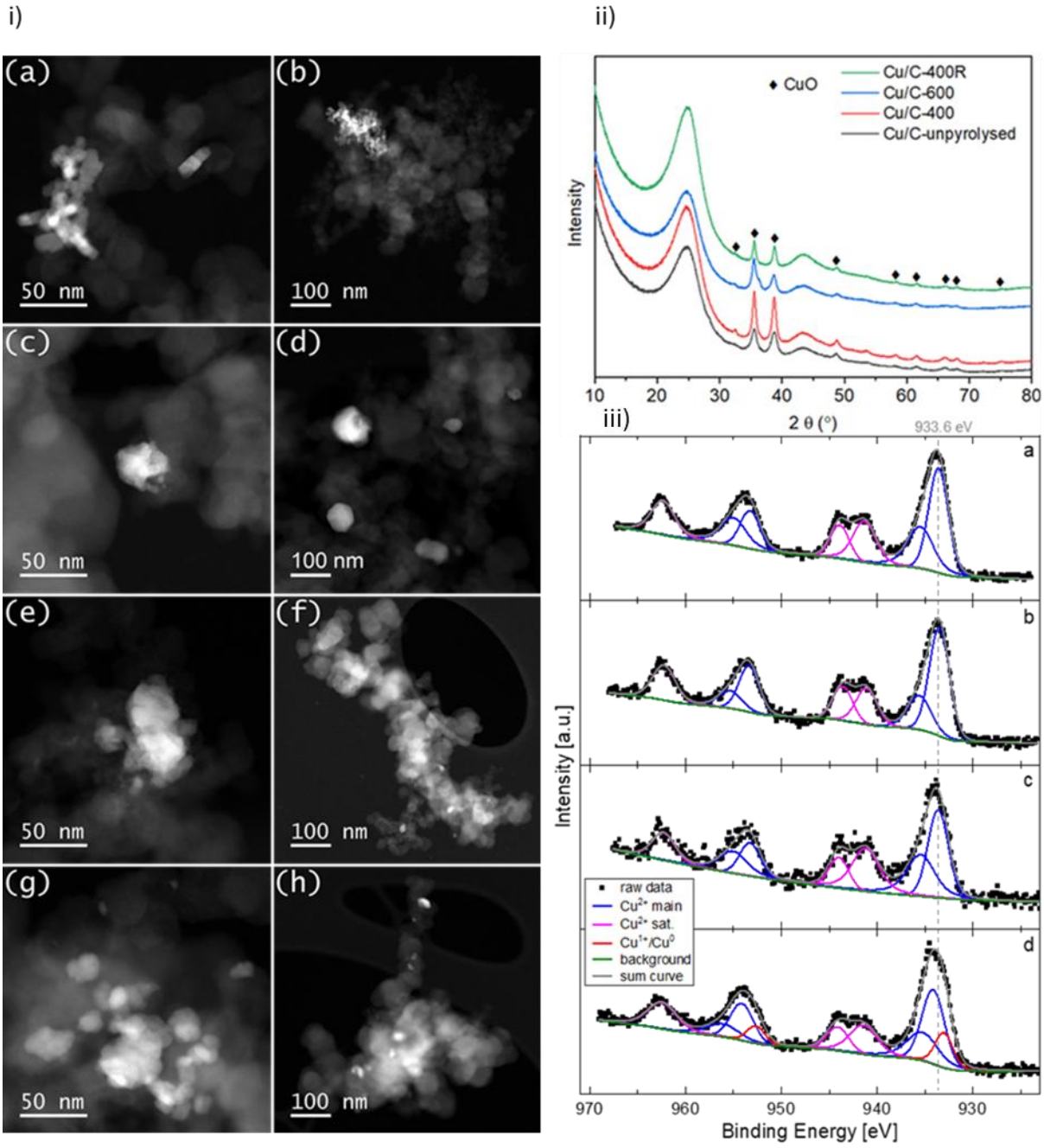
Table 3. Oxidative amination of benzyl alcohol: Evaluation of catalytic activities**.**

Cu-based catalysts were characterized using state-of-the-art analytical techniques such as scanning transmission electron microscopy (STEM), X-ray diffraction (XRD), electron energy-loss spectroscopy (EELS), energy-dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS) were conducted. STEM analysis of the of unpyrolyzed material (CuO@C-unpyrolyzed), the agglomeration of particles in bar-like oxidic structures in the range of 20 to 180 nm was observed (**Scheme 24** (i) a, b). In case of most active CuO@C-400 formation of CuO particles in an irregular shape with sizes ranging from 20 to 130 nm was seen (see **Scheme 24** (i) c, d). The material prepared at higher pyrolysis temperature (CuO@C-600) contained also CuO particles in an irregular shape with sizes ranging from about 4 to 150 nm (**Scheme 24** (i) e, f). The STEM measurements of CuO@C-400 after one run, CuO@C-400R, resembled CuO@C-400, however the size range of particles was larger (from about 3 to 300 nm) and was less compact (**Scheme 24** (i) g, h).

Moreover, in case XRD analysis patterns of both pyrolyzed catalysts (CuO@C-400 CuO@C600) and unpyrolyzed (CuO@C) and recycled ones (CuO@C-400R), showed the presence of CuO particles (**Scheme 24** ii). In the unpyrolyzed material, agglomerations of bar-like structures can be seen, while more compact oxidic copper can be observed in the pyrolyzed catalysts. Further analysis of the catalyst surface by X-ray photoelectron spectroscopy (XPS) showed the presence of C, O, Cu, and N elements.

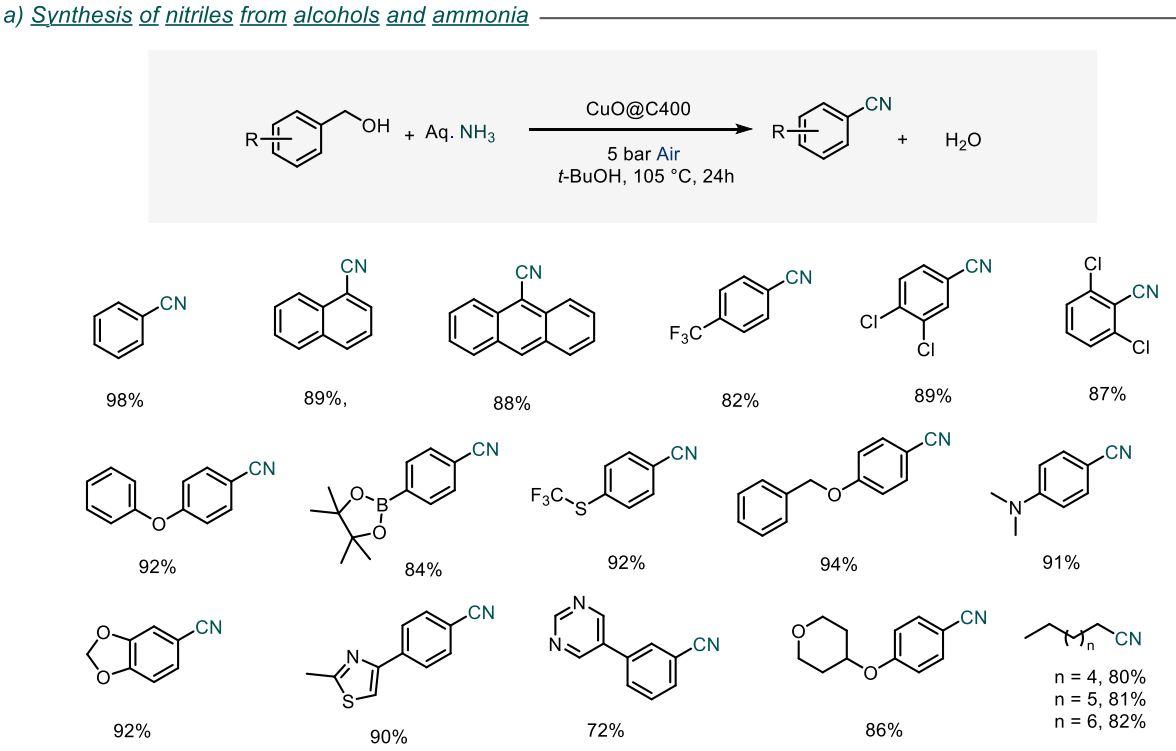
The Cu 2p spectra shown in **Scheme 24** (iii) reveal the presence of peaks at 933.6 eV and 954.0 eV, which are corresponding to Cu $2p_{3/2}$ and Cu $2p_{1/2}$. The strong satellite features around 942.5 eV and 962.5 eV together with the binding energy of the Cu $2p_{3/2}$ peak clearly prove CuO as the main oxidation

state. The unpyrolyzed catalyst as well CuO@C-400 and CuO@C-600 show very similar Cu 2p spectra and the same oxidation state (**Scheme 24** (iii) a-c) with decreasing concentration of Cu at the surface.



Scheme 24:. (i) STEM images of copper-based nanocatalysts (ii) XRD patterns of Cu-based materials. (iii) Deconvoluted XPS of Cu-based materials.[7.2]

However, for the recycled catalyst CuO@C-400R a slightly higher amount of Cu can be observed as well as differences in the Cu 2p spectra.

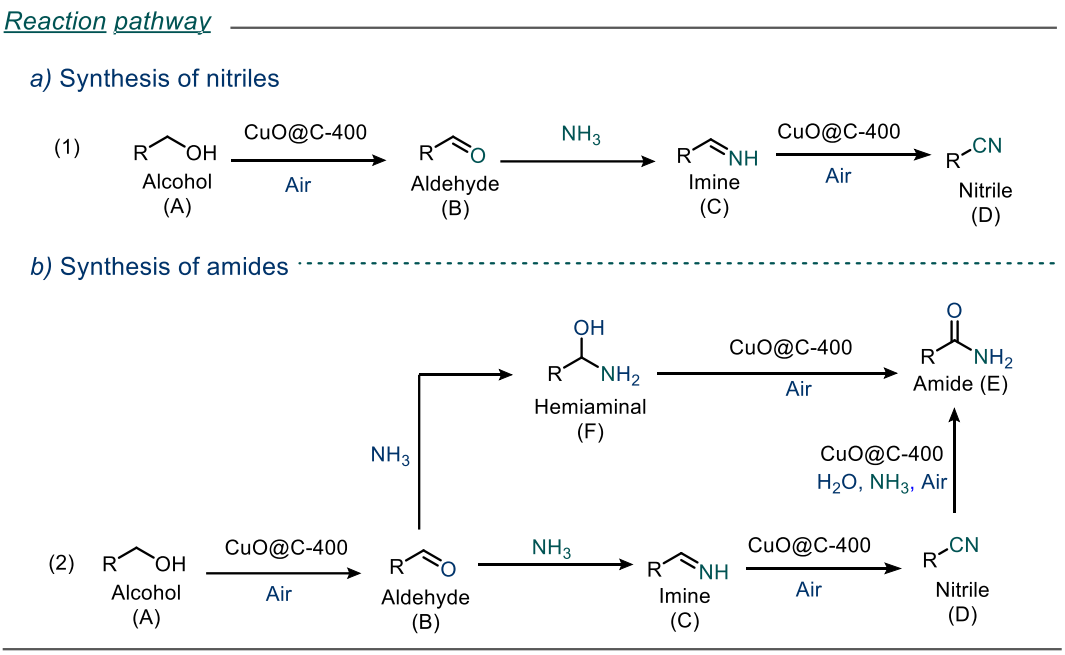


Scheme 25: Selected examples of nitrile and primary amide synthesis from CuO-400 catalyst

After characterization of the prepared catalysts CuO@C-400 was tested for the synthesis of diverse functionalized benzonitriles and simple and substituted benzonitriles were synthesized and obtained up to 95% yield (**Scheme 25** a).

Alcohols containing aromatic, aliphatic, sterically hindered and halogenated alcohols were conveniently transformed into corresponding nitriles. Several functional groups including ether-, ester-, boronic ester-, thio ether-, primary amine-, N,N-dimethylamine- and cyano- groups were tolerated and corresponding nitriles were obtained in excellent yields. Moreover, diverse heterocycles such as pyridine, quinoline, thiophene, furan, dioxole-, thiazole- and pyran-based nitriles were prepared in up to 98% yield. As an example of allylic nitrile, cinnamonitrile was accessed from cinnamyl alcohol in a 73% yield.

Subsequently, diverse primary amides were prepared using CuO@C-400 catalyst in the presence of ammonia using water as solvent (**Scheme 25** b). Primary amides including functional groups such as halogenated, trifluoromethyl-, ether, thio-ether etc were prepared in excellent yield. Further, different heterocyclic amides such as isonicotinamide, thiophene-2-carboxamide, furan-2-carboxamide, benzothiophene-2-carboxamide, and benzodioxole-5-carboxamide were prepared in up to 91% yield. However, unlike to nitrile synthesis CuO@C-400 catalyst was not active for the transformation of aliphatic alcohols towards primary amides.

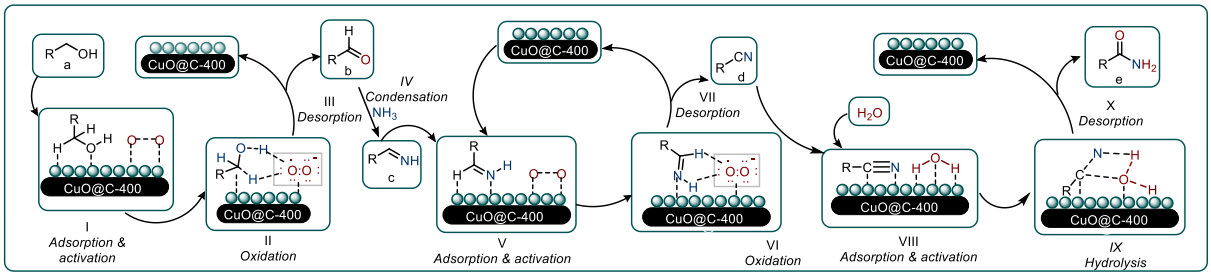


Scheme 26: Oxidative amination of alcohols: reaction pathway

Several control experiments and kinetic experiments suggested reaction pathways for nitrile as well as amide formation (**Scheme 26**). In case of nitrile formation, in the presence of CuO@C-400 catalyst and air the oxidation of alcohol to aldehyde (B) takes place. So formed aldehyde couples with ammonia and generates primary imine (C). Imine intermediate undergoes oxidation in presence of catalyst to form the corresponding nitrile. In case of synthesis of amides, two reaction pathways are possible: i) the aldehyde formed by the oxidation of alcohol can react with ammonia and generates hemiaminal as the intermediate, which can convert to the corresponding primary amide, or b) the benzonitrile produced from alcohol can undergo hydrolysis to form the primary amide in presence of water.

Based on control experiments and obtained results, we propose a plausible reaction mechanism of the Cu-catalysed aerobic oxidation process to prepare nitriles and primary amides in (**Scheme 27**). Initially,

adsorption and activation of both alcohol and oxygen take place on the surface of CuO@C-400 catalyst, with generation of super oxide as oxygen reactive species (I). Oxidation of activated alcohol proceeds using super oxide species (II). Next, the desorption of aldehyde with the regeneration of catalyst (III) occurs and the so formed aldehyde condenses with ammonia and forms imine as intermediate (IV). In the subsequent catalytic cycle imine undergoes adsorption and activation on the catalyst (V) surface followed by oxidation (VI). Finally, the nitrile desorbs with the regeneration of catalyst (VII). For the formation of amide, the nitrile and water adsorb and activate on catalyst surface (VIII) and then hydrolysis occurs (IX). Finally, desorption of amide takes place with the regeneration of catalyst (X).[7.3]



Scheme 27: Oxidative amination of alcohols: Plausible reaction mechanism

6. Conclusion and outlook

This thesis presents the development of three novel methodologies for the C-N bond formation reactions. By replacing petroleum-derived chemical feedstocks with more abundant chemical toolkit and by utilizing base metals for organic transformations current work embody a small contribution to more sustainable, efficient and circular approach towards carbon-nitrogen bond formation. A cobalt triphos system has been developed for the hydrogenative amination of polyesters including post-consumer products and used cooking oil using wide array of amines and corresponding amines were synthesized with high selectivity. The utilization of post-consumer polyesters and used cooking oil in chemical synthesis has the potential to contribute to a circular economy, particularly with regard to the elimination of waste and the synthesis of value-added products from *end-of-life* materials. The development of a homogeneous base metal catalyst capable of selectively forming primary amines from carboxylic acids and esters remains an unsolved challenge in chemical research. A cobalt-based system has been evaluated for its potential in the amination of a diverse array of carboxylic acids and esters, including those derived from commercial vegetable oils. Furthermore, a green and sustainable copper-based heterogeneous catalytic approach was developed for the efficient synthesis of nitriles and primary amides from alcohol and ammonia using air as the oxidant. In all cases, the conversion of the starting material was high, and the selectivity towards the desired final product was excellent. Furthermore, detailed mechanistic investigations of the reaction network and catalyst species were successfully performed. Future advancements in the domain of C-N bond formation reactions must prioritize the utilization of more environmentally friendly solvents and milder reaction conditions. In particular, base metal catalysts that can facilitate reactions with reduced catalyst loading, milder reaction temperatures, pressures, and shorter reaction times are of significant interest for enhancing the existing systems. Additionally, the development of ligands that are more straightforward and amenable to synthesis is of paramount importance prior to the large-scale implementation of these technologies in industrial contexts. The present work signifies an inaugural endeavor within the domain of base metal-catalyzed C-N bond formation reactions, employing more sustainable feedstocks. Nevertheless, the further development of more environmentally friendly approaches is of significant interest.

7. Publications

7.1. A catalytic approach to the valorization of polyesters and biogenic waste for the production of amines

Fairoosa Poovan, Rajenahally V. Jagadeesh, Matthias Beller, *Chem*, **2025**, *12,* 102667.

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Author contributions:

For this manuscript, I performed all the experimental work, including optimization, ligand synthesis, evaluation of the substrate scope as well as mechanistic experiments. In addition, I evaluated all analytical data, wrote the first draft of the manuscript and the supporting information. My contribution to this work is approximately to 80%.

Article

A catalytic approach to the valorization of polyesters and biogenic waste for the production of amines

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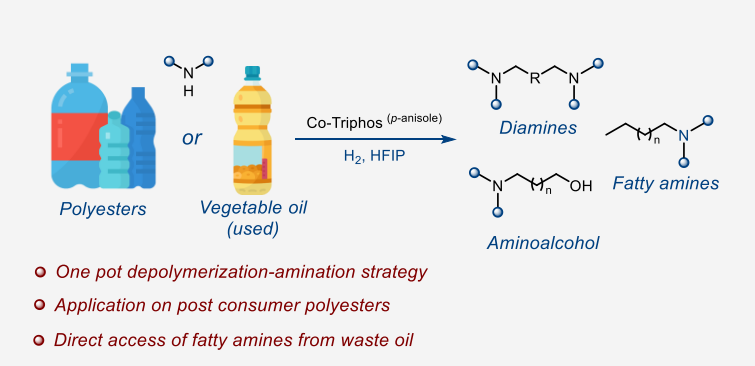
SUMMARY

Despite the numerous applications of polymers in human life, their excessive use has caused serious environmental hazards. Among polymer recycling methods, chemical recycling offers a streamlined approach to polymer degradation by enabling depolymerization without compromising functionality. Specifically hydrogenolysis of polymers, a depolymerization technique that utilizes hydrogen to cleave bonds, has emerged as a powerful strategy for depolymerization, facilitating the upcycling of plastics into high-value chemicals. Previous research in this area has predominantly focused on noble metal catalysts, and the potential of base metals remains unexplored. In this work, we propose a cobalt-based hydrogenative amination approach for the selective depolymerization of polyesters to versatile diamines as well as amino alcohols. This strategy can also be applied to the one-pot synthesis of industrially relevant fatty amines from used cooking oil. The current system opens new avenues for the upcycling of waste into valuable amines, providing a viable solution to plastic pollution and a way to utilize waste as a resource.



Keywords: polyesters, cobalt, depolymerization, homogenous catalysis, selective amination

THE BIGGER PICTURE

The implementation of catalysts with precise bond activation and cleavage provides the basis for selective depolymerization of polymers. Several homogeneous catalytic systems with said properties have been described for the hydrogenative depolymerization of polyesters, but most of them focus on noble metals. Herein, we propose a Co(II)-triphos(*p*-anisole) system for the selective synthesis of various amines and amino alcohols from polyesters and biogenic waste (used cooking oil).

The use of various amine precursors in the presence of molecular hydrogen facilitated efficient depolymerization of polyesters. Selective synthesis of primary fatty amines was achieved by hydrogenative amination of used cooking oil. Interestingly, despite the high reactivity of the aliphatic amines formed, the current amination protocol did not exhibit self-coupling of primary amines. By facilitating the up-cycling of waste materials into valuable amine derivatives, this innovative approach not only addresses pressing environmental issues associated with plastic waste, but also transforms them into useful resources.

INTRODUCTION

The chemical conversion of post-consumer products into value-added small molecules offers an effective approach towards sustainability.[1-6] Extensive amounts of end-of-use plastics cause severe environmental hazards and introducing plastic waste into the chemical production stream will abate these challenges significantly.[7-11] Upcycling technologies, which allow the synthesis of molecules that are different from the parent monomer, have gained wide appeal in recent polymer research. Among the various polymer classes, polyesters can be an effective benchmark for exemplifying diverse depolymerization techniques.[12-16] Poly(ethylene terephthalate) (PET), a significant petroleum-based polyester plastic, accounts for ~12% of global plastic waste and due to its inert nature, slower natural degradation has led to numerous detrimental impacts.[17,18] Mechanical processing (melting and re-extrusion) is widely used for PET recycling, but it often leads to deterioration of the polymer properties.[19-21] In this context, chemical recycling offers an efficient alternative for PET recycling and this approach allows depolymerization without compromising functionality. Chemical recycling not only minimizes the negative environmental effects of plastic wastes but also opens new avenues for the access of valuable chemicals.[22-24] Conventional chemical recycling methods for polyesters include, glycolysis, alcoholysis, hydrolysis, aminolysis and aerobic oxidation.[25-27] Additionally, research focusing on biocatalysis for PET depolymerization is expanding and has been commercialised recently.[28-30] Depolymerization products derived from glycolysis as well as methanolysis of PET have been widely used as gasoline and jet fuels (C7–C8 cycloalkanes and aromatics) after further hydrogenation. Moreover, the conversion of ethylene glycol (EG) (obtained from upcycling techniques) into valuable chemicals such as glyoxal, formate, and glycolic acid (GLA) has garnered significant research interest recently[7].

Compared to conventional approaches, hydrogenolysis (using hydrogen to cleave bonds) of polymers is an efficient depolymerization technique for polymer degradation, and this strategy allows upcycling of polymers into value-added chemical functionalities.[31,32] For this reason, several heterogeneous as well as homogeneous catalyzed hydrogenative depolymerizations have become prominent in this field.[33,34] As a result PET has been converted into several valuable products such as 1,4-benzenedimethanol and ethylene glycol (EG)[35], terephthalic acid and ethylene[36], and *p*-xylene and methylbenzene[37] (Figure 1). Prevailing research in the field of homogeneous hydrogenative depolymerization shows that most studies focus on noble metal catalysis (Figure 1).[35] In 2014, Roberson *et al*. published the first report of transition metal-catalyzed depolymerization of the polyesters in the presence of a Ru(II)-pincer complex ([Ru(II)PNN]).[38] An efficient transesterification-hydrogenation relay strategy using quinaldine-based Ru(II)-pincer catalysts was disclosed recently.[39] Protocols using base metals for depolymerization reactions toward diols have recently emerged, but the application of these catalytic systems for post-consumer products has not yet been explored.[40,41] Herein, we propose a Co-based hydrogenative amination strategy for the selective depolymerization of polyesters. The central part of our research focuses on the synthesis of a large class of highly relevant diamines from various technical grade as well as post-consumer polyesters.

The ubiquity of amine derivatives in agrochemicals, pharmaceuticals, biological probes, and natural products has encouraged researchers to rationalize their synthesis. Among them, diamines are important precursors for the selective formation of various polymers, drugs, agrochemicals, ligands, ionic liquids, and other organic materials (Figure 1).[42-49] Due to their cationic properties, diamines (primary) are also modulators of various ion channels in nature.[50] Furthermore, carbon dioxide capture by amines is considered to be one of the most economical strategies for post-combustion CO2 capture.[51,52] Due to their extensive utilization, global diamines market was valued at 6.5 billion USD in 2024 with annual growth rate (CAGR) of 7% from 2024 to 2030[53-57]. The well established diamine synthesis routes relies on energy-intensive petrochemical processes, which depends on fossil fuels and leads to a significant carbon footprint. These methodologies also use of toxic chemicals (e.g., HCN), contribute to greenhouse gas emissions and waste generations resulting in both environmental and cost concerns[58-60]. Moreover, circular end-of-life (EoL) analysis performed in terms of CO2 emissions for set of polymers including PET indicates that, the quality of the recycled product significantly enhances the environmental performance[61]. Among various recycling technologies upcycling performs better in LCA (Life cycle analysis) studies due to its lower resource use and extended material life[62]. Upcycling polymers into new chemicals can have a lower environmental impact across multiple categories, such as carbon footprint and energy consumption[63]. Recently many studies have been focussing on chemical recycling of polyesters[64-76] to obtain monomers[77] as well as upcycling technologies such as hydrogenolysis[78-79], ammonolysis/ aminolysis[80-89]. However to the extent of our knowledge, hydrogenative amination approach for polymer upcycling has not yet been explored. With increasing concern on environmental problems and sustainable development, upcycling of PET products to synthesize valuable amines offers an efficient pathway to transform plastic waste into useful resources.

Analogous to the use of polymers as feedstocks for valuable chemical syntheses, the use of renewable resources for synthetic transformations also offers new pathways to sustainability. In an effort to utilize more end-use materials as feedstocks for small molecule synthesis, we investigated the generality of the Co-triphos(*p*-anisole) system for the synthesis of fatty amines from used cooking oil (UCO). UCO belongs to the family of municipal wastes that pose high end environmental problems.[90,91] The total annual production of used vegetable oils exceeds 190 million metric tons and are used as major raw materials in many industrial processes.[92] Their specific composition can also be exploited as sources of chemicals for the production of fuels, bio-plasticizers, surfactants, absorbents for volatile organic compounds (VOCs) etc.[93,94] Especially, among the known oleochemicals, fatty amines own high significance and find applications in the production of various specialty chemicals. The production capacity of fatty amines is >1 million metric tons per year and their market size is expected to grow from $3.44 billion to $4.87 billion by 2026.[95-100] Considering the ever-increasing applications of amine derivatives, here we describe a Co-based catalytic framework for the selective formation of synthetically relevant amines from post-consumer as well as bio-based resources. Compared to existing valorization technologies and amination protocols, the proposed system not only mitigates waste accumulation concerns but also aligns efficiently with sustainability as well as circularity principles.

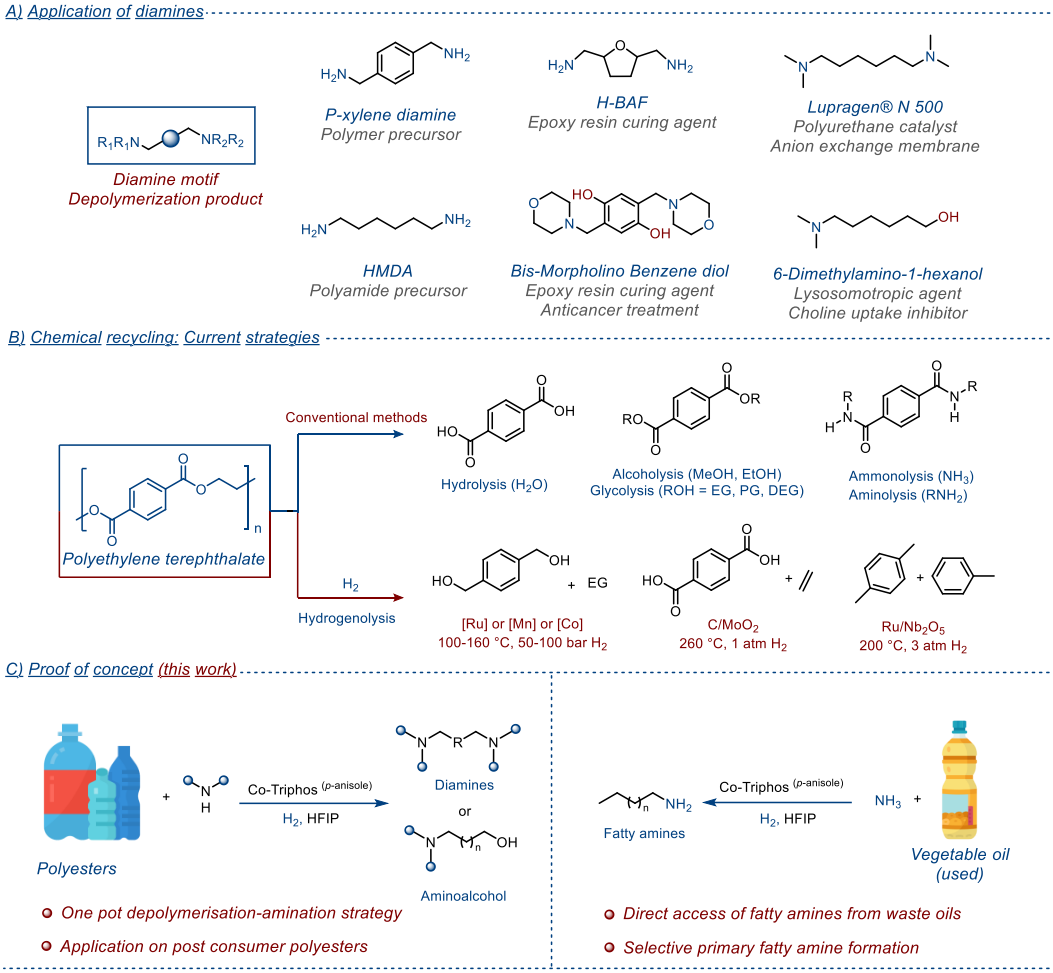


Figure 1. Development of catalytic system for hydrogenative amination
A, Applications of diamines. **B**, Selected examples of current strategies. **C**, This work: Cobalt-catalyzed hydrogenative amination of polyesters and used cooking oil.

RESULTS

Catalyst design

Rational catalyst design that enables precise bond activation as well as selective bond cleavage is critical for polymer degradation. Chemical resistance as well as thermal stability (PET, T_g = 74 °C, T_m = 246 °C) of polyesters often make their depolymerization quite challenging. A molecular Ru-triphos catalytic system that can selectively depolymerize a wide variety of polyesters has been reported by Klankenmayer *et al*.[35] Leveraging our advancements in Co-catalyzed hydrogenation reactions[101-104], we focused on the development of a cobalt-based catalytic system for depolymerization reactions. Initial optimization for amination was performed by employing PET **1a** (technical grade polymer, for details on polymer grade, see the Supplemental information) as the model compound in the presence of gaseous ammonia and hydrogen (referring to the repetition unit of the polymers, 0.5 mmol of each polymer granulate was transformed). To achieve efficient conversion, the solubility of plastics or oils in suitable solvent is a key factor.[105] Hence, to promote hydrogenative amination with sufficient selectivity, hexafluoroisopropanol (HFIP) was used as a solvent.[106] Initial screening performed using cobalt tetrafluoroborate and triphos (1,1,1-tris(diphenylphosphinomethyl)ethane; tripodal-triphos; **L1**) ligand showed 60% conversion of PET with 53% selectivity towards *p*-xylenediamine **3a** and ethylene glycol (Table S1). The reaction was performed at 140 °C in the presence of 5 bar ammonia and 60 bar hydrogen. Inspired by the critical role of triphos ligands in ester hydrogenations as well as reductive amination reactions, we synthesized three electronically diverse triphos ligands (**L2**–**L4**) (S2).[102-104] Next, the corresponding in-situ generated cobalt-phosphine complexes were tested for the depolymerization reaction, and triphos ligands substituted with electron-donating groups (methyl, methoxy, **L2**-**L3**) displayed increasing activity and selectivity for the formation of the desired product **3a** with high conversion (Table S1 entries 2-3). In contrast, the chloro-substituted ligand **L4** showed lower conversion and lower selectivity. Testing the isolated Co-(**L3**)2 (C1) complex for the model reaction, increased the yield of **3a** up to 82% (Table S1, entry 5; S3). Because of the role of additives in reductive depolymerization reactions[35], several acidic and basic co-catalysts were tested, and in the presence of inexpensive aluminium isopropoxide (Al(O-*i*Pr)3) 90% of p-xylylenediamine **3a** was obtained

(Table S2, entry 5). Other cobalt (II) metal precursors tested for the reactions showed no improvement in the catalysis. Testing of different solvents confirmed that fluorinated solvents worked best for the selective formation of p-xylylenediamine **3a** (Table S3, entry 6). Compared to other solvents tested HFIP has unique properties and dissolves PET at very mild temperature.[107] The H-bond donating ability of HFIP is known for enhancing chemical reactivity and studies suggesting HFIP utilizing its strong hydrogen bond donating ability to lower the activation barriers for various transformations is reported.[108-110] We also suggest substrate activation via enhanced acidity due to the presence of two trifluoro methyl groups makes HFIP suitable for the depolymerization.[111,112] The lower boiling point (58.2 °C) makes this solvent easy for distillation and the used HFIP was conveniently recycled and reused for several cycles (Figure S10).[113]

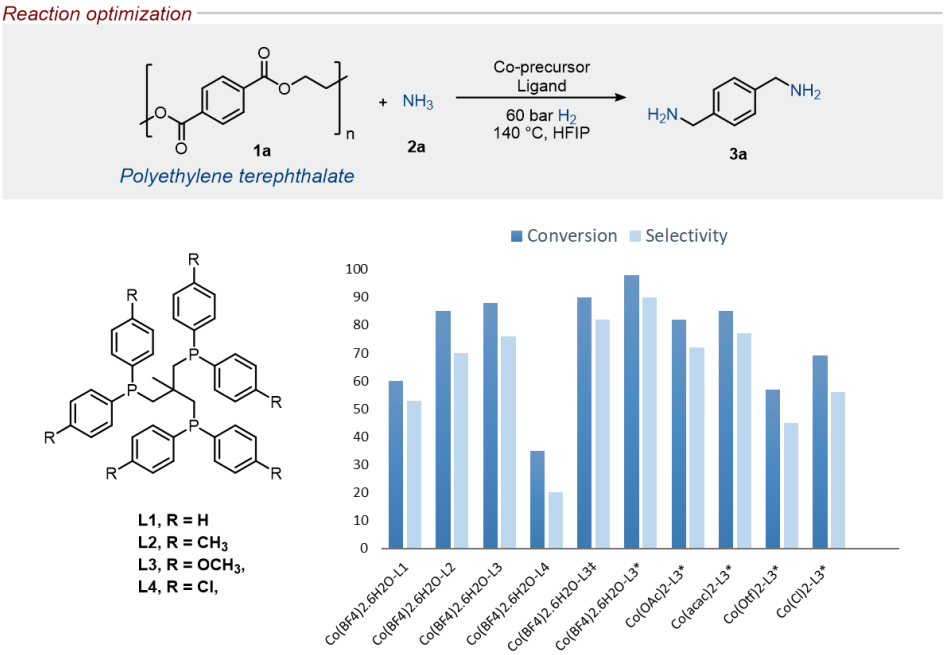


Figure 2. Overview of tested cobalt-phosphine catalysts.

Reaction conditions. 0.5 mmol PET, 5 bar NH_3, 8 mol% metal precursor, 16 mol% ligand, 60 bar H_2, 1 mL HFIP, 140 °C, 24 h. ‡, isolated complex. *Reaction in the presence of aluminium isopropoxide. Yields were determined by GC using mesitylene as standard.

Depolymerization of polyesters

After successful optimization of the depolymerization of PET **1a**, amination of other polyesters was performed under the above mentioned conditions using various amine sources (Figure 2). Synthesis of primary amines from carboxylic acids or esters is more challenging with respect to their secondary or tertiary counterparts.[104] In this context, we examined depolymerization of polyesters in the presence of ammonia **2a**. Interestingly, 85% of *p*-xylylenediamine **3a** was obtained when polybutylene terephthalate (PBT) **1b** was employed in the reaction. Efficiency of the catalyst for depolymerization of more challenging aliphatic polyesters was studied. Remarkably, reaction of polyethylene adipate (PEA) **1c**, and polyethylene succinate (PES) **1d** in the presence of ammonia **2a** gave the corresponding cyclic amides, caprolactam **3b** and butyrolactam **3c** in 88% and 86% yield respectively. Such lactams are versatile bulk chemicals, which are used to produce polyamides as well as prominent drug candidates.[114-116] For example, caprolactam is a key precursor for the manufacture of Nylon 6 and various derivatives of butyrolactam, referred as racetams (e.g. Aniracetam, Oxiracetam, Piracetam) are widely used in pharmaceutical industries as nootropics. Notably, experiments performed for the further hydrogenation of corresponding lactams were not successful even at higher catalyst loading, higher pressure or under longer reaction times.

Polycaprolactone (PCL) **1e** is a significant biodegradable synthetic polyester that found applications in various industrial fields including biomedical sectors and its production via ring-opening polymerization of *ε*-caprolactone exceeds million tons/year.[117,118] Hydrogenation of polycaprolactone **1e** in the presence of ammonia **2a** gave *ε*-caprolactone in 73% yield under optimized conditions. Prolonging the reaction time to 36 hours yielded desired 6-aminohexan-1-ol **3d** in excellent yield. Amino alcohols are important structural motif with diverse pharmaceutical applications and as per FDA report over 30% of small-molecule drugs contain residues of amino alcohols.[119-121] To the best of our understanding this strategy is one of the first base metal catalyzed hydrogenative amination approach for amino alcohols synthesis from *ε*-caprolactone.

Even though ammonolysis as well as aminolysis of polyesters giving corresponding diamides are well explored, reductive depolymerization of polyesters towards amines is challenging therefore, we explored different amine derivatives for current depolymerization strategy. PET **1a** and PBT **1b** were reacted with aniline **2b** and corresponding N,N'-(1,4-

phenylenebis(methylene))dianiline **3e** were obtained up to 75% isolated yield. Morpholine **2c** is one of the most frequently used heterocycle in bioactive compounds and is an ubiquitous candidate in several approved and experimental drugs.[122,123] Owing to the high significance of these amine functionality we explored depolymerization of PET **1a** in the presence of morpholine **2c**. Corresponding diamine was obtained in very good, isolated yield. In the next steps we employed *N,N*-dimethyl amine **2d** for depolymerization reactions and gratifyingly 1,4-phenylene)bis(*N,N*-dimethylmethanamine) **3h** and tetramethylhexane-1,6-diamine **3i** was obtained in good yield. It is worth mentioning that tetramethylhexane-1,6-diamine **3i** also known as Lupragen®N201 is a polyurethane catalyst and used as anion exchange membrane.[124,125] Motivated by the formation of amino alcohol **3d** from polycaprolactone **1e** we tested N,N-dimethyl amine **2d** for the depolymerization of polycaprolactone **1e**, and to our delight 6-dimethylamino-1-hexanol **3i** was obtained in very good yield.

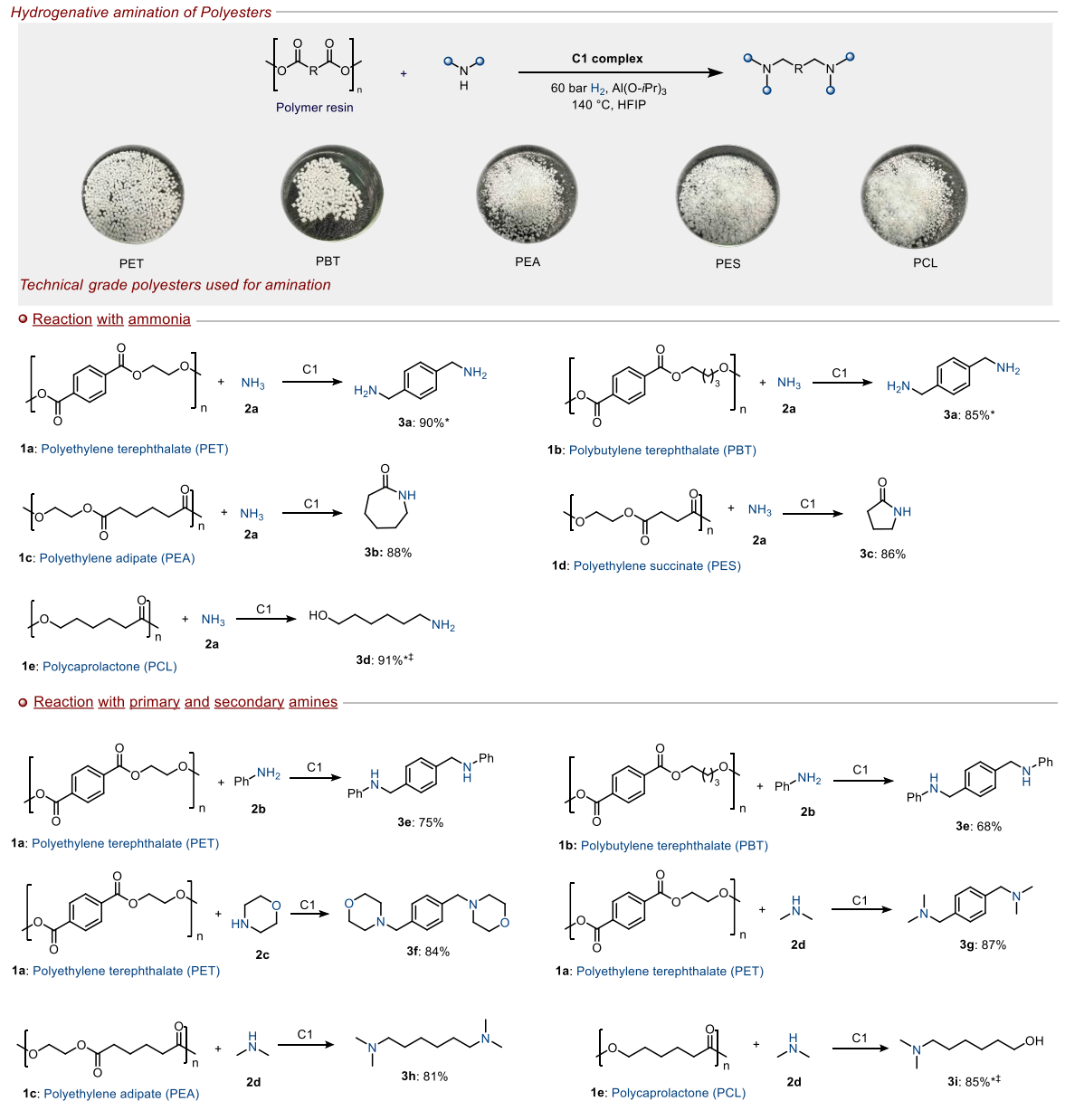


Figure 3. Depolymerization of technical grade polyesters.

Reaction conditions. 0.5 mmol PET, 5 bar NH_3 or 1 mmol amine or 200 µL *N, N*-dimethylamine (12 M in ethanol), 8 mol% catalyst, 60 bar H_2, 1 mL HFIP, 140 °C, 24 h. isolated yields. ‡, 0.5 mmol PCL, 5 bar NH_3 or 200 µL N, N-dimethylamine (12 M in ethanol), 8 mol% catalyst, 20 mol% Al(O-iPr)$_3$, 60 bar H_2, 1 mL HFIP, 140 °C, 36 h. * GC yields were determined using mesitylene as internal standard.

Next, to broaden the applicability of the catalyst, depolymerization of PET based post-consumer products were tested. For the direct amination of PET-based waste products such as water bottles **1f**, PET-bags **1g**, polyester cloth **1h**, and parcel boxes **1i** were collected and cut into small pieces (ca. 5-8 mm) (Figure 4). In the first set of experiments, all mentioned polymeric waste materials were treated with ammonia and para-xylylenediamine **3a** was obtained up to 80% yield. In case of polyester cloth **1h** the yield of desired amine was comparatively lower attributing to non-PET components present in the fabric. Similarly, plastic bottles and boxes can also be transformed with aniline **3b**, morpholine **2c** and dimethylamine **2d** to give the corresponding diamines in up to 70% isolated yields. Furthermore, The scalabilty of the current system was tested. For this purpose, PET bottles were collected and cut into pieces and 5 gram was tested for reaction and 67% of para-xylylenediamine **3a** was isolated. The broader applicability of current system was tested employing polylactic acid as well as polycarbonates, however, in both the cases satisfactory yield of desirer products were not obtained.

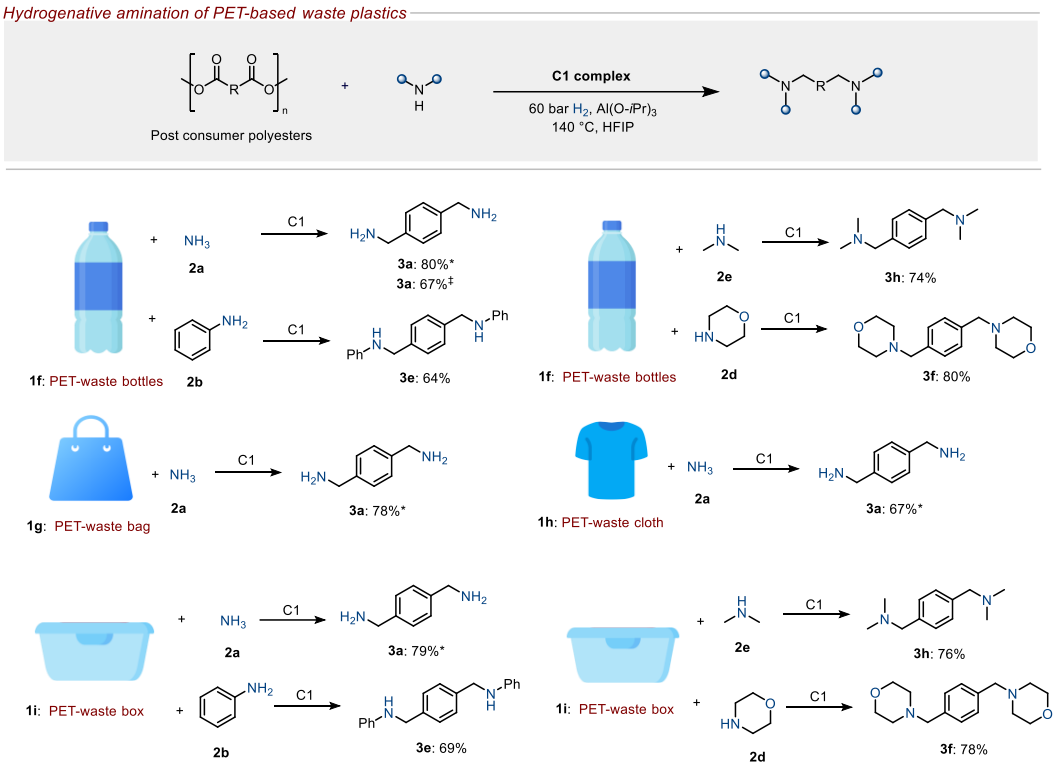


Figure 4. Depolymerization of post-consumer polyesters.

Reaction conditions. 0.5 mmol polymer, 5 bar NH_3 or 1 mmol amine or 200 µL *N,N*-dimethylamine (12 M in ethanol), 8 mol% catalyst, 20 mol% Al(O-*i*Pr)3, 60 bar H_2, 2 mL HFIP, 140 °C, 24 h. isolated yields. ‡Scale up - 5 gram PET-waste bottles, 5-7 bar NH_3, 8 mol% catalyst, 20 mol% Al(O-iPr)$_3$, 60 bar H_2, 60 mL HFIP, 140 °C, 24 h isolated yiled. *GC yields were determined using mesitylene as internal standard.

Hydrogenative amination of used cooking oil

Production of fatty amines are vastly increasing each year and their industrial synthesis generally is from triglycerides via "nitrile route".[120] During this process fatty acids formed from the hydrolysis of the triglycerides is treated with ammonia to obtain the corresponding nitriles, which are further reduced to the desired amines. Fatty alcohols are also employed these days and subsequent primary, secondary or tertiary fatty amines are obtained.[126] This well-established "nitrile route" for fatty amine synthesis possesses certain challenges including harsh reaction conditions, multiple steps, and formation of undesired mixtures of primary, secondary and tertiary amines which are difficult to separate. Moreover; considering the environmental impact of the process, a more efficient and sustainable alternative is essential as the current process contribute significantly to carbon footprints from energy intense steps and waste generation[127]. One pot catalytic system which can selectively transform vegetable oils to primary fatty amines minimises the mentioned challenges significantly. Platinum based heterogenous catalyst for amination of triglycerides was reported by Jamil *et al.* and after the reaction 51% of dodecylamine as well as 32% of didodecylamine was obtained via reductive homocoupling.[128] However, long reaction time (96 hours) as well as higher temperature (220 °C) constraints the applicability of this protocol. To the extent of our knowledge one pot synthesis of primary fatty amine from vegetable oil (used) has not yet studied.

For the ease of analysis during reaction optimization for amination of used cooking oils, triglyceride **1j** (C18) was chosen as model substrate. The reaction under standard condition for polyester depolymerization gave 19% of desired amine **3j** and 76% of corresponding amide **3k** (Table S4). Extending the reaction time showed no improvement. Interestingly increasing the catalyst loading to 6 mol% per ester unit gave stearyl amine **3j** in 88% yield. It was also observed that amount of co-catalyst is highly influential for higher fatty amine yield (Table S4). Amination of aliphatic substrates using ammonia are more challenging due to the high basicity of corresponding products and can lead to self-coupling, which

preferably forms secondary as well as tertiary amines.[129] In case of triglyceride no self-coupling was observed after the reaction and high primary amine selectivity was achieved. After optimising the reaction conditions, we applied Co-catalyst (**C1**) for the synthesis of fatty amines from used cooking oil. For this purpose, sunflower oil **1k** used for cooking was collected, filtered and fatty acid composition was analysed (see S8 for used cooking oil assay). It was observed that used sunflower oil contains 6.3% of C16 fatty acid (6.2% saturated, 0.1% unsaturated) and 91.55% C18 fatty acid (3.2% saturated, 88.35% unsaturated) composition along with 2.15% of other components. Interestingly, 70% of total fatty amine yield was obtained when the reaction was performed in the presence of ammonia and molecular hydrogen.

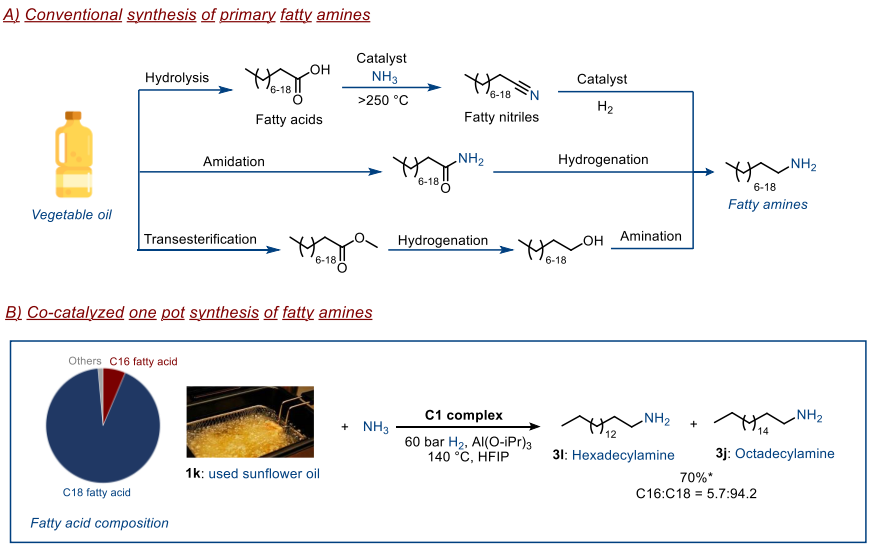


Figure 5. Hydrogenative amination of used cooking oil.

A) Conventional fatty amine synthesis. B) Co-catalyzed amination of used cooking oil.
Reaction conditions. 0.1 mmol oil, 5 bar NH_3, 6 mol% catalyst for each ester unit, 20 mol% Al(O-*i*Pr)$_3$ for each ester unit, 60 bar H_2, 2 mL HFIP, 140 °C, 24 h * GC yields were determined using mesitylene as standard.

Effect of polymer additives and control experiments

Polymer additives are chemicals added to the polymer to enhance polymer properties such as processability, life span, desired physical or chemical properties in the final product.[130] Even though the content of additives in polymers is mostly few percent, they have significant impact on polymer stability as well as properties. Types of additives include plasticizers, light stabilizers, flame retardants, anti-aging agents, anti-ozonants etc[131]. To evaluate the tolerance of developed catalyst in the presence of different polymer additives we performed model reaction in the presence of polymer stabilizers. Remarkably, employing *N*-isopropyl-*N*′-phenyl-1,4-phenylenediamine (IPPD; anti-ozonant) **4a** and methylene bis-benzotriazolyl tetramethylbutylphenol (bisoctrizole; light stabilizer) **4b** for the reductive depolymerization showed no catalyst inhibition and desired diamines were obtained in similar yield showcasing the applicability of the catalyst system for conversion of "real" plastics. Moreover, N-isopropyl-N′-phenyl-1,4-phenylenediamine (IPPD; anti-ozonant) **4a** was also tested as an amine source for depolymerization reaction, however only corresponding diol product 1,4-benzenedimethanol was obtained portraying IPPD was not reactive under standard conditions.
Hydrogenolysis as well as aminolysis (or ammonolysis) are two distinct depolymerization techniques widely used in polyester disassembling. While hydrogenolysis utilizes hydrogen to cleave the polymer into shorter chains, aminolysis involve the nucleophilic attack of the primary amino groups on the ester bond resulting in formation of new amide bonds. Present hydrogenative amination of polyesters can proceed via two general pathways: a) initial hydrogenolysis of polymer followed by reductive amination and b) depolymerization via ammonolysis followed by corresponding amide hydrogenation (supplemental Information, Scheme 2a). To unravel mechanistic insights of hydrogenative amination of polyesters several control experiments were performed. Depolymerization of PET resin **1a** performed in the absence of ammonia gave 1,4-benzenedimethanol (BDM) **3m** and EG in excellent yield, conforming the possibility of proposed hydrogenolysis pathway. Reductive amination of terephthalaldehyde **1i** in the presence of ammonia gave 92% of desired diamine product under optimized conditions. Interestingly, formation of the 60% terephthalamide **3n** was observed in the absence of the cobalt catalyst, demonstrating the possibility of ammonolysis mediated polymer disassembly. Possibility of terephthalamide **3n** hydrogenation under standard conditions were explored and excellent yield of *p*-xylene diamine **3a** was obtained. In case of aliphatic polyesters preferred ring closure was observed instead of diamine formation. We assume in the presence of cobalt catalyst depolymerization is happening via sequential hydrogenolysis or ammonolysis pathway. Subsequent imine hydrogenation in case of hydrogenolysis or amide hydrogenation in case of ammonolysis can form the corresponding amine intermediate. So formed amine can cleave C-O bond of polyester via intramolecular aminolysis reaction to form corresponding lactams (Supplemental information, Figure S11b)[132-133]. Notably depolymerization of polycaprolactone under standardized reaction conditions gave caprolactone [134], however extending the reaction time resulted in excellent yield of 1,6-aminoalcohol (Supplemental information, Figure S11). Interestingly, in case of PEA **1c**, and PES **1d** neither extending reaction time nor increasing catalyst loading or pressure gave hydrogenated products of caprolactam **3b** and butyrolactam **3c**. Hydrogenative amination reactions performed using lactams (caprolactam **3b** and butyrolactam **3c**) and lactone (ε-caprolactone) as starting material found C1 complex was capable of hydrogenating caprolactone **3p**, not caprolactam **3b** and butyrolactam **3c** (Supplemental information, Figure S11d). Experimental results and literature

precedents, suggest that current depolymerization technique involve domino hydrogenolysis-ammonolysis pathway in which hydrogenolysis-reductive amination strategy can be the major route.

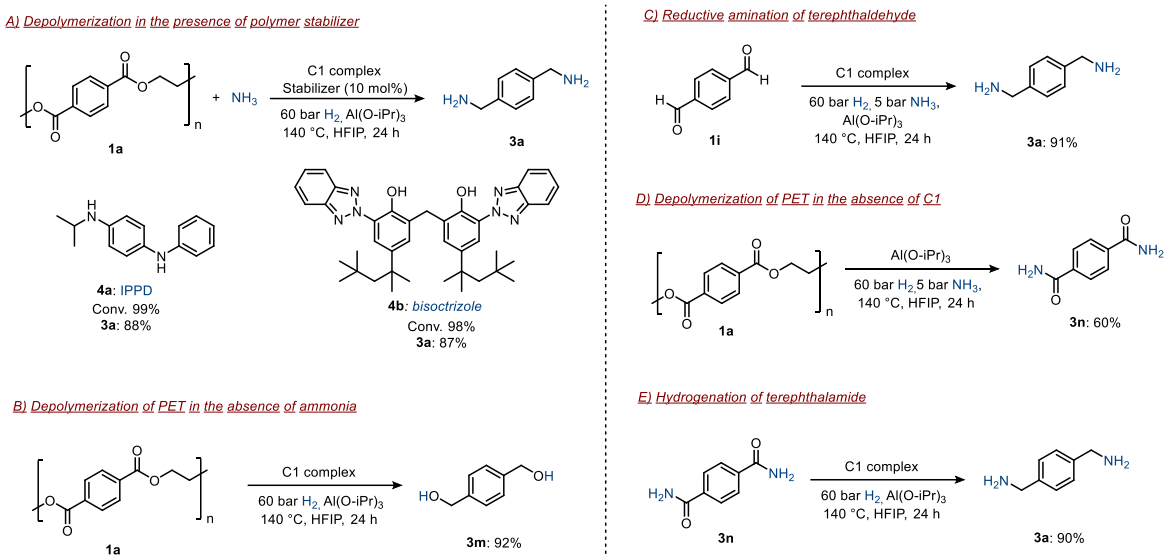


Figure 6.Effect of polymer additives and control experiments.

A) Depolymerization in the presence of polymer additives. B) Depolymerization in the absence of ammonia C) Reductive amination of terephthaldehyde D) Depolymerization of PET in the absence of C1 system E) Hydrogenation of terephthalamide.
Reaction conditions. 0.5 mmol of polymer or terephthalamide or terephthaldehyde, 5 bar NH_3, 8 mol% catalyst, 20 mol% $Al(O\text{-}iPr)_3$, 60 bar H_2, 1 mL HFIP, 140 °C, 24 h * GC yields were determined using mesitylene as standard.

CONCLUSION

The selective depolymerization of polyesters to amines represent a promising strategy for alleviating plastic waste and producing valuable chemicals. Herein, we introduce a highly efficient and thermally stable Co(II)-triphos(*p*-anisole) catalytic system for the hydrogenative depolymerization of polyesters and biogenic waste (used cooking oil). This approach leverages various amine precursors in the presence of molecular hydrogen to achieve selective depolymerization of technical grade as well as post-consumer polyesters to synthesize diverse amines and amino alcohol. Moreover, one pot synthesis of primary fatty amines from used cooking oil reported herein, not only overcomes the inherent challenges in industrial fatty amine synthesis but also can contribute to achieve the important 'waste-to-wealth' mission. While this approach aligns with waste mitigation and valuable chemical synthesis, further development of more economical ligands and solvents is of interest.

EXPERIMENTAL PROCEDURES

Resource availability

All experimental procedures are detailed in the supplemental information.

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Matthias Beller (matthias.beller@catalysis.de).

Materials availability

All reagents in this study are either commercially available or can be prepared as indicated in the supplemental information. All materials generated in this study are available from the lead contact upon reasonable request.

Data and code availability

All data needed to support the conclusions of this manuscript are included in the main text and/or the supplemental information.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://www.cell.com/chem.

Dedication

This work is dedicated to Professor Anilkumar Gopinathan, Mahatma Gandhi-University, Kerala, in recognition of his many contributions to science and education over the course of his distinguished career.

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AUTHOR CONTRIBUTIONS

F. P., R.V.J., and M. B. conceived and designed the experiments. R.V. J., and M.B. supervised the project F. P performed the catalytic experiments. F.P., R.V.J. and M.B. co-wrote the paper. All authors reviewed and contributed to the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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7.2. A highly selective cobalt catalyst for primary amine synthesis from carboxylic acids, esters and vegetable oils

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Author contributions:

For this manuscript, I performed the experimental work, including optimization, evaluation of the substrate scope and mechanistic experiments. In addition, co-wrote the manuscript and wrote the supporting information. As a first author my contribution to this work is approximately to 70%.

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A highly selective cobalt catalyst for primary amine synthesis from carboxylic acids, esters and vegetable oils

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ABSTRACT: The prevalence of carboxylic acids and esters in nature renders them as diverse and conveniently accessible building blocks for chemical synthesis. In this report, we present a straightforward cobalt-based catalytic system for the selective synthesis of primary amines from carboxylic acid derivatives and ammonia. The current system has been demonstrated to provide an efficient synthesis route for various amine derivatives. It exhibits excellent chemoselectivity, despite the complex reaction network. The optimal catalyst offers broad functional group tolerance, with both (hetero)aromatic and aliphatic substrates yielding the desired primary amines in good to excellent yields. The sophisticated Co-triphos$^{(p\text{-anisole})}$ system has also been demonstrated to be efficacious in the direct synthesis of fatty amines from a variety of vegetable oils. In comparison with the industrially applied fatty amine process, the approach of a one-pot fatty amine synthesis presented here represents a significant advancement in the field. This approach not only overcomes the inherent challenges but also aligns with sustainability goals by utilizing renewable feedstocks.

INTRODUCTION

Primary amine compounds play a pivotal role among the various known amine compounds. They offer a wide range of further transformations and are utilized extensively as starting materials and intermediates in chemical synthesis. As indicated in **Scheme 1a**, they are a crucial structural motif in active pharmaceutical ingredients (APIs), ligand libraries, CO_2 capturing agents, dyes, and polymers.[1-9] Apart from traditional stoichiometric methods such as Gabriel synthesis, Curtius rearrangement, and well-established reduction of nitrile or nitro groups, various catalytic protocols to synthesize primary amines have been developed.[10]

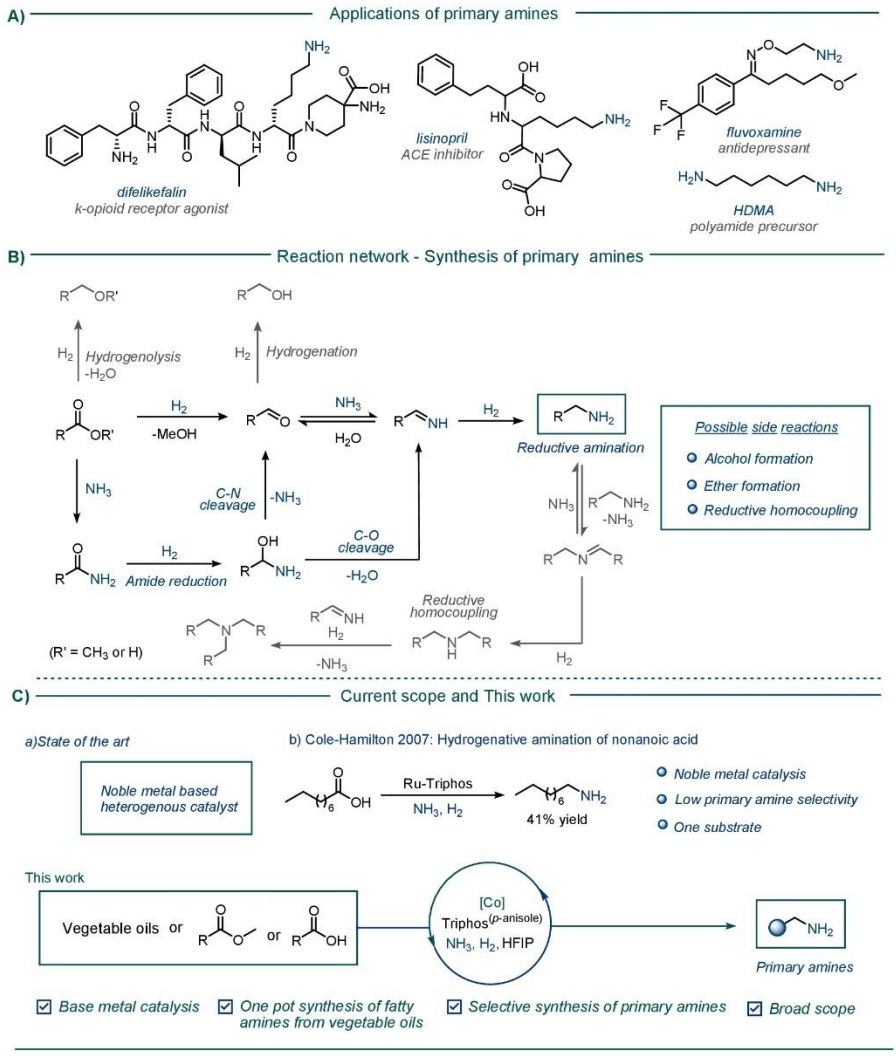
Even though there are many protocols available, most C-N bond formations in the chemical industry are done using only a few well-known synthetic methods. In this respect, one of the most important chemical reactions in the industry to form C-N bonds is the catalytic reduction of aldehydes or ketones using ammonia.[11] However, the sensitivity, high reactivity, and limited availability of aldehydes often impede their application in advanced chemical synthesis. In general, the synthesis of amines from more stable carboxylic acids and esters presents a viable alternative to the established approach.[12-14] Favourably, these substrates are more abundant in nature than olefins or aldehydes, which are derived from classic petrochemical feedstocks. Furthermore, the Haber-Bosch process, which utilizes green hydrogen, is anticipated to produce "green" ammonia in the forthcoming years. This ammonia is expected to be a readily available feedstock.[15-16] Consequently, the development of a synthetic toolbox for primary amines from carboxylic acid derivatives, hydrogen, and ammonia can be a significant sustainable approach.

Despite the steady progress in transition metal catalysis over the past decade with ammonia serving as a nitrogen source,[17-20] the selective formation of primary amines under mild conditions remains a formidable challenge. The deactivation of the catalyst by the formation of stable transition metal-ammonia complexes leading to less reactive metal-amine species,[21] and chemoselectivity issues arising from the reactivity of the initially generated primary amines compared to ammonia, which leads to secondary or tertiary amines are inherent obstacles in this field. Additionally, the control of chemoselectivity in reductive aminations employing carboxylic acids or esters is a highly challenging endeavor. The presence of multiple intermediates, along with the potential for side reactions stemming from the intrinsic reactivity of these intermediates, contributes to the complexity of the aforementioned reaction network (**Scheme 1b**). For instance, the partial reduction of esters or carboxylic acids to aldehydes is a slow process, and the generated aldehydes are more prone to reduction. Likewise, the presence of etherification and amide formation reactions complicates the selectivity to a considerable extent. Moreover, the primary amine selectivity can be decreased via reductive homocouplings, which result in the formation of the corresponding secondary or tertiary amines.

In the year 1994 Barrault et al. reported a $CuCrO_2$-based heterogeneous catalyst for the reductive amination of carboxylic acid and ester to primary amines. The reaction using methyl dodecanoate and dodecanoic acid in the presence of ammonia and hydrogen gave upto 27% of primary amines at 300 °C.[22] Further catalysts developed to date for the formation of primary amine from acids or esters are mostly heterogeneous catalysts based on Ru, Au, Ag or Pt, which require very high reaction temperatures (>200 °C) similar to seminal work.[23-24] Moreover, In the case of Ru-based catalytic system, it was difficult to prevent hydrogenation of the aromatic ring while employing aromatic substrates.[23] The first and only homogeneous catalyst developed for the conversion of carboxylic acids to primary amines was disclosed by Cole-Hamilton and co-workers.[25] In this study, the ruthenium-1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) system was employed for the amination of nonanoic acid (studied only one substrate) with ammonia. Unfortunately, the selectivity exhibited towards primary amines was found to be minimal.

In the past decade, a substantial number of studies in the area of homogeneous catalytic hydrogenation reactions have focused on the use of non-noble metal-based catalysts.[26] Based on our long-standing interest in this area,[27-29] a novel amination of polymers and (bio)waste was achieved recently.[30] Based on the realization of this waste-to-value concept, we present here a general hydrogenative amination of all kinds of carboxylic acids and esters, includingrenewables, using ammonia. This novel process facilitates the synthesis of a diverse array of primary amines with excellent selectivity (**Scheme 1c**).

Scheme 1. Overview: Cobalt catalyzed hydrogenative amination (A: Applications of primary amines; B: Reaction network; C: Current scope and this work).

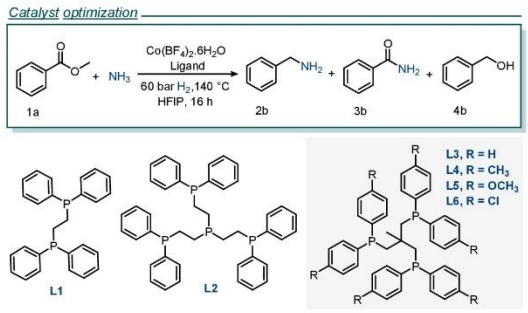


RESULTS AND DISCUSSION

Catalyst Development and Optimization of the Reaction System. In order to develop a general synthesis methodology of primary amines from readily accessible esters and acids, the direct amination of methyl benzoate with ammonia in the presence of molecular hydrogen was utilized as a model reaction. Traditional reductive aminations of carbonyl compounds have been predominantly carried out by employing heterogeneous noble metal-based materials.[17,31-32] However, over the past two decades, there has been a rapid emergence of molecularly defined 3d metal catalysts for a wide range of reductive transformations.[33-35] An illustrative elegant example, the groups of de Bruin and Elsevier reported a Co-triphos complex for challenging carboxylic acid hydrogenation.[36] A critical factor for the application of this and related catalysts is the stability of the active metal complex, which can be achieved using multi-dentate ligands. Therefore, the present investigation was initiated using a model system with cationic Fe,

Mn, Co, Ni, and Cu salts in the presence of various bi-, tri-, and tetradentate ligands, specifically dppe; (1,2-bis(diphenylphosphino)ethane; **L1**) tetraphos (tris[2-(diphenylphosphino)ethyl]phosphine; **L2**), and tripodal-triphos (tri-(1,1,1-tris(diphenylphosphinomethyl)ethane; **L3**) (**Table 1; Table S1**). To identify potential catalysts in a fast and reliable manner, *in situ* generated complexes were applied. Notably, in the hydrogenative amination of methyl benzoate **1a** with ammonia, in addition to the desired benzylamine **2b**, other byproducts such as benzamide **3b**, and benzyl alcohol **4b** can be anticipated as side products. As shown in the **Table S1**, with the exception of the triphos-ligated Co catalyst (Co-**L3**), the tested complexes did not promote the formation of **2b** but provided only **3b** (47-85%) and **4b** (8-24%). In contrast, applying Co-**L3**, resulted in the detection of 25% of the desired product **2b** accompanied by the formation benzamide **3b** and benzyl alcohol **4b** as provided in **Table S1**.

Table 1. Co-catalyzed hydrogenative amination: Testing different phosphine derivatives.



Entry	Co-Ligand	Conv. [%]	2b [%]	3b [%]	4b [%]
1	Co-**L1**	85	-	60	24
2	Co-**L2**	78	-	58	19
3	Co-**L3**	89	25	55	8
4	Co-**L4**	85	65	12	7
5	Co-**L5**	98	79	11	4
6	Co-**L6**	70	10	48	10
7	Co-**L5** (1:1.1)	54	11	39	2
8	Co-(**L5**) (1:2.1)	>99	82	10	5
9	Co-(**L5**)* (1:2.1)	>99	92	5	2

Reaction conditions. 0.3 mmol methyl benzoate, 5 bar NH_3, 8 mol% $Co(BF_4)_2.6H_2O$, 16 mol% ligand, 60 bar H_2, 1 mL HFIP, 140 °C, 16 h. *Similar conditions with 20 mol% Al(O-*i*Pr)$_3$. Conversion and yields were determined by GC using mesitylene as standard.

In order to enhance the selectivity of the process, three electronically distinct substituted triphos ligands (**L4-L6**) were prepared (Supplementary materials 2) and the corresponding *in situ* generated cobalt complexes were tested in the benchmark reaction (Table 1; Table S2). Here, triphos-substituted ligands with electron-donating groups (methyl, methoxy, **L4-L5**) displayed an increase in activity and selectivity for the formation of the desired product 2 (see **Table 1**, **Table S2**, entries 2-3 for further details). Conversely, the chloro-substituted ligand **L6** exhibited diminished activity and selectivity (see **Tables 1 and Table S2**). As demonstrated in **Table 1** (entry 8) using 1:2.1 Co-**L5** ratio the yield of **2b** was increased to 82%. In light of the elementary reaction steps implicated in the hydrogenative amination of methyl benzoate, we assumed that the employment of acidic or basic additives could enhance the overall transformation. Indeed, higher yields of the desired benzylamine **2b** were obtained in the presence of acidic co-catalysts (**Table S3**). Among these, inexpensive aluminum isopropoxide (Al(O-iPr)$_3$) demonstrated the most favorable outcome, with a 92% yield of the desired product (**Table 1**, entry 9).

Testing different solvents revealed that fluorinated ones, especially HFIP showed best activity and selectivity in the benchmark reaction (**Table S4**). Similar positive effects of fluorinated solvents have been observed in conventional reductive aminations[32-33], as well as other reactions in organic synthesis.[36-40] At this point, it should be noted that the HFIP solvent can be conveniently recycled and reused, which has been demonstrated (**Figure S2**).

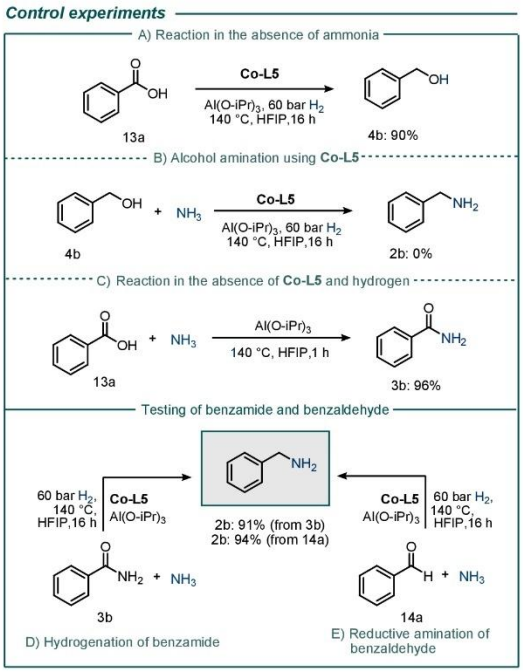
Additionally, the thermal stability of the cobalt system was investigated. It is noteworthy that the majority of 3d-metal phosphine complexes exhibit increased sensitivity in comparison to their noble congeners. Nevertheless, the catalyst demonstrated no deactivation in the model reaction at 180°C and exhibited remarkable chemoselectivity (see **Figure S3**).

Mechanistic investigation. As illustrated in **Scheme 1**, the reaction of **1a** with ammonia and hydrogen can result in the formation of multiple products. Achieving chemoselectivity necessitates the control of this intricate reaction network. From a mechanistic perspective, two general pathways exist for achieving the desired transformation: A. The catalytic hydrogenation of **1a** results in the formation of benzaldehyde, which reacts with ammonia to form an imine intermediate. Subsequent catalytic hydrogenation yields the primary amine **2b**. B. Alternatively, the primary amide **3b** could be formed first, followed by hydrogenation to give the desired amine **2b**. To differentiate between the two reaction pathways, a series of control experiments were conducted and the progression of the reaction and the intermediates were meticulously monitored (**Scheme 2**).

Under optimized reaction conditions excluding ammonia **13a** yielded benzyl alcohol **4b** in 90% yield (**Scheme 2a**). It is evident that under these conditions transformation of **4b** to **2b** is not possible (**Scheme 2b**), thereby precluding the possibility of an alcohol amination mechanism. Conversely, hydrogenation of benzamide **3b** also occurred under these conditions (**Scheme 2d**). As anticipated, reductive amination of benzaldehyde **13a** proceeded satisfactorily under these conditions, yielding 94% of the desired product, benzylamine **2b** (**Scheme 2e**). Notably, the Lewis acid-catalyzed formation of amide **3b** took place within 1 hour under standard reaction conditions (**Scheme 2c**) and this latter finding suggests that hydrogenative amination of esters and acids likely proceeds through a reaction pathway involving the corresponding amide as a major intermediate. To determine whether a reductive amination sequence is possible directly from carboxylic acids and esters under the employed conditions, the reaction system was investigated in more detail using further studies. The reaction of $Co(BF_4)_2{\cdot}6H_2O$ with **L5** (at a 1:2 metal-to-ligand ratio) was investigated, with the addition of hydrogen (60 bar) under varying temperatures using *insitu* NMR spectroscopy. Initial experiments were conducted in a Young NMR tube under argon atmosphere and the mixture of $Co(BF_4)_2{\cdot}6H_2O$ and **L5** was analyzed. The formation of a $[Co_2(triphos)_2(\mu\text{-}OH)_2](BF_4)_2$ complex, which exhibits antiferromagnetic properties, is reported when $Co(BF_4)_2{\cdot}6H_2O$ and triphos are mixed in a metal-to-ligand ratio of 1:1.[41] However, using two equivalents of **L5** in the current system resulted in a mixture of complexes (see SI for details). Specifically, the ^{31}P NMR spectrum showed that only a small

fraction of the triphos ligand initially coordinated to the metal (**Figure S4a**).

Scheme 2. Mechanistic studies: Control experiments.



Reaction conditions: 0.3 mmol substrate, 8 mol% $Co(BF_4)_2.6H_2O$, 2.1 equiv. of **L5** to [Co], 5 bar NH_3, 20 mol% Al(O-iPr)$_3$, 60 bar H_2, 1 mL HFIP, 140 °C, 16 h. GC yields using mesitylene as standard.

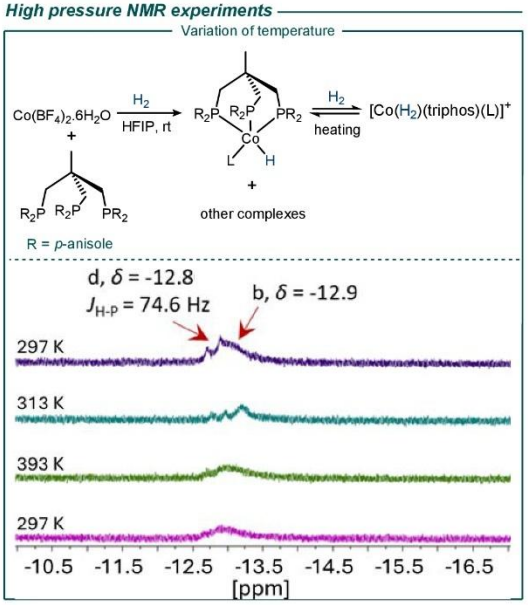
Moreover, an intense broad resonance corresponding to non-coordinated P-atoms was observed at -31.39 ppm. The broadening of the phosphorus signals can be attributed to the coupling of the quadrupolar Co nucleus. Following the addition of hydrogen at room temperature (297 K) within a sapphire NMR tube, a clear broad signal manifested in the hydride region of the ^{1}H NMR spectrum at -12.9 ppm (**Figure 1**). The corresponding ^{31}P NMR spectrum shows a decrease in the intensity of the signal attributed to non-coordinating P-atoms of **L5** at -31.3 ppm, and also the resonance at -0.5 ppm decreases (**Figure S4 b**). At the same time, a new broad resonance in the region for coordinated P ligand was detected at 20.4 ppm (**Figure S4 b**). This suggests the formation of a monohydride Co complex [HCo(triphos$^{(p\text{-anisole})}$)(L)], where L could be a P atom from another triphos ligand, given the addition of excess equivalents of ligand were added with respect to Co.[42]

The performance of NMR experiments at 120 °C (393 K) under 60 bar hydrogen revealed complications with the lock and shimming, indicating the potential formation of paramagnetic species, particularly at elevated temperatures. As the temperature increased, a doublet in the hydride region of the ^{1}H NMR spectrum was detected at -12.8 ppm. ^{1}H{^{31}P} measurements confirmed the $^2J(^{31}P,^1H)$ coupling as illustrated in **Figure 1**. The value of 74.6 Hz corresponds to trans coupling in a distorted geometry and is assigned to a dihydrogen cobalt complex [Co(H_2)(triphos$^{(p\text{-anisole})}$)(L)]$^+$. Such complexes have been previously reported for a similar system.[43] In the ^{31}P NMR spectrum at 120 °C, most of the signals of coordinated phosphorus could not be detected most likely due to broadening of the phosphorus signals, which is a known feature at increased temperatures.[42] Intriguingly, a signal at -17.4 ppm, corresponding to non-coordinating P-atoms became discernible at 40 °C. After cooling down the mixture to rt (297 K), a new broad signal in the ^{31}P NMR spectrum at -5.8 ppm was detected. Concurrently, the doublet in the hydride region of the ^{1}H NMR spectrum became more pronounced (**Figure S4b**). No further signals were detected in the region for non-coordinated phosphorus species.

Furthermore, we performed experiments to investigate the stability of *in situ* formed Co-H complex. Subsequent to the high-pressure measurements, hydrogen was released and the solution was transferred into a Young NMR tube under argon atmosphere. Then, the broad signal of the main complex in the hydride region of the ^{1}H NMR spectrum at -12.9 ppm, attributed to [HCo(triphos$^{(p\text{-anisole})}$)(L)] vanished completely (**Figure S4c**). The lability of this type of complex can be explained by its tendency to be protonated under acidic conditions to form the Co(III) dihydride [H_2Co(triphos$^{(p\text{-anisole})}$)(L)], followed by the irreversible loss of H_2.[42] This process is favored under an inert atmosphere but is inhibited under hydrogen (see SI for details). Furthermore, the doublet assigned to the stable hydrogen complex [Co(H_2)(triphos$^{(p\text{-anisole})}$)(L)]$^+$ at -12.8 ppm decreased notably in intensity and a new doublet appeared at δ = -11.6 ppm (2JP-H = 58.9 Hz), which can be attributed to an isomeric form.

The catalyst formation reaction was studied further using electron spray ionization mass spectrometry (ESI-MS). In the presence of benzoic acid as a model substrate, a sample from the reaction solution was analyzed after 1 hour of reaction time. The presence of the catalyst prototype [Co(triphos$^{(p\text{-anisole})}$)(benzoate)]$^+$ was detected by ESI-MS analysis at m/z = 984 (**Figure S5**).

Figure 1. Mechanistic studies: NMR experiments



Since traces of paramagnetic species were detected during the NMR measurements, we further explored the reaction mechanism using EPR spectroscopy. The EPR analysis of the *in situ* Co

catalyst (metal to ligand ratio 1:2) in HFIP at 95K exhibits an EPR signal of rhombic symmetry at $g_1 = 2.250$, $g_2 = 2.070$, $g_3 = 1.978$, and $A_1 = 174$ MHz, $A_2 = 148$ MHz, $A_3 = 148$ MHz (estimated from EPR simulation, **Figure 2**) with a complex hyperfine splitting due to the coupling of the unpaired electron (S = 1/2) with ^{59}Co nuclear

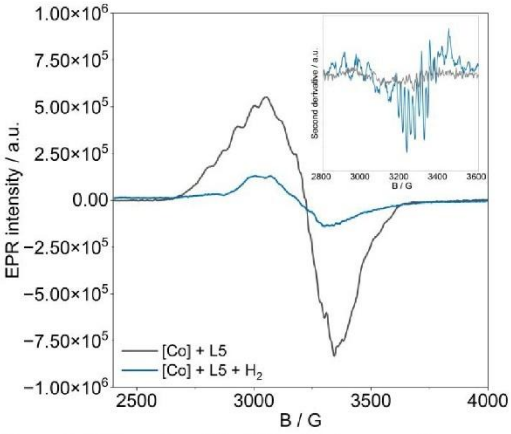


Figure 2. EPR spectra of **Co-L5** in the absence and presence of hydrogen in HFIP measured at 95K.

spins (I = 7/2, 100%). The eight-line hyperfine structure of the second component can be seen more clearly in the second derivative EPR spectra (**Figure 2**). Subsequently, we investigated the *in situ* prepared [Co] catalyst under hydrogen atmosphere. The obtained EPR spectra showed a single broad signal at g = 2.1 with lower intensity compared to **Figure 2** and without hyperfine structure (**Figure 2**). Therefore, we assume that during the reaction structural reorganization of the initial [Co] complex takes place. Moreover, the EPR analysis of the [Co] catalyst with BzOH in HFIP (**Figure 3**) showed an EPR signal of rhombic symmetry with minor differences in parameters at $g_1 = 2.205$, $g_2 = 2.006$, $g_3 = 1.983$, and $A_1 = 174$ MHz, $A_2 = 147$ MHz, $A_3 = 162$ MHz and with the well-resolved eight-line hyperfine structure. Additional splitting of the hyperfine interaction with three ^{31}P nucleus (I = 1/2) was observed in the second derivative EPR spectra. These Hamiltonian parameters are similar with those of Co phosphine complexes with square-planar or square-pyramidal geometries of low-spin Co (II) ions.[41,44]

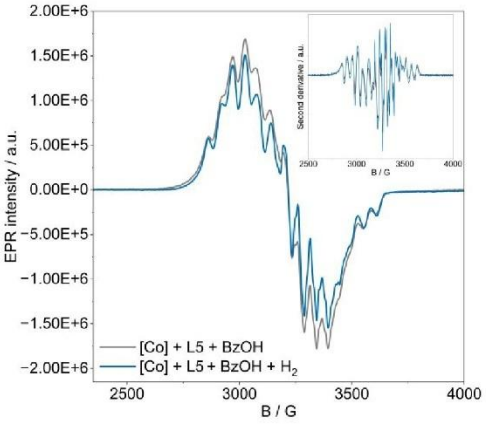
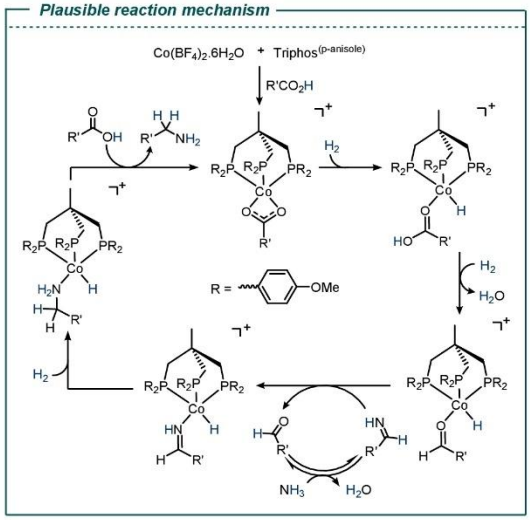


Figure 3. EPR spectra of **Co-L5** and benzoic acid in the absence and presence of hydrogen in HFIP measured at 95K.

To learn more about the active cobalt species, we performed EPR measurements on the reaction mixture after catalysis. The resulting reaction mixture showed a similar Co(II) signal to that shown in **Figure 2**. but with slightly lower intensity. Furthermore, these results suggest the presence of a cobalt substrate complex, [Co-triphos$^{(p\text{-anisole})}$benzoate]$^+$, which was confirmed by ESI-MS. Additionally, no radical intermediate signal was detected during further control measurements, which excludes a radical mechanism. A mercury poisoning test was conducted with the **Co-L5** catalyst, and no considerable inhibition of catalysis was observed, confirming that the reaction proceeds via homogeneous catalysis and that the formation of Co nanoparticles does not occur (see Supporting information, **Figure S6**).

Scheme 3. Mechanistic proposal for the "non-amide" involved reaction pathway.

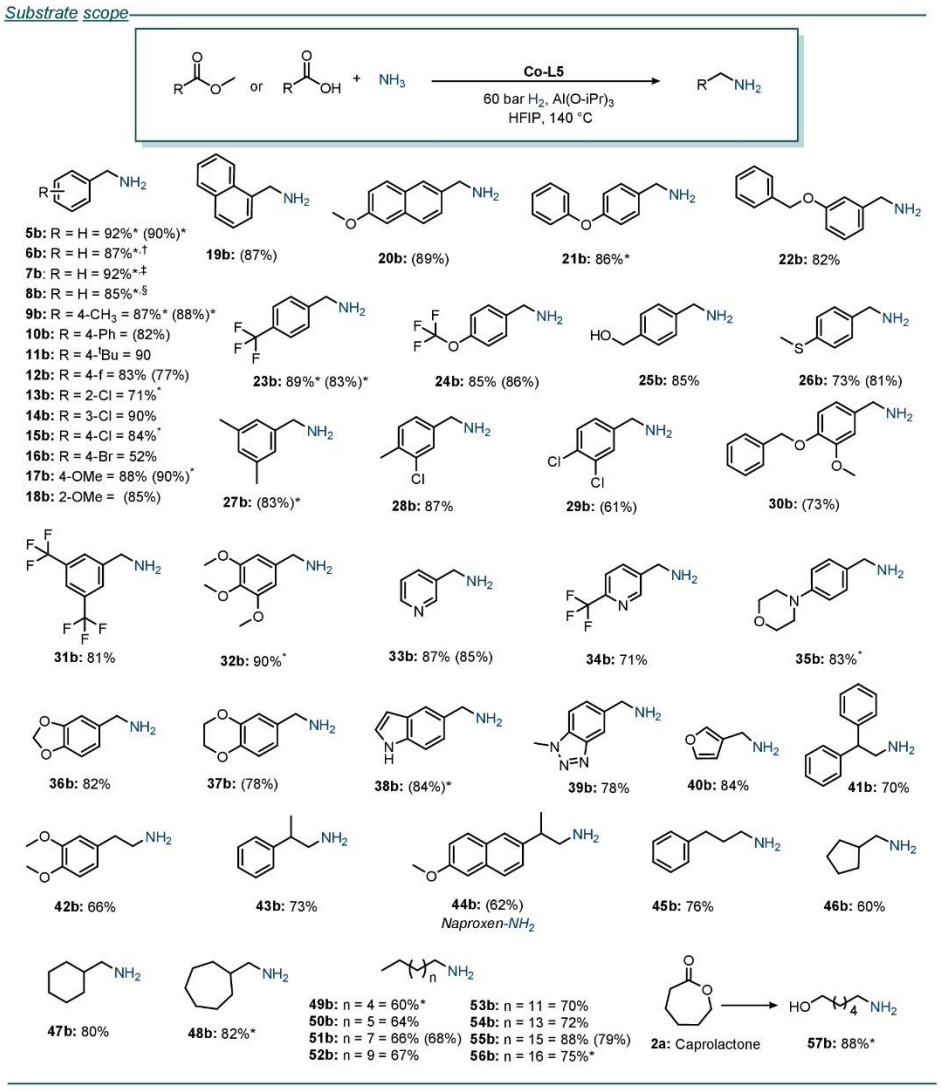


Based on all the experimental data obtained and the literature precedents, we propose the following mechanism. First, the formation of Co(triphos(p-anisole))(alkanoate) species takes place followed by heterolytic hydrogen splitting, leading to a Co-H complex. After hydride addition to the carbonyl carbon, subsequent second heterolytic hydrogen splitting step takes place. After one equivalent of water is expelled, a [Co(triphos$^{(p\text{-anisole})}$)(H)(aldehyde)]$^+$ species is formed. Next, the primary imine formed from the aldehyde in the presence of ammonia generates the Co-imine complex. Finally, after β-hydride addition and H_2 coordination, followed by hydrogenolysis, the primary amine is released, and the catalytically active species is regenerated (**Scheme 3**).

Synthesis of primary amines from esters and carboxylic acids: Scope and applications. In order to illustrate the synthetic utility of the presented catalyst system, an investigation was conducted into the applicability of the Co-L5 system for the hydrogenative amination of diverse esters and carboxylic acids (Scheme 4). As demonstrated in Scheme 4, a range of carboxylic acids, including aromatic, heterocyclic, and aliphatic derivatives, along with esters, were subjected to amination reactions with ammonia. This process resulted in the generation of primary amines, exhibiting yields that ranged from good to excellent. Amination of methyl esters and the

corresponding carboxylic acids showcased similar activity and selectivity during the process. In addition to conventional substrates, a number of functionalized substrates gave the corresponding primary amines in high yields. For instance, halogenated benzylamines were obtained in yields up to 90% (**12b-16b**). Substrates containing methoxy-, benzyloxy-, trifluoromethoxy-, hydroxy-, and thioether groups yielded the corresponding benzylamines in up to 89% (**17b-26b**).

Scheme 4. Substrate scope – **Co-L5** hydrogenative amination of various carboxylic acids and esters.

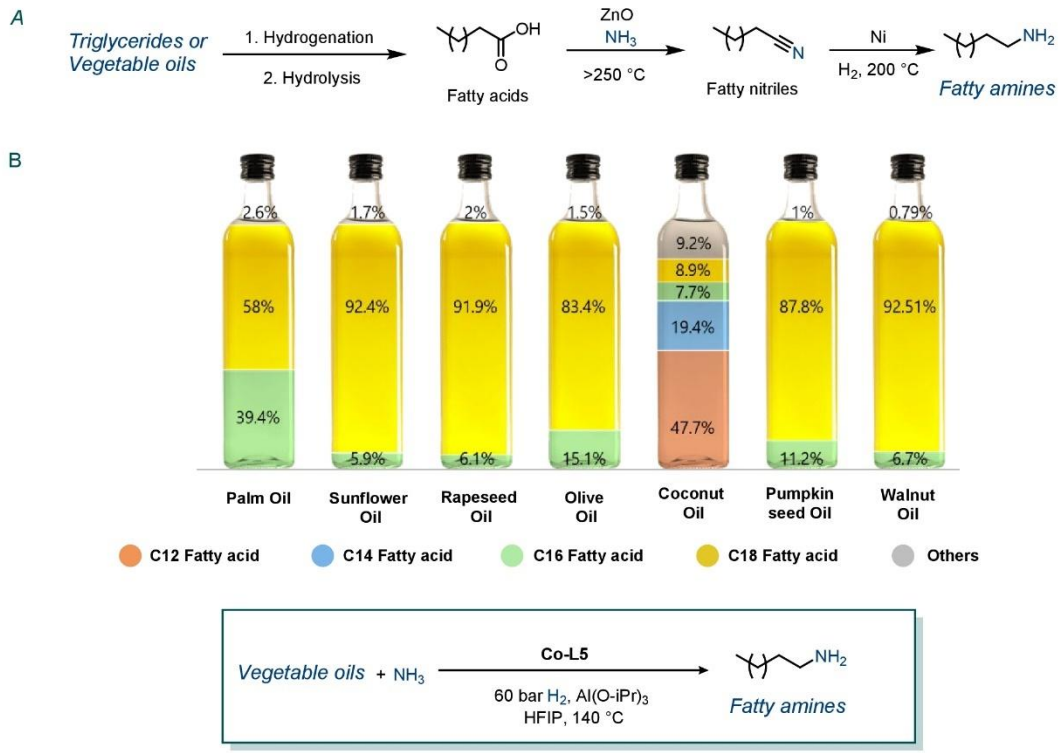


Reaction conditions: 0.5 mmol ester or acid, 8 mol% $Co(BF_4)_2.6H_2O$, 2.1 equiv. of **L5** to [Co], 5 bar NH_3, 20 mol% $Al(O\text{-}iPr)_3$, 60 bar H_2, 1 mL HFIP, 140 °C, 16-20 h, isolated yields. *GC yields using mesitylene as standard. †From ethyl benzoate, ‡from butyl benzoate, §from tert-butyl benzoate. Note: Yields given in the parenthesis corresponds to primary amines obtained from acids.

Additionally, the amination of di- and tri-substituted methyl benzoates and acids were efficiently executed (**27b-32b**). Furthermore, a series of amines comprising significant heterocycles, including pyridine, furan, benzodioxole, benzodioxane, indole, benzotriazole, and morpholine were synthesized from the corresponding heterocyclic esters and acids (**33b-40b**). In general, the re-duction of aryl-alkyl and aliphatic substrates is more challenging due to the reduced selectivity and self-coupling reactions, which typically results in the formation of secondary amines.

Nonetheless, these substrates were also selectively synthesized with up to 82% yield, representing a substantial advancement over the previously reported cobalt-catalyzed reductive amination of aldehydes (**41b-56b**).[31] Apart from methyl esters, different kinds of esters, e.g. ethyl, butyl- and tertiary butyl benzoates provided the respective primary amines (**6b-8b**). In addition, ε-caprolactone was used as an example of lactones, which can be converted to the corresponding amino-alcohol (**57b**). Amino alcohols are important structural motifs with a wide range of diverse pharmaceutical applications.

Scheme 5. Straightforward synthesis of fatty amines from vegetable oils.



6a: Palm oil

54b: n = 12, Hexadecylamine
55b: n = 14, Octadecylamine
71%
C16:C18 = 40.7:59.2

7a: Sunflower oil

54b: n = 12, Hexadecylamine
55b: n = 14, Octadecylamine
74% (68%)*
C16:C18 = 5.5:94.4

8a: Rapeseed oil

54b: n = 12, Hexadecylamine
55b: n = 14, Octadecylamine
70% (59%)*
C16:C18 = 5.4:94.6

9a: Olive oil

54b: n = 12, Hexadecylamine
55b: n = 14, Octadecylamine
73%
C16:C18 = 14.6:85.3

10a: Walnut oil

54b: n = 12, Hexadecylamine
55b: n = 14, Stearylamine
69%
C16:C18 = 5.5:94.4

11a: Pumpkin seed oil

54b: n = 12, Hexadecylamine
55b: n = 14, Octadecylamine
68%
C16:C18 = 11.3:88.6

12a: Coconut oil

52b: n = 8, Dodecylamine
53b: n = 10, Tetradecylamine
54b: n = 12, Hexadecylamine
55b: n = 14, Octadecylamine
60%
C12:C14:C16:C18 = 54.6:27.2:8.3:9.8

Reaction conditions: 0.1 mmol vegetable oil, 6 mol% $Co(BF_4)_2.6H_2O$ each ester unit, 2.1 equiv. of **L5** to [Co], 20 mol% $Al(O\text{-}iPr)_3$ for each ester unit, 5 bar NH_3, 60 bar H_2, 2 mL HFIP, 140 °C, 24 h. Yields given corresponds to total yield of all fatty amines obtained after reaction, GC yields determined by using mesitylene as standard. *Isolated yield.

According to a report by the FDA, the presence of amino alcohol residues has been detected in over 30% of small-molecule drugs, underscoring their importance in contemporary drug design.[45-47] The developed protocol has demonstrated broad applicability, providing products with yields ranging from good to excellent. Nevertheless, a few limitations were observed, e.g. in case of halogenated substrates (**13b and 16b**), reductive dehalogenation of bromo and chloro substituents could be observed in varying amounts.

Conversion of renewable vegetable oils to primary fatty amines. Among the array of renewable feedstocks, vegetable oils have emerged as a predominant biomass-based feedstock in terms of scale. Indeed, the annual production of vegetable oils exceeds 200 million metric tons, and has multitude of applications,[48-49] and potential use in biorefinery concepts.[50-51] These applications are relevant to the production of numerous everyday products, including soaps, candles, cosmetics, and food products.[52]

Notably, naturally occurring and commercially available vegetable oils constitute mixtures of different triglycerides of fatty acids. The valorization of these compounds typically necessitates a series of functionalization and purification steps. For instance, the predominant current production of primary fatty amines - a highly significant class of chemicals due to their wide applications in personal care products, household products, and allied industries,[53-56] - proceeds via the so-called nitrile route from vegetable oils. The process consist of three distinct steps (**Scheme 5a**): The first step of the synthesis of fatty amines involves involves the hydrogenation of the fatty acid alkyl chain followed by the hydrolysis of vegetable oil to release fatty acids. The second step includes the amination-dehydration of fatty acids at a high temperatures (>250°C) in the presence of metal oxide catalysts, such as alumina or zinc oxide. The third step is a final catalytic hydrogenation of fatty nitriles, which results in the desired amine products.[57-60] Despite being well-established, this method of fatty amine synthesis is characterized by several drawbacks such as harsh reaction conditions and multiple steps. In addition, the formation of undesired mixtures of primary, secondary, and tertiary amines complicates the process, as their separation is difficult.

A more straightforward aopproach, which can selectively transform vegetable oils to primary fatty amines would minimize the above mentioned challenges significantly. First report of hydrogenative amination of triglycerides were shown in a patent application by Henkel, using $ZnO\text{-}Al_2O_3$. The seminal work showed excellent selectivity towards amines however significantly harder reaction conditions (250 bar H_2 and 310 °C) were required.[61] In the year 2016 a homogeneous catalytic method for the direct synthesis of N-alkylated amines from triglycerides under hydrogen was reported by our group using the $[Ru(acac)_3]$/Triphos/$HNTf_2$ catalytic system (acac - acetylacetonate; $HNTf_2$ - triflimide). Although this study represented a significant step forward in this area, the catalytic system was not tested for primary amine synthesis.[13] In 2019, Shimizu and co-workers demonstrated platinum based heterogenous catalyst for direct conversion of triglycerides to fatty amines. The reaction performed using different triglycerides gave upto 51% of dodecylamine and 32% of didodecylamine.[63] Although the system was tested for 6 different triglycerides, the long reaction time (96 hours) as well as high temperature (220 °C) constraints the applicability of this protocol. During the preparation of the manuscript, Mizugaki and co-workers presented a general direct reductive amination of triglycerides to fatty amines using a titanium oxide-supported platinum–molybdenum (Pt–Mo/TiO_2) catalyst. Reactions were performed milder conditions (10 bar H_2, 180 °C, and 16-48 h) compared to previous reports. The reusability of the catalyst as well as testing wide variety of triglycerides for the synthesis of amines are advantages of the developed system. However, employing ammonia for reductive amination yielded 74% of secondary amine instead of primary fatty amine.[62]

Using our **Co-L5** system, different fatty amines can be conveniently obtained from pure triglycerides (Supporting information **Figure S7**) as well as natural vegetable oils (**Scheme 5**). For the initial screening 3 diverse commercially available triglycerides were chosen (C7, C16, and C18). Under standard reaction conditions the amination of commercially available triglyceride **5a** gave the corresponding primary fatty amines in less yields along with generation of corresponding fatty amide (Supporting information **Figure S7**). Prolonging the reaction time to 24 hours and 6 mol% catalyst loading for each ester unit gave 86% yield of stearyl amine.

After triglyceride optimization 7 distinct vegetable oil were chosen for hydrogenative amination. Fatty acid assay was generated after hydrolysis for each vegetable oil for the ease of analytics before reaction (**Table S6**). For the majority of vegetable oils characteristic C16 and C18 fatty acids were prominent whereas, coconut oil had a high composition of C12 fatty acid and the presence of C14 fatty acid was also observed (**table S6**). Palm oil **6a**, sunflower oil **7a**, rapeseed oil **8a**, olive oil **9a**, walnut oil **10a**, pumpkin seed oil **11a**, and coconut oil **12a** underwent reductive amination with ammonia and molecular hydrogen to give primary fatty amines C12-C18 in up to 74% yields (**Scheme 5B**, products **52b-55b**). In agreement with the results using triglycerides, the developed catalyst demonstrated a high degree of selectivity for the formation of primary amines, with no evidence of homocoupling of primary amines. It is also noteworthy that the hydrogenation of the double bond was observed in all of the oils utilized in this study, which in turn simplifies downstream processing in fatty amine synthesis.

CONCLUSIONS

In summary, a general catalytic route towards the synthesis of primary amines from carboxylic acids derivatives and ammonia in the presence of molecular hydrogen is presented. This approach is characterized by its selectivity as well as efficiency, making it a promising methodology for preparation of diverse class of valuable compounds. The success of this straightforward hydrogenative amination process is contingent upon the implementation of two critical components: the use of the stable and robust cobalt-based catalyst **Co-L5** and the employment of HFIP as solvent. Among various triphos derivatives synthesised, the triphos$^{(p\text{-anisole})}$ ligand demonstrated superior activity and selectivity. A broad variety of carboxylic acids and esters provided both (hetero)aromatic and aliphatic primary amines in high to excellent yields. The advantages of this straightforward methodology are exemplified by the utilization of renewable feedstocks and vegetable oils for the one-pot synthesis of fatty amines. Starting from a series of seven distinct commercial-grade vegetable oils, each exhibiting a unique fatty acid composition, provided fatty amines with yields up to 74% with excellent selectivity towards primary amines. Compared to existing industrially synthesis of fatty amines, the current strategy of one-pot fatty amine synthesis

presented herein represents a considerable step forward in this field.

ASSOCIATED CONTENT

Supporting Information.

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Author Contributions
F. P., R.V.J., and M. B. conceived and designed the experiments. R.V. J., R.J. and M.B. supervised the project F. P. performed the catalytic experiments. F.P. and V.C. synthesized triphos ligands. F.P. and D.P.F performed high pressure NMR experiments. T.H.V. and J.R. performed EPR measurements. F.P., R.V.J. and M.B. co-wrote the paper. All authors reviewed and contributed to the manuscript.

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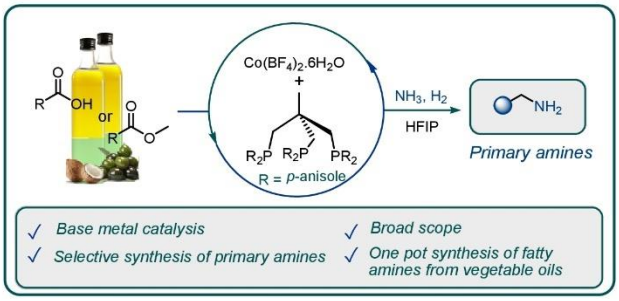
Co(BF4)2.6H2O
NH3, H2
HFIP
NH2
Primary amines
R = p-anisole
✓ Base metal catalysis
✓ Selective synthesis of primary amines
✓ Broad scope
✓ One pot synthesis of fatty amines from vegetable oils

7.3. Cu-Oxide Nanoparticles Catalyzed Synthesis of Nitriles and Amides from Alcohols and Ammonia in Presence of Air

Thirusangumurugan Senthamarai, Fairoosa Poovan, Asma M. Alenad, Nils Rockstroh, Jabor Rabeah, Stephan Bartling, Eszter Baráth, Kishore Natte, and Rajenahally V. Jagadeesh

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Electronic supporting information is available online.

Author contributions:
In this work, I involved in the catalyst development and evaluation of substrate scope, I performed reproducibility tests as well as revision works of the manuscript. As a second author my contribution to this work is approximately to 30%.

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Cu-Oxide Nanoparticles Catalyzed Synthesis of Nitriles and Amides from Alcohols and Ammonia in Presence of Air

*Thirusangumurugan Senthamarai, Fairoosa Poovan, Asma M. Alenad, Nils Rockstroh, Jabor Rabeah, Stephan Bartling, Eszter Baráth, Kishore Natte, and Rajenahally V. Jagadeesh**

The synthesis and functionalization of nitrogen-containing compounds continue to be important due to their wide applications. In particular, the preparation of nitriles and amides applying cost-effective and green methodologies is of central importance because these products represent valuable fine and bulk chemicals and serve as key precursors and central intermediates in organic synthesis and drug discovery as well as materials. Here, the preparation of nitriles and primary amides from alcohols and ammonia by a heterogeneous Cu-catalyzed aerobic oxidation process is reported. The optimal catalyst for this synthesis is based on supported copper oxide-nanoparticles, which are prepared by the impregnation and pyrolysis of simple copper nitrate on carbon. Applying these reusable nanoparticles, various simple, substituted, and functionalized aromatic, heterocyclic, and aliphatic nitriles are synthesized starting from inexpensive and easily accessible alcohols and ammonia in the presence of air. In addition, the synthesis of selected primary amides in a water medium is also performed using these Cu nanoparticles.

1. Introduction

The development of cost-effective and sustainable catalytic methodologies for the synthesis and functionalization of nitrogen-containing compounds, which represent highly valuable and widely used products, continues to be important.[1–11] Among N-containing compounds, nitriles[3–7] and amides[8–11] constitute valuable fine and bulk chemicals, which are used as precursors and intermediates for essential chemical products, pharmaceuticals, agrochemicals, and biomolecules as well as materials. Noteworthy, nitrile and amide functionalities serve as vital motifs in many life science molecules.[5–13] Regarding the synthesis of nitriles, simple ones are produced industrially by ammoxidations, which in general are performed in the gas phase at drastic conditions (>300 °C).[12–14] Unfortunately, these reactions cannot be applied to the synthesis of structurally challenging nitriles.[12–14] On the other hand, the preparation of functionalized nitriles still relies on nucleophilic cyanation reactions of aryl or alkyl halides using toxic and waste-generating reagents such as HCN or metal cyanides.[15,16] For a sustainable point of view, the synthesis of functionalized and structurally diverse nitriles from inexpensive and easily accessible starting materials using green and more abundant reagents is highly beneficial and scientifically interesting. In this regard, the preparation of nitriles from alcohols and ammonia by catalytic aerobic oxidations is considered to be an appropriate and green methodology.[17–28]

In general, the creation of an amide bond is of fundamental importance in organic synthesis, medicine, and biology.[8–11] Classically, primary amides are prepared by the reaction of activated carboxylic acid derivatives such as chlorides and anhydrides with ammonia or from carboxylic acids with ammonia in presence of coupling agents.[11,29–31] However, these methodologies employ stoichiometric quantities of activating reagents, which generate significant amounts of wastes and are low atom-efficient reactions. Notably, the catalytic synthesis of primary amides starting from alcohols and ammonia in water represents a convenient and green methodology.[18,32–34]

Noteworthy, alcohols serve as potential feedstocks to produce various chemicals because they are easily accessible and inexpensive as well as some of them can be obtained from renewable resources.[35–37] Hence, alcohols are considered as suitable starting materials for the synthesis of nitriles and amides.[17–29,32–34] The other starting, ammonia is an abundant and green chemical, which is produced in >175 million tons per year scale.[38,39] Noteworthy, this bulk chemical is extensively used to produce urea and other fertilizers as well as various fine and bulk chemicals.[38,39] In order to synthesize nitriles

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and amides from alcohols, the use of an oxidant is essential. Among various oxidants, the air is "ideal" because it is more abundant, inexpensive, green, safer to use, and produces only water as the by-product.[40]

To carry out aerobic oxidation of alcohols to prepare nitriles and amides the applicability of catalysts is crucial. In the past, catalysts based on heterogeneous Au, Ru, Fe, Co, Mn, and V,[17–28] as well as homogeneous Fe-[23] and Cu-[22] based ones have been successfully applied for the synthesis of various nitriles from alcohols and ammonia; most of these utilize molecular oxygen as oxidant. For the synthesis of primary amides from alcohols and ammonia Mn, Co, V, and Au-[18,28,32–34] based systems are reported.

Despite these achievements, the development of appropriate catalysts, which should work in a selective and efficient manner, especially in the presence of air, is still desired. Regarding potential catalysts, earth-abundant metal-based ones are desirable due to their relatively low costs and availability. More specifically, heterogeneous materials are in general preferable for sustainable and cost-efficient chemical synthesis.[41–50] Here, we report the preparation of carbon-supported copper nanoparticles, which constitute excellent aerobic oxidation catalysts for the synthesis of aromatic, heterocyclic, and aliphatic nitriles starting from alcohols and ammonia. Moreover, using these Cu-nanoparticles the synthesis of primary amides directly from alcohols and ammonia in water is also performed.

2. Results and Discussion

2.1. Preparation and Catalytic Evaluation of Cu-Based Nanoparticles

Among heterogeneous catalysts, supported nanoparticles are more desirable due to their advantages such as tunable activities and selectivities as well as stability and convenient recycling and reusability.[41–50] In recent years we focused on the development of such nanostructured materials for organic synthesis.[18,47–50] As a result, Fe-, Co- and Ni-based nanoparticles-based catalysts have been prepared and applied for the hydrogenation, amination, and oxidation reactions involving functionalized and structurally complex molecules.[18,47–50] However, until now, we have not developed related Cu-based nanocatalysts for essential organic reactions.

In this regard, we turned our interest to prepare Cu-nanoparticles-based catalysts for the synthesis of nitriles and amides using air. To prepare these nanoparticles, we applied a general and commonly used impregnation and pyrolysis method (**Figure 1**). In a typical experiment, $Cu(NO_3)_2.3H_2O$ was dissolved in DMF by stirring at 150 °C for 30 min. To this solution, Vulcan XC-72R (as carbon powder) was added and stirred for 4 h at 150 °C. Next, DMF was evaporated slowly and dried to obtain immobilized solid materials. Finally, this material was pyrolyzed at different temperatures under argon to obtain carbon-supported copper oxide nanoparticles (Figure 1).

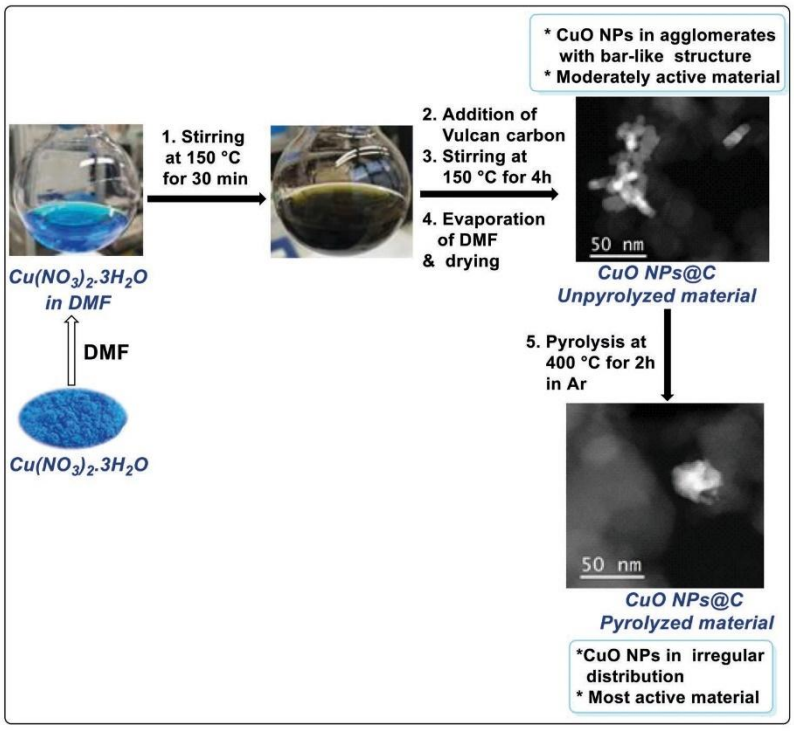
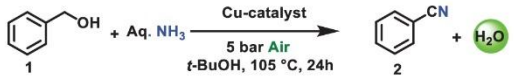


Figure 1. Preparation of carbon-supported CuO nanoparticles.

Table 1. Cu-catalyzed synthesis of benzonitrile from benzyl alcohol and ammonia in the presence of air: Evaluation of catalytic activities.



Entry	Catalyst	Conv. [%]	Yield [%]
1	$Cu(NO_3)_2.3H_2O$	3	2
2	$Cu(NO_3)_2$-carbon	37	33
3	CuO@C unpyrolyzed	67	60
4	CuO@C-300	75	70
5	CuO@C-400	>99	98
6	CuO@C-600	85	83
7	CuO@C-800	83	79

Reaction conditions: 0.5 mmol alcohol, 200 µL aq. NH_3 (28–30% in water), 30 mg heterogeneous catalyst (3-4 mol% of Cu), 5 bar air, 2 mL *t*-butanol, 105 °C, 24 h. Conversions and yields were determined by GC using n-hexadecane as standard. In the case of homogeneous catalysis conditions 4 mol% of $Cu(NO_3)_2.3H_2O$ was used.

In order to select the optimal Cu-based catalyst, all the prepared materials were tested for the synthesis of benzonitrile from benzyl alcohol and aqueous ammonia in the presence of air as the model reaction. First, $Cu(NO_3)_2.3H_2O$ was tested and found that it was not active (**Table 1**, entry 1). Next, the mixture of copper nitrate and Vulcan carbon powder was tested and some activity from this system was observed (37% Conv., 33% yield; Table 1, entry 2). To our surprise, the impregnated, non-pyrolyzed material, CuO@C, produced 60% of the desired product (Table 1, entry 3). After pyrolysis of this CuO@C material, we observed a further increase in the activity. As a result, materials pyrolyzed at different temperatures (CuO@C-300-800; 300-800 indicates the applied pyrolysis condition in °C) were tested and the one pyrolyzed at 400 °C was found to be the most active and selective catalyst (Table 1, entries 4–7). From this material (CuO@C-400), complete conversion of benzyl alcohol took place and produced 98% of the desired product, benzonitrile (Table 1, entry 5). On the other hand, the materials pyrolyzed at 600 (CuO@C-600) and 800 °C (CuO@C-800) also exhibited good activities, but less compared to CuO@C-400.

2.2. Characterization of Cu-Oxide Nanoparticle-Based Catalysts

To know the structural features and the varying catalytic activities, these novel Cu-based materials were characterized using state-of-the-art analytical techniques such as X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy (EDX), electron energy-loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS). XRD patterns of both unpyrolyzed (CuO@C) and pyrolyzed catalysts (CuO@C-400 and CuO@C600) as well as recycled ones (CuO@C-400R), showed the presence of mainly CuO particles (**Figure 2**).

In the case of unpyrolyzed material, (CuO@C-unpyrolyzed), the agglomeration of particles in bar-like oxidic structures in the range of 20 to 180 nm is observed (**Figure 3**a,b and

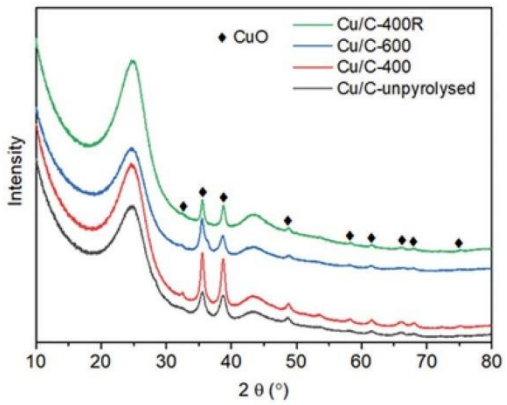


Figure 2. XRD patterns of Cu-based materials.

Figures S1 and S2, Supporting Information). Scanning transmission electron microscopy (STEM) of the most active material CuO@C-400 showed the formation of CuO particles in an irregular shape with sizes ranging from about 20 to 130 nm (see Figure 3c,d). Electron energy-loss spectroscopy (EELS) of CuO@C-400 revealed the presence of both Cu(II)- and Cu(I)-oxide nanoparticles (see Figure S3, Supporting Information). The material obtained at higher pyrolysis temperature (CuO@C-600) also contained CuO particles in an irregular shape with sizes ranging from about 4 to 150 nm (Figure 3e,f). In CuO@C-600, we also observed some extent of agglomeration of CuO particles. The sample obtained after one run, CuO@C-400R, looks very similar to CuO@C-400, but the size range of particles is larger (from about 3 to 300 nm) and is less compact (Figure 3g,h). This is again supported by the XRD patterns, where less intense and broader reflections are observed for Cu@C-400R. In the unpyrolyzed material, agglomerations of bar-like structures can be seen, while more compact oxidic copper can be observed in the pyrolyzed catalysts. Among these Cu-materials, the one pyrolyzed at 400 (CuO@C-400) is more active compared to the catalysts pyrolyzed at higher temperatures >600 (CuO@C-600-800). This varying activity is due to the formation and distribution of Cu-oxide nanoparticles. In case of CuO@C-400, particles are not agglomerated and are well defined. On the other hand, the particles in CuO@C-600 are in agglomeration, which could be the reason for the less activity of this material.

Further analysis of the catalyst surface by X-ray photoelectron spectroscopy (XPS) showed the presence of C, O, Cu, and N elements (**Table 2**). Additionally, small amounts of Si and S can be found which may be originated from the support (Vulcan XC-72R). The Cu 2p spectra in **Figure 4** reveal the presence of peaks at 933.6 eV and 954.0 eV, which are corresponding to Cu $2p_{3/2}$ and Cu $2p_{1/2}$. The strong satellite features around 942.5 and 962.5 eV together with the binding energy of the Cu $2p_{3/2}$ peak clearly prove CuO as the main oxidation state.[51] The unpyrolyzed catalyst as well CuO@C-400 and CuO@C-600 show very similar Cu 2p spectra and the same oxidation state (Figure 4a–c) with decreasing concentration of Cu

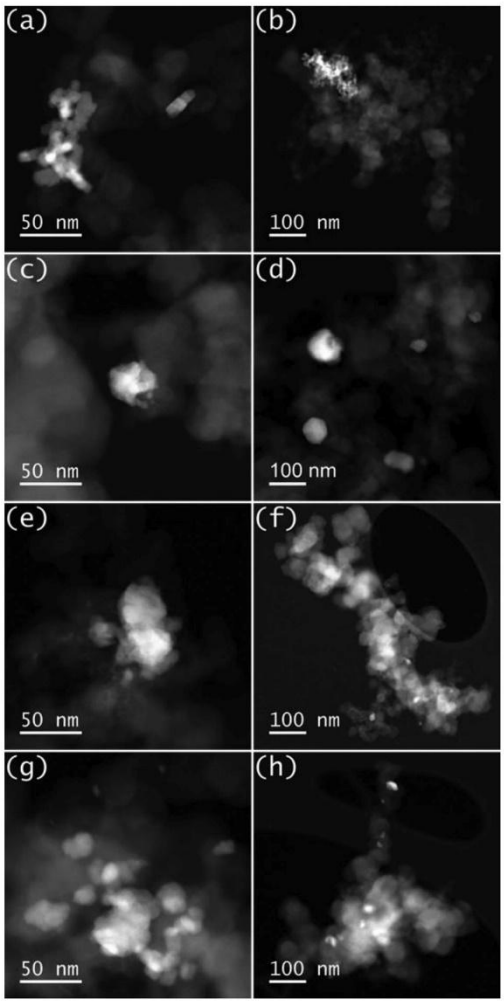


Figure 3. STEM images of copper-based nanocatalysts. STEM-HAADF images of a,b) CuO@C-unpyrolyzed, c,d) CuO@C-400, e,f) CuO@C-600, and g,h) CuO@C-400R-recycled.

Table 2. Amount of C, O, N, and Cu (in %) on the surface of Cu-materials obtained by XPS.

Catalyst	C	O	N	Cu
CuO@C unpyrolyzed	96.0	2.3	0.3	0.7
CuO@C-400	97.0	1.7	0.2	0.5
CuO@C-600	97.5	1.6	–	0.3
CuO@C-400R	95.6	2.1	1.6	0.7

Reaction conditions: 0.5 mmol alcohol, 200 µL aq. NH_3 (28–30% in water), 30 mg CuO@C-400 (3.3 mol% Cu), 80 mg of radical quenching /trapping agent, 5 bar air, 2 mL *t*-BuOH, 105 °C, 24 h, conversions, and yields were determined by GC yields using n-hexadecane as standard.

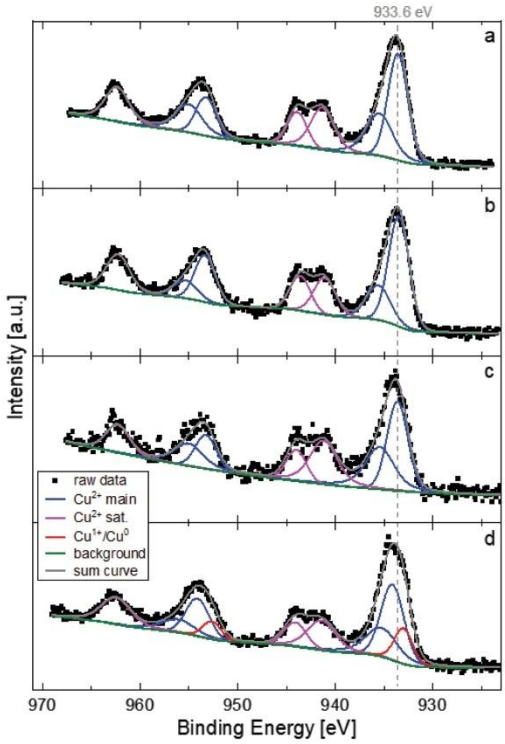


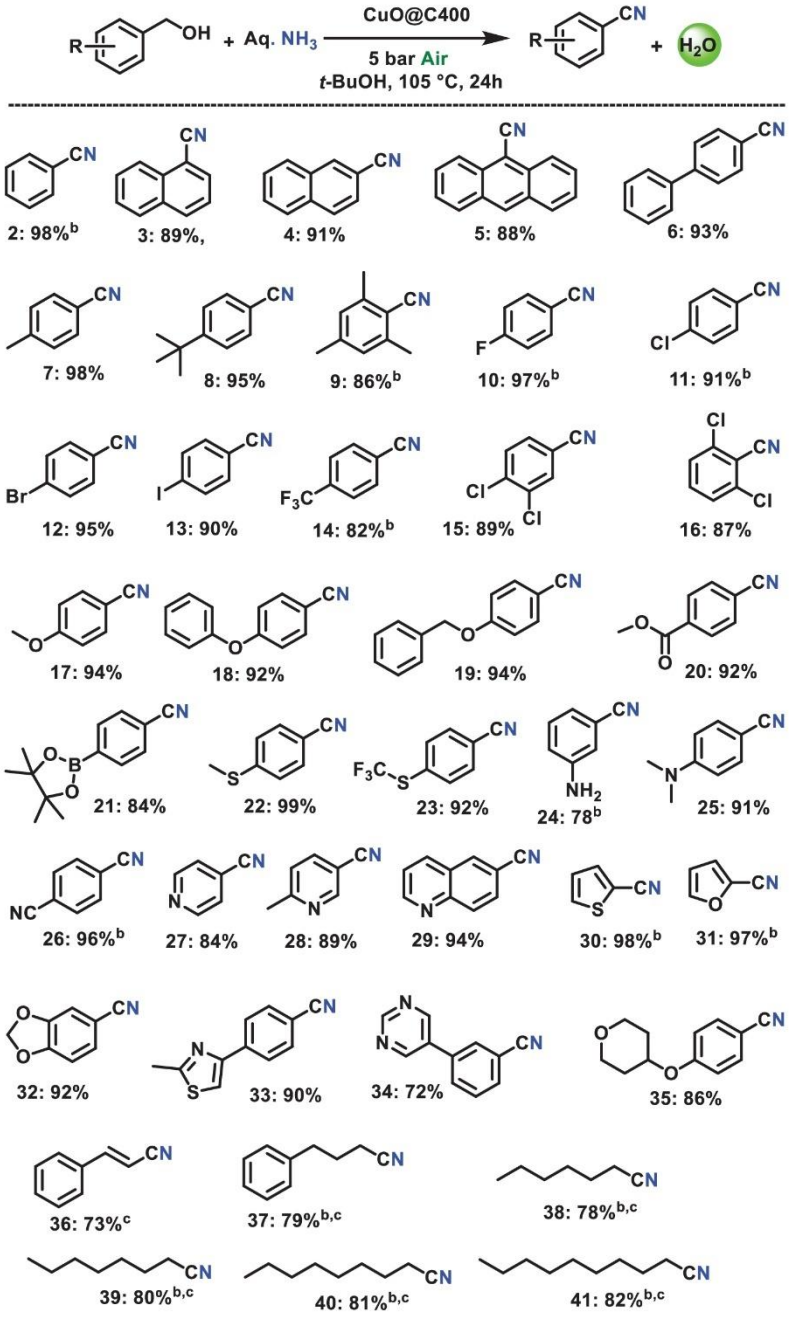
Figure 4. Deconvoluted XPS Cu 2p spectra of a) CuO@C-unpyrolyzed, b) CuO@C-400, c) CuO@C-600, and d) CuO@C-400R.

at the surface. However, for the recycled catalyst CuO@C-400R a slightly higher amount of Cu can be observed as well as differences in the Cu 2p spectra. Here, the satellite features are not as pronounced and a peak at lower binding energy (around 932.7 eV) appears. This indicates the presence of Cu^+/Cu^0, which cannot be distinguished, as the second oxidation state to a minor extent.[51]

The N 1s spectra of catalysts reveal the presence of pyrrolic-N (≈399.4 eV)[52] as the main component (Figure S4, Supporting Information) with a low total concentration of N (Table 2). However, in the recycled catalyst CuO@C-400R a slightly higher N concentration can be observed, also showing pyridinic and graphitic nitrogen to a minor extent (Figure S4, Supporting Information).

2.3. CuO-Nanoparticles Catalyzed Synthesis of Nitriles

With the most active catalyst (CuO@C-400) in hand, we demonstrated its general applicability for the synthesis of different kinds of nitriles, which are of commercial and industrial interest, starting from various alcohols and ammonia (**Scheme 1**). Among cyano-compounds, benzonitriles constitute integral parts of advanced products and pharmaceuticals



Scheme 1. Synthesis of nitriles from alcohols and ammonia by CuO@C-400 catalyzed aerobic oxidation[a]. Reaction conditions: [a]0.5 mmol alcohol, 200 µL aq. NH_3 (28-30% in water), 30 mg CuO@C-400 (3.3 mol% Cu), 5 bar air, 2 mL *t*-butanol, 105 °C, 24 h, isolated yields. [b]GC yield using n-hexadecane as standard. [c]0.5 mmol alcohol, 400 µL aq. NH_3 (28–30% in water), 45 mg CuO@C-400 (4.9 mol%), 5 bar air, 2 mL *t*-butanol, 130 °C, 36 h.

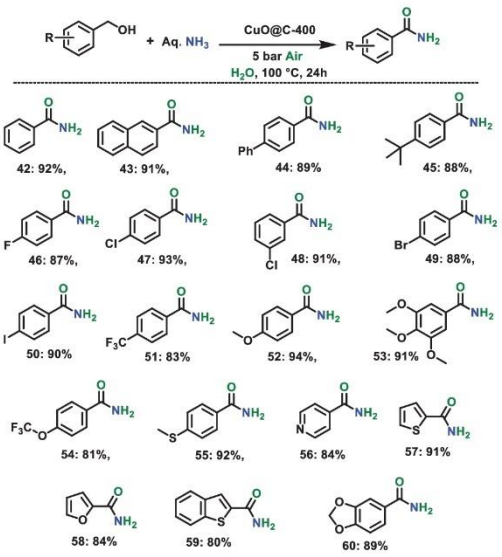
and play significant roles in their physical, chemical, and bioactivities.[14] In addition, aryl nitrile-containing compounds have been developed as selective enzyme inhibitors for the treatment of estrogen-dependent diseases.[14]

Noteworthy, applying CuO@C-400, substituted and functionalized benzonitriles were prepared in good to excellent yields (Scheme 1, products 2-26). Simple and substituted benzonitriles were obtained in up to 95% yield (Scheme 1, products 2-8). The sterically hindered, 2,4,6-trimethyl benzyl alcohol, which is difficult to react, was successfully proceeded to give 86% of the corresponding nitrile (Scheme 1, product 9). Interestingly, halogenated benzonitriles (their synthesis is problematic in both ammoxidation and nucleophilic cyanation reactions), were conveniently obtained in up to 97% yield (Scheme 1, products 10-16). Notably, such functionalized aryl halides are of interest in organic synthesis because these compounds can easily undergo various reactions to access different types of value-added products. Among these, 2,6-dichlorobenzonitrile (DCBN), is a special product that is considered as a potential herbicide as well as serves as a key intermediate in the production of pesticides and the thermally resistant plastics. Again, the preparation of this compound by traditional methods is highly challenging. However, starting from inexpensive and commercial 2,6-dichlorobenzyl alcohol, DCBN was obtained with 87% yield. (Scheme 1, product 16). In synthetic organic chemistry and drug discovery, the preparation and reaction of functionalized compounds are of central importance. In this regard, different functionalized benzonitriles were synthesized. As an example, ether-, ester-, boronic-ester-, thio-ether-, primary amine-, *N,N*-dimethylamine- and cyano-substituted benzonitriles were selectively prepared starting from corresponding alcohols (Scheme 1, products 17-26).

Heterocycles are an essential class of compounds and are of increasing interest in medicinal and biological chemistry. Among these, cyano-heterocycles are specifically important in organic synthesis as well as drug discovery. Applying our Cu-based catalyst, different heterocyclic nitriles such as cyno-pyridine, cyano-quinoline-, cyano-thiophene-, and cyano-furan as well as dioxole-, thiazole- and tetrahydro pyran-based nitriles were prepared in up to 98% (Scheme 1, products 27-86). As an example of allylic nitrile, cinnamonitrile was accessed from cinnamyl alcohol in a 73% yield (Scheme 1, product 36). Among alcohols, aliphatic ones in general are difficult to react and require highly active catalysts or drastic conditions. Nevertheless, CuO@C-400 catalyst is also active for the aliphatic substrates; albeit requires higher temperature and longer reaction time. As a result, 4-phenylbutane *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane nitriles were prepared in up 81% yield (Scheme 1, products 36-41).

2.4. CuO-Nanoparticles Catalyzed Synthesis of Primary Amides in Water

After the successful preparation of nitriles, we turned our interest in the synthesis of primary amides using CuO@C-400. As shown in **Scheme 2**, 19 primary amides were prepared in good to excellent yields from benzylic and heterocyclic alcohols and ammonia in presence of air in water. Interestingly, F-, Cl-, Br-, and I-substituted benzylic alcohols were smoothly reacted and provided corresponding halogenated primary amides (Scheme 2, products 46-50). In addition, trifluoromethyl-, ether, thio-ether substituted primary amides were obtained in up to 93% yield (Scheme 2, products 51-54). Further, different heterocyclic amides such as isonicotinamide (product 56), thiophene-2-carboxamide (product 57), furan-2-carboxamide (product 58, benzothiophene-2-carboxamide (product 59), and benzodioxole-5-carboxamide (product 60) were prepared in up to 91% yield. Unfortunately, CuO@C-400 did not show sufficient activity for the synthesis of aliphatic primary amides, although it showed good activity to access aliphatic nitriles.



Scheme 2. CuO@C-400 catalyzed synthesis of primary amides from alcohols and ammonia in water. Reaction conditions: 0.5 mmol alcohol, 300 µL aq. NH_3 (28–30% in water), 30 mg CuO@C-400 (3.3 mol% Cu), 5 bar air, 2 mL H_2O 100 °C, 24 h, isolated yields.

It is important to note that sulfur-containing compounds create a common poisoning effect for heterogeneous catalysts. However, favorably, our Cu-based nanocatalyst is well tolerated and exhibited good to excellent activity for the preparation of several sulfur-containing products (Schemes 1 and 2, products 22, 23, 30, 33, 55, 57, 59).

2.5. Catalyst Recycling and Reusability

In the context of practical and cost-effective synthetic processes, recycling and reusability of a given catalyst are key factors. As shown in **Figure 5**, the catalyst can be conveniently recycled and reused up to 3 runs without any significant loss of activity or selectivity. However, after the 4th run the activity of catalyst decreased, which is due to the leaching of Cu-particles from the catalyst (wt% of Cu in the fresh catalyst = 3.5% and in the recycled catalyst after 4th run = 2.5%).

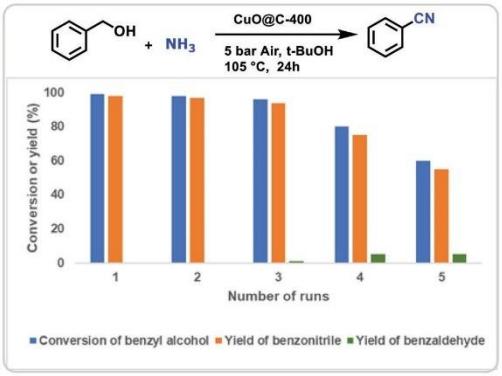


Figure 5. Recycling and reusability of CuO@C-400 for the synthesis of benzonitrile. Reaction conditions: 1 mmol alcohol, 400 µL Aq. NH_3 (28-30% in water), 60 mg CuO@C-400 (3.3 mol% Cu), 5 bar air, 4 mL *t*-butanol, 105 °C, 24 h, GC yields using n-hexadecane as standard.

2.6. Kinetic and Mechanistic Investigations

After having demonstrated the synthetic applicability, we performed mechanistic investigations and monitored the reaction profile. For the model reaction, we studied the effect of (a) reaction time, (b) amount of catalyst, (c) reaction temperature, and (f) substrate (benzyl alcohol) concentration (**Figure 6**). Increasing the reaction time, temperature, and amount of catalyst the yield of benzonitrile was increased, and the best result was achieved at 105 °C with 30 mg of catalyst for 24 h. In contrast, varying the concentration of benzyl alcohol (substrate) the yield of benzaldehyde was decreased, indicating that the higher amount of the starting material on the surface hinders the reaction.

To identify the formation of possible reactive oxygen species (ROS) during this CuO@C-400 catalyzed synthesis of benzonitrile, we conducted radical quenching/trapping experiments. For this purpose, under standard conditions, we tested the reaction in presence of PBQ (*p*-benzoquinone, NaN_3, and *i*-PrOH, which are generally used as radical quenchers/trapping agents for superoxide ($O_2^{\bullet-}$), singlet oxygen ($^{[1]}O_2$) and hydroxyl radical ($^{\bullet}OH$) (**Table 3**) respectively. These experiments showed that the reaction has been inhibited in presence of 80 mg PBQ. On the other hand, there is no effect on the reaction after adding NaN_3 or *i*-PrOH. These observations infer the formation of superoxide ($O_2^{\bullet-}$) species is more likely during this Cu-catalyzed nitriles synthesis protocol. Next, we also conducted an experiment to trap superoxide ($O_2^{\bullet-}$) species using butylated hydroxytoluene (BHT) (**Figure 7**). In absence of benzyl alcohol, the reaction was performed using 30 mg of Cu@C-400 and 0.5 mmol BHT in presence of 1 bar of air at 80 °C in 2 mL n-heptane for 24 h and detected the formation of BHT-OOH by GC MS analysis (Figure 7).

Further, in situ electron paramagnetic resonance (EPR) studies for the aerobic oxidation of benzyl alcohol over CuO@C-400 catalyst in *t*-butanol were carried out in the presence of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a spin trap. The

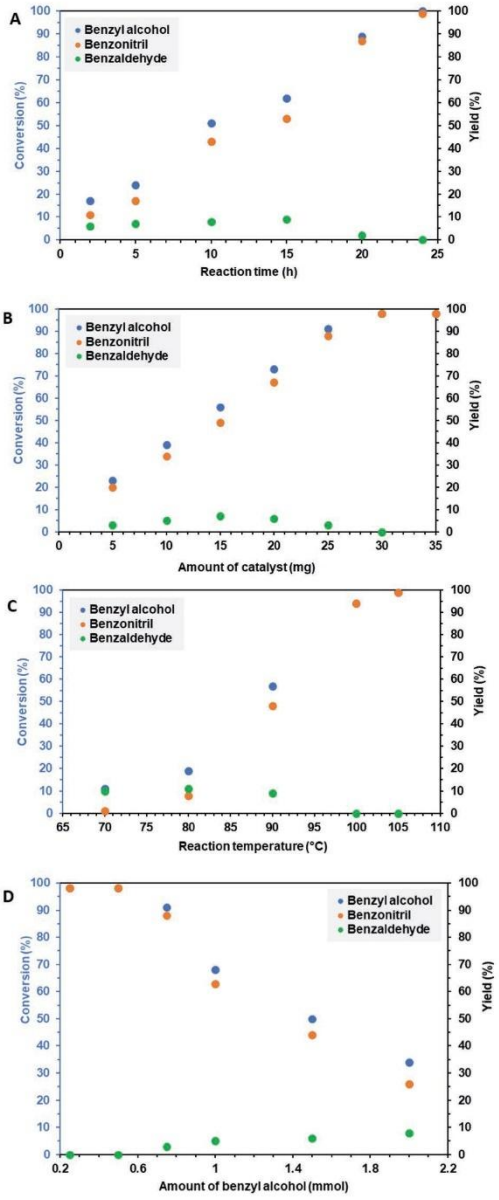
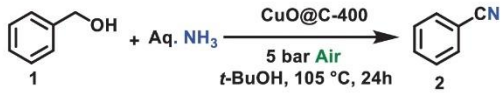


Figure 6. Kinetic investigations on the CuO@C-400-catalyzed synthesis of benzonitrile from benzyl alcohol and ammonia in the presence of air. A) Yield versus reaction time, B) yield versus amount of catalyst, C) yield versus reaction temperature, and D) yield versus concentration of benzyl alcohol (substrate).

EPR spectrum of the reaction mixture shows a six-line signal at $g = 2.006$, which can be simulated with $A_N = 18.28$ MHz and $A_{\beta H} = 55.98$ MHz characteristic for DMPO-R spin adduct.

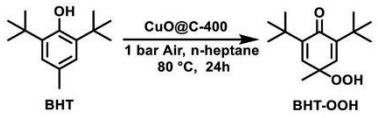
Table 3. Effect of different radical quenching/trapping agent on CuO@C-400 catalyzed conversion benzyl alcohol benzonitrile.



Entry	Radical quenching/ trapping agent	Reactive oxygen species	Conv. [%]	Yield [%]
1	–	–	>99	98
2	PBQ	Superoxide ($O_2^{\bullet-}$)	5	3
3	NaN_3	Singlet oxygen ($^1O_2$)	96	94
4	*i*-PrOH	Hydroxyl radical (•OH)	94	92

These results indicate that the reaction mechanism involves the formation of carbon radical intermediate with the interaction of superoxide radical species (**Figure 8**).

Regarding the reaction pathway (**Scheme 3**) for the preparation of nitrile (D), first the oxidation of alcohol to aldehyde (B) takes place in presence of CuO@C-400 and air. Then, the aldehyde couples with ammonia and generates primary imine (c). This intermediate is unstable and undergoes oxidation in presence of CuO@C-400 to produce the corresponding nitrile. For the synthesis of amides, two pathways are possible: a) the aldehyde formed by the oxidation of alcohol can react with ammonia and generates hemiaminal as the intermediate, which could be then converted to the corresponding primary amide, or b) the benzonitrile produced from alcohol which can undergo hydrolysis to form the primary amide in presence of water.



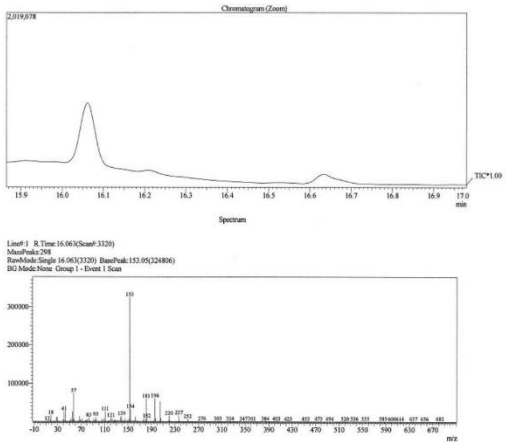


Figure 7. Trapping of super oxide ($O_2^{\bullet-}$) using butylated hydroxytoluene (BHT) and mass spectrum BHT-OOH.

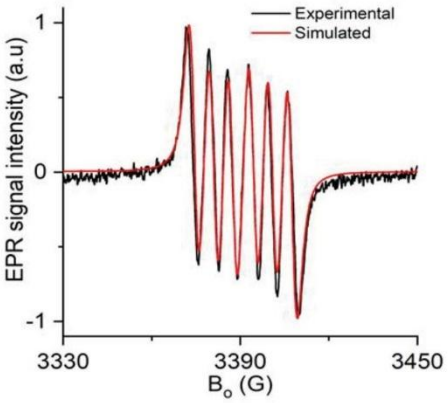
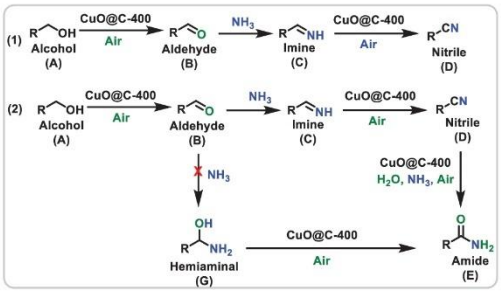


Figure 8. EPR spectra of CuO@C-400 (10 mg) + benzyl alcohol (20 µL) + DMPO (10 µL) in *t*-BuOH (0.5 mL) were measured at 20 °C after heating the suspension at 80 °C for 2 min under O_2 (black experimental and red simulated spectra).

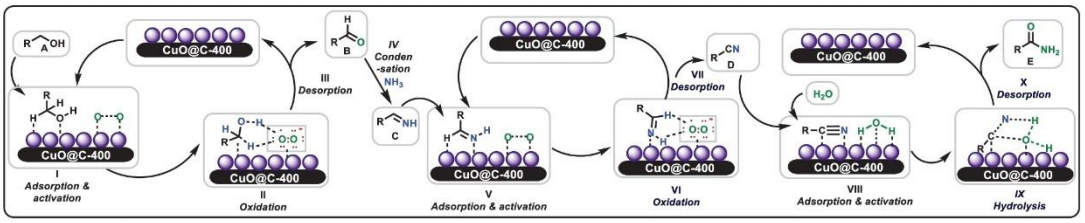
To confirm the formation of primary amide, the reaction of benzonitrile in presence of ammonia and air using CuO@C-400 was conducted at 100 °C for 24 h in water. This reaction provided benzylamide in a 90% yield (Figure S10, Supporting Information), which confirmed that the formation of amide occurs mainly by the hydration of benzonitrile. The catalytic hydration of nitriles is also another green method to prepare amides.[53,54]

Compared to nitriles, the formation of amides from alcohols is challenging because it involves a two-step reaction. In particular, the hydrolysis of aliphatic nitriles is difficult compared to aromatics ones and hence this might be the reason that using CuO@C-400 catalyst was very poor or no yield of aliphatic nitriles was observed.

Based on reaction pathways and obtained results, we propose the plausible reaction mechanism of the Cu-catalyzed aerobic oxidation process to prepare nitriles and primary amides in **Scheme 4**. First, on the surface of CuO@C-400 catalyst, adsorption and activation of both alcohol and oxygen take place



Scheme 3. Reaction pathways for the Cu-nanoparticle catalyzed synthesis of nitriles and primary amides from alcohols and ammonia in presence of air.



Scheme 4. Proposed mechanism for the CuO@C-400-catalyzed synthesis of nitriles and amides from alcohols and ammonia in presence of air.

with the generation of superoxide as oxygen reactive species (I). Next, oxidation of activated alcohol proceeds using superoxide species (II). Further, the desorption of aldehyde with the regeneration of catalyst (III) occurs. The formed aldehyde condenses with ammonia and forms imine as an intermediate (IV). In the next catalytic cycle imine undergoes adsorption and activation on the catalyst (V) surface followed by oxidation (VI). Finally, the nitrile desorbs with the regeneration of catalyst (VII). For the formation of amide, the nitrile and water adsorb and activate on catalyst surface (VIII) and then hydrolysis occurs (IX). Finally, desorption of amide takes place with the regeneration of catalyst (X).

3. Conclusion

Pyrolysis of simple copper nitrate on carbon generated efficient and selective copper oxide nanoparticles-based aerobic alcohol oxidation catalysts (CuO@C-400). Applying optimal CuO-based nanocatalyst, ammoxidation of various alcohols with ammonia in presence of air has been performed and produced various simple, substituted, and functionalized aromatic, heterocyclic, and aliphatic nitriles in good to excellent yields. In addition, this Cu-based aerobic oxidation protocol has been used for the synthesis of primary amides in a water medium. Superoxide ($O_2^{\bullet-}$) radical species are identified as the reactive oxygen species in this Cu-NPs catalyzed aerobic oxidation process. Finally, reaction pathways and plausible mechanism for the CuO-NPs catalyzed synthesis of nitriles and amides from alcohols and ammonia in presence of air have been proposed.

4. Experimental Section

Procedure for the Preparation of CuO NPs-Based Catalysts: In a 50 mL round-bottomed flask, 142 mg of $Cu(NO_3)_2.3H_2O$ and 25 mL of DMF were added and the mixture was stirred at 150 °C for 30 min. Then, 885 mg of Vulcan XC 72R carbon powder was added and the whole reaction mixture was stirred again at 150 °C for 4 h fixing a reflux condenser to the round-bottomed flask. Then after, the reflux condenser was removed and the round-bottomed flask containing the reaction mixture was allowed to stand for 24 h at 150 °C for the slow evaporation of DMF to obtain Cu-carbon based solid material. After the evaporation of the solvent and drying, the solid material was cooled to room temperature and ground to a fine powder. Finally, the powdered material was pyrolyzed at different temperatures (300–800 °C) for 2 h under argon atmosphere. Elemental analysis of optimal catalytic material CuO@C-400 (wt%): C = 88.5, N = 0.76, Cu = 3.5% H = 0.25%.

Elemental analysis recycled catalyst CuO@C-400R (after 4th run): C = 85.4, N = 1.26, Cu = 2.57%, H = 0.20%.

Procedure for the Synthesis of Nitriles and Amides: To a glass vial (8 mL), the magnetic stirring bar and 0.5 mmol alcohol were added and then 2 mL *t*-butanol as solvent (in case of amides synthesis, 2 mL water was used as solvent) were added. Then, 30 mg CuO@C-400 catalyst was added followed by the addition of 200 µL aq. NH_3 (in case of amides synthesis 230 µL aq. NH_3 was used). Afterward, the reaction vial was fitted with a septum, cap, and needle. The reaction vials (8 vials with different substrates) were placed into a 300 mL autoclave and the autoclave was pressurized with 5 bar air. The autoclave was placed into a preheated aluminum block at 115 °C (110 °C in case of amides synthesis) and reactions were allowed to progress under stirred conditions for 24 h. During the reaction, the inside temperature of the autoclave is measured to be 105 °C (100 °C in case of amides synthesis) and this temperature has been considered as the reaction temperature. After the completion of the reactions, the autoclave was cooled down to room temperature and the remaining air was slowly discharged. The catalyst was filtered-off, and washed with ethyl acetate. The products were purified by column chromatography and analyzed by GC, GC-MS, and NMR spectroscopy. In the case of yields determined by GC, 100 µL *n*-hexadecane was added to the reaction vial containing products and diluted with ethyl acetate. Then, the crude mixture containing catalyst and products was filtered through a plug of silica and the filtrate containing products were analyzed by GC.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

aerobic oxidation, alcohols, amides, ammonia, Cu nanoparticles, nitriles

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8. Curriculum Vitae

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EDUCATION

2021-2025 – Doctoral studies in Organic Chemistry at the Leibniz Institute for Catalysis (present)

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2017-2019 - MSc. Chemistry (Organic) Mahatma Gandhi University Kerala

Master Thesis - “Identification of a New Class of Pyridine Derivatives as Antihyperlipidemic Agents.” Carried out under the supervision of Dr. Kishor Mohanan, Senior scientist, in the division of Medicinal and Process Chemistry, CSIR-Central Drug Research Institute Lucknow, India

2014-2017 – BSc. Chemistry Kannur University Kerala

PARTICIPATION IN CONFERENCES

1. Poster “Mechanistic insights of hydrogenative lignin depolymerization reactions” at the Symposium (Dream reaction, with and without Hydrogen), University of Münster, Germany.

2. Oral communication - “Cobalt catalyzed valorization of vegetable oils“ at Institute seminar on Circular economy, 2024, LIKAT.

3. Poster “Cobalt catalyzed amination of esters and carboxylic acids” at the 57th Annual Meeting of German Catalysts. Wimar 2024, Germany.

4. Poster “Cobalt catalyzed valorization of vegetable oils and polyesters” at the ISHC 2024 - International Symposium on Homogeneous Catalysis, Trieste.

VOLUNTEERING AND PARTICIPATIONS

11/2021 - 10/2023 - Worked on EHLCATHOL 2020 project

11/2023 - 12/2024 PhD-Postdoc representative at LIKAT, Rostock.

Attended RDM School of Catalysis, Frankfurt, 2024.

PUBLICATIONS

1. A catalytic approach to the valorization of polyesters and biogenic waste for the production of amines, Fairoosa Poovan, Rajenahally V. Jagadeesh, Matthias Beller, *Chem*, **2025**, *12, 102667.* https://doi.org/10.1016/j.chempr.2025.102667.

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3. Synergy between homogeneous and heterogeneous catalysis, Fairoosa Poovan, Vishwas G. Chandrashekhar, Kishore Natte and Rajenahally V. Jagadeesh, *Catal. Sci. Technol*., **2022**, *12*, 6623-6649. https://doi.org/10.1039/D2CY00232A

4. Cu-Oxide Nanoparticles Catalyzed Synthesis of Nitriles and Amides from Alcohols and Ammonia in Presence of Air, = Thirusangumurugan Senthamarai, Fairoosa Poovan, Asma M. Alenad, Nils Rockstroh, Jabor Rabeah, Stephan Bartling, Eszter Baráth, Kishore Natte, Rajenahally V. Jagadeesh, *Adv. Sustain. Syst*, **2022**, 6, 2200263. https://doi.org/10.1002/adsu.202200263

5. Streamlining the synthesis of amides using Nickel-based nanocatalysts, Jie Gao, Rui Ma, Fairoosa Poovan, Lan Zhang, Hanan Atia, Narayana V. Kalevaru, Wenjing Sun, Sebastian Wohlrab, Denis A. Chusov, Ning Wang, Rajenahally V. Jagadeesh and Matthias Beller, *Nat Commun*, **2023,** *14*, 5013. https://doi.org/10.1038/s41467-023-40614-1

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