Review

Green Catalytic Synthesis of Ethylenediamine from Ethylene Glycol and Monoethanolamine: A Review

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ABSTRACT: Ethylenediamine (EDA) is a crucial chemical raw material and fine chemical intermediate. Compared with the industrial approach of ammonolysis of 1,2-dichloroethane, the catalytic amination of ethylene glycol (EG) is an economical and environmentally benign route that will be the future trend for EDA synthesis. Herein, we systemically review the recent progress in direct and indirect catalytic conversion of EG to EDA. Furthermore, different types of catalysts are discussed: (i) supported metal and multimetallic catalysts, (ii) solid acid catalysts, and (iii) other active catalysts (e.g., ionic liquids and metal complexes). Finally, we conclude with the frontiers and future prospects of the catalytic synthesis of EDA from EG and monoethanolamine, providing readers a snapshot of this field.
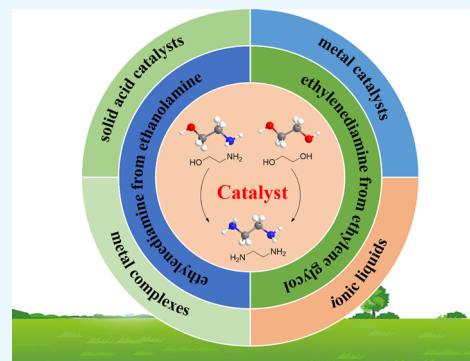
1. INTRODUCTION

Ethylenediamine (EDA) is an important organic intermediate with many uses, including in broad spectrum fungicides, chelating agents, epoxy curatives, hot melt adhesives, corrosion inhibitors, and lubricating oil additives.[1−4] At present, the ammonolysis of ethylene dichloride (EDC) accounts for more than 60% of the total EDA market share. In the EDC process, EDC is aminated by anhydrous or liquid ammonia, and afterward the amines are freed from their chlorhydrates by the action of sodium hydroxide. The main disadvantages of this process consist of the severe corrosion of the apparatus by ammonium chloride and in the difficulty in quantitatively recovering the amines from their diluted aqueous solution charged with sodium chloride. Hence, this process suffers from obvious drawbacks like a mass production of inorganic salt as a byproduct, serious equipment corrosion, and growing difficulties in environmentally acceptable disposal.[5]

Ethylene glycol (EG) is an important chemical intermediate that is widely used in the production of polyester and antifreeze. The main EG production technologies include oil-based, coal-based, and natural gas-based routes. Additionally, new routes were also explored to synthesize EG from renewable biomass feedstocks.[6−8] Recently, the global EG industry has faced the problem of overcapacity due to the continuous development of coal chemical industry.[9] Therefore, it is of great significance to transform EG into high value-added chemicals such as EDA, which would not only promote energy-based structure optimization but also contribute to achieving carbon neutrality.

Intensive endeavors have been undertaken to achieve the selective amination of EG to EDA. These efforts encompass both direct conversion processes stemming from EG and indirect conversion methods originating from monoethanolamine (MEA). Both of these processes produce products and water after the reaction, making them green and sustainable practices in the synthesis of EDA. Nevertheless, although great progress has been achieved in this field, there still remain substantial challenges for EDA synthesis (e.g., low selectivity and harsh reaction conditions). To the best of our knowledge, there has been no review that systematically summarizes the advances in the selective amination of MEA and EG.[5] This Review presents the current status and progress in the production of EDA from EG and MEA by using different catalysts such as metals and solid acids. Furthermore, the frontiers and prospects of the catalytic synthesis of EDA are concluded. This Review provides a promising perspective of EDA synthesis and enhances the development of the high-value utilization of EG.

2. DIRECT SYNTHESIS OF EDA FROM EG

The EG amination method uses EG and liquid ammonia (NH$_3$) as raw materials and achieves products in addition to

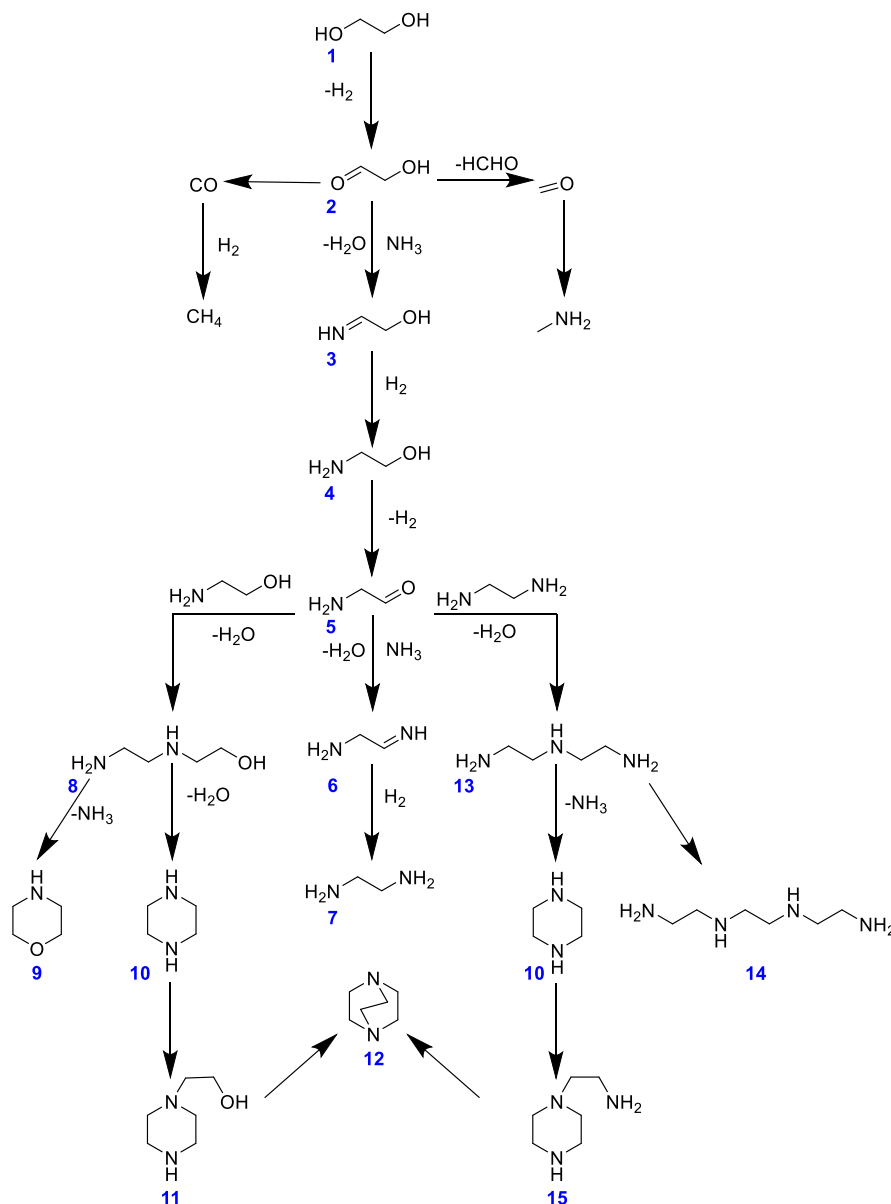**Scheme 1. Proposed Reaction Pathway of EG Reductive Amination**

water after the reaction, which is considered as a clean and green production process. Two types of catalytic materials are suitable for the heterogeneously catalyzed amination of EG: hydrogenation—dehydrogenation catalysts, which are usually supported metals, and solid acid catalysts, such as phosphates and zeolites. In addition, homogeneous catalysts like ionic liquids and metal complexes are also developed for the EG amination process. Detailed discussions of reaction routes and catalysts can be found in the following sections.

2.1. Reductive Amination Route. *2.1.1. Reaction Mechanism.* In essence, the reductive amination of EG takes place via the so-called borrowing hydrogen methodology[10,11] or hydrogen-transfer methodology.[12] On the basis of a few mechanistic studies, the key reaction steps and typical side reactions during the metal-catalyzed amination of EG are illustrated in Scheme 1.[13] The main reaction steps include (i) the dehydrogenation of the −CH₂OH group to a carbonyl group, (ii) the condensation of the carbonyl group with NH₃ to form an imine, and (iii) hydrogenation of the imine to

produce amine. Meanwhile, a series of side reactions such as condensation, disproportionation, and cyclization occur simultaneously. Typical byproducts like piperazine (PIP, **10**) and diethylenetriamine (DETA, **13**) are produced. Additionally, EG degradation products (such as CO, methane, and formaldehyde) and methylamine are also produced (Scheme 1).

2.1.2. Catalysts for the Reductive Amination Route. Various transition metals, especially Cu and Ni, have been explored as active components for the EG reductive amination reaction due to their ability to facilitate the dehydrogenation—hydrogenation process in the hydrogen transfer reaction.[14] The addition of metals, such as Re, Co, Zr, Ti, Sn, Mn, etc., may improve the catalytic activity, selectivity, and stability. In addition, metal oxides like SiO₂, TiO₂, and Al₂O₃ are usually used as supports to stabilize the dispersed metals. Since DuPont pioneered the first CuNi-catalyzed EG amination system in 1964,[15] various strategies have been explored to attain high selectivity for EDA.

2.1.2.1. Bi- and Polymetallic Catalysts. Generally, the bi-polymetallic alloys have a synergistic effect on the hydrogen transfer reaction due to the electronic and geometric effects.[14,16] Therefore, the addition of a second/third metal to form alloys is a promising strategy to enhance the catalytic activity and tune product selectivity.[17−19] For instance, patent US 3137730 disclosed a Cu−Ni catalyst supported on activated Al_2O_3 for the direct synthesis of EDA from EG, NH_3, and H_2 under 212−414 atm at 200−300 °C.[15] After reaction, EDA was separated from the resulting reaction mixture by fractional distillation, achieving a yield of about 46% based on the EG consumed in the process. BASF developed a two-stage process for the production of EDA and MEA through hydrogenation−amination of EG. In the first-stage reactor or reactor region, a temperature within the range from 130 to 230 °C, particularly from 150 to 170 °C, is preferred. The second stage can preferably be operated at a temperature from 150 to 240 °C, particularly from 160 to 190 °C. The performance of $RuCo/Al_2O_3$ catalyst in the transformation of EG to EDA is illustrated in Table 1.[20−24]

**Table 1. Amination of EG with NH_3 over $RuCo/Al_2O_3$**

entry	T (°C)	p (atm)	n_{H2}/n_{EG}	WHSV (kg/l·h)	n_{NH3}/n_{EG}	conv. (%)	sel. (%)
1	180	200	1.5	0.25	10	53.2	47.2
2	180	200	0.5	0.25	10	43.4	57.0
3	180	200	0.5	0.25	10	40.4	55.5
4	170	200	3.0	0.37	10	35.7	30.1
5	150−170	200	0.6	0.10	15	42.6	49.5

The harsh reaction conditions, especially the high pressure, hinder the widespread application of the above systems. Hence, various catalytic systems have been developed to realize the amination of EG under mild conditions. In 2022, a supported bimetallic catalyst $Co-Cu/\gamma-Al_2O_3$ was investigated by An et al., delivering an EG conversion of 54.4% and an EDA yield of 24.7% at 200 °C and 4 MPa H_2.[25] The interaction between Cu and Co reduces the reduction temperature of the catalyst, while Cu and Co facilitate the dehydrogenation of EG and the following amination reaction, respectively. Hence, the synergy of different metals plays a key role in the catalytic activity and selectivity of EG amination.[26−30]

2.1.2.2. Support Effect. Comprehension of the nature of supports is crucial to regulate the activity and selectivity of EG amination to EDA.[31] Yang reported a catalyst with sulfuretted and/or fluorinated Al_2O_3 as the support, Ni and Co as main active components, and Zn, Fe, Cu, and Re as promoters,

achieving an EDA selectivity of 60.8% with an EG conversion of 70.8% at 180 °C under 10 MPa.[32] The introduction of S and/or F in the carrier effectively improves the acid−base environment of the active components in the catalyst, thus enhancing the activity and stability of the catalyst. Subsequently, An's group confirmed that the catalytic activity of amphoteric metal oxide-supported Co is significantly higher than that on acidic metal oxides (Table 2).[31] Density functional theory (DFT) calculations showed that the basic sites of $Co/\gamma-Al_2O_3(110)$ promote the cleavage of the O−H bond, while the acidic ones facilitate the fracture of the C−H bond as compared with $Co/SiO_2(100)$. Moreover, the basic sites made EG more prone to chemical absorption on $\gamma-Al_2O_3$, leading to a higher concentration of alkoxy intermediates and thereby promoting the overall reaction rate. Consequently, the synergistic effect of acid−base sites plays a critical role in the EG amination reaction (Scheme 2). Patent WO 2018108698 also accomplished an EG amination process in the gas phase by using a calcined catalyst with low basicity.[33]

Scheme 2. a Proposed Reaction Mechanism for EG Dehydrogenation over $Co/\gamma-Al_2O_3$[a]
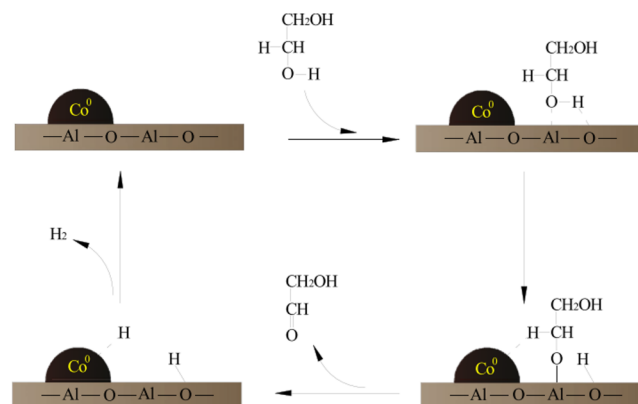
[a]Reproduced with permission from reference 31. Copyright 2022 Elsevier B.V.

2.1.2.3. Promoting Effect. Over recent decades, extensive efforts have been devoted to improving the selectivity for EDA by introducing various additives, which might be attributed to the promoting effect. In order to reduce the sintering and deactivation of Cu, catalysts that include Cu and Ni as primary components and Zn, Al, Ti, Mn, and Ce as additives were introduced, achieving up to 81% selectivity for EDA.[34] Similarly, a series of catalysts composed primarily of Cu and

Table 2. Acidity and Basicity of Co/SiO_2 and $Co/\gamma-Al_2O_3$ Catalysts[a,b]

catalyst	acid density (μ mol/m^2)	base density (μ mol/m^2)	conv. (%)	sel. (EDA + MEA) (%)	yield (EDA + MEA) (%)	sel. (EDA) (%)	yield (EDA) (%)
Co/SiO_2	0.52	0.14	2.2	23.9	0.5	1.6	<0.1
$Co/\gamma-Al_2O_3$	4.38	4.31	57.5	54.3	31.2	29.3	16.8
Co/Nb_2O_5	2.29	0.08	3.1	5.0			
Co/TiO_2	1.46	0.02	1.3	5.8			
Co/ZrO_2	3.98	1.22	23.9	75.2			
Co/Y_2O_3	2.32	2.85	15.5	75.2			
Co/MgO	1.04	4.58	15.4	69.8			
Co/CaO	0.85	34.34	28	53.8			

[a]Reaction conditions: 3 MPa H_2, 12 h, 4.46 g of EG, 0.89 g of catalyst, and 14.81 g of NH_3. [b]Reproduced with permission from ref 31. Copyright 2022 Elsevier B.V.
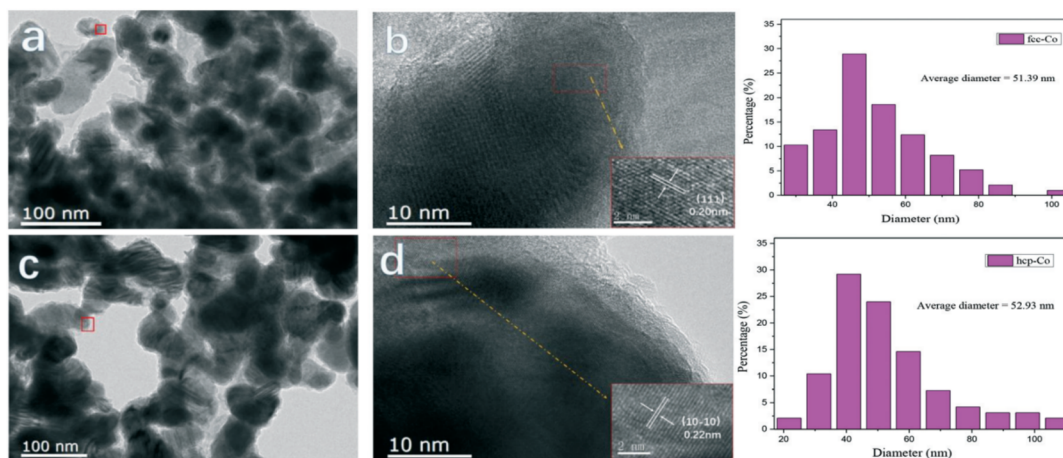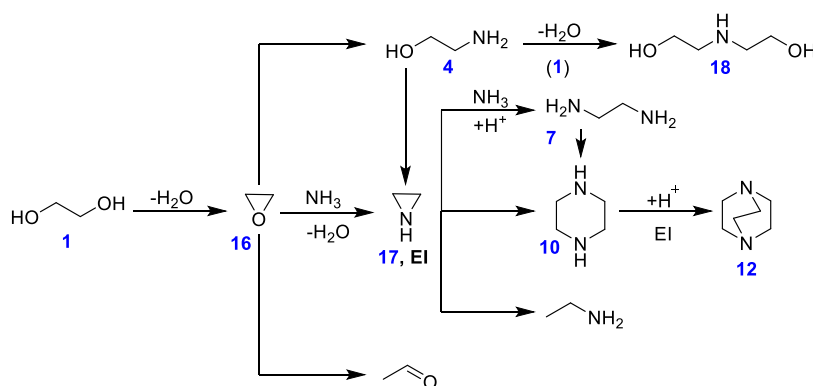
Figure 1. TEM images of the (a and b) fcc-Co and (c and d) hcp-Co catalysts. Reproduced with permission from ref 13. Copyright 2022 Royal Society of Chemistry.

Scheme 3. Proposed Reaction Pathway of EG Condensation Amination[a]

[a]Reproduced with permission from ref 5. Copyright 1997 Elsevier B.V.

Ni, along with additives like Mn, Co, Zr, Ti, and Sn, were reported by Xu's group. Under the established catalytic systems, an EDA selectivity of up to 87% and an EG conversion of 93% were achieved using an optimized Cu/Ni/Ti/Zr/Sn/Co/Mn/ZSM-5 catalyst under a pressure of 14 MPa at 250 °C.[35] Then, a comparable dehydrogenation−hydrogenation catalyst containing Ni, Cu, Cr, and Ru delivered an MEA conversion of 40% and an EDA selectivity of 81% at 200 °C in the batch reaction.[36−38]

2.1.2.4. Facet Effect. The crystal facet represents a crucial characteristic of crystalline materials. Different crystal facets have different geometric and electronic structures, exhibiting various surface physicochemical properties and intrinsic reactivity.[39] The catalytic performance of Ni and Co for EG amination were studied by An et al. Interestingly, Co was found to be more active than Ni. DFT calculations demonstrated that the energy barriers for the dissociation of O−H and C−H bonds in an EG molecule are smaller on the Co(0001) plane, accounting for the higher EG conversion and EDA yield on a metal Co catalyst.[40] Therefore, face-centered cubic (fcc) and hexagonal close-packed (hcp) Co nanoparticles were synthesized for the EG amination reaction (Figure 1). First-principle calculations revealed that the Co(111) facet favors the cleavage of O−H and C−H bonds in the EG molecule, resulting in higher EG conversion and EDA yield on the fcc-Co catalyst.[13]

2.2. Condensation Amination Route. *2.2.1. Reaction Mechanism.* The condensation amination of EG proceeds through ethylene oxide (EO, **16**) by dehydration, then a condensation reaction of EO with ammonia occurs to produce an ethylenimine (EI, **14**) intermediate over the active sites of the catalyst. EI is protonated by the stronger acidic sites with an excess amount of NH_3 to produce EDA. Meanwhile, typical byproducts like MEA, acetaldehyde, ethylamine, and homologues of PIP are produced after the reaction[41] (Scheme 3).

2.2.2. Catalysts for the Condensation Amination Route. Based on the mechanistic understanding of EG condensation amination, BASF explored metal-exchanged zeolites such as MOR, FAU, CHA, and GME for EG amination. The Cu-MOR with 2.6 wt % Cu showed the highest catalytic performance, giving a yield of 9.6% at 340 °C under a gas stream containing 40 vol % Al_2O_3 and 20 vol % H_2.[42,43] The synergy between acidic sites and metallic species is beneficial to the condensation amination of EG to EDA.

2.3. Homogeneous Catalysts. Compared to heterogeneous catalysts, homogeneous catalysts usually present excellent catalytic activity and product selectivity. In particular, the chemically well-defined nature of their active structures allows for more rational design through structure−activity relationships.[44,45] In 2012, a well-defined $RuHCl(CO)(PPh_3)_3$ catalyst (Figure 2) was established to enable the reaction of alcohol with NH_3. Impressively, the catalyst enabled complete
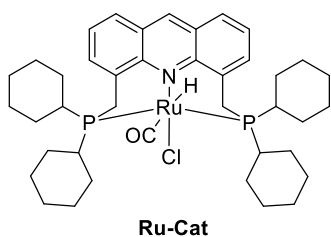
Figure 2. Structure of the RuHCl(CO)(PPh₃)₃ complex.

conversion of EG with an EDA selectivity of 21.2% under relatively mild conditions (180 °C, 1 mol % KOtBu).[46]

Ionic liquids (ILs) have attracted considerable interest because of their unique properties, such as low vapor pressure, wide liquid range, high thermal stability, structural designability, and high solubility in various solvents.[47−49] Combining metal complexes with ILs tends to be an effective method to overcome the limitations of the direct formation of EDA from EG. In 2016, Xu and co-workers synthesized a series of ILs from four-coordinate transition-metal anion complexes (CuCl$_4^{2-}$, CoCl$_4^{2-}$, MnCl$_4^{2-}$, NiCl$_4^{2-}$, and ZnCl$_4^{2-}$) and Brønsted acid-modified bisimidazolium cations (Figure 3). For
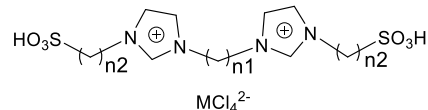
n1, n2: Number of carbon atoms; M: Transition metal

Figure 3. Structure of the ionic liquid.

EG amination, an EG conversion of 92% and an EDA selectivity of 85% were obtained under a pressure of 14 MPa at 250 °C in 8 h.[50] In the catalyst, the sulfonic group-functionalized Brønsted acid and the Lewis acidic bisimidazolium cation promote the dehydrogenation of EG, and the transition-metal anion (MCl$_4^{2-}$) facilitates the hydrogenation of imines. These two catalytic species cooperatively accelerate the conversion of EG to EDA.

3. INDIRECT SYNTHESIS OF EDA FROM MEA

Due to the long reaction process and a dozen or more byproducts for EG amination, researchers have shifted their focus to the amination of MEA, which is an intermediate in EG amination, and have achieved significant progress. Similar to EG amination routes, metal catalysts for the reductive amination process and solid acids for the condensation amination process have been developed for the synthesis of EDA from MEA.

3.1. Reductive Amination Route. *3.1.1. Catalysts for the Reductive Amination Route.* Metals and supported metals have been reported to be efficient in the reductive amination of alcohols.[14] Catalysts for the selective synthesis of EDA from MEA primarily focus on Cu-, Ni-, and Co-based nanomaterials. Besides, promoters such as Cr, Re, Zn, and Ir are able to enhance the activity, selectivity, or stability. Additionally, neutral or weak acid/alkaline metal oxides (e.g., SiO₂, TiO₂, and Al₂O₃) are often used as supports to stabilize the dispersed metals. Since DuPont developed the first Ru-catalyzed MEA amination system in 1956,[51] various methods have been explored to attain high selectivity for EDA. Tables 3 and 4

summarize the representative catalytic systems used in the reductive amination of MEA to EDA.

Table 3. Summary of Typical Catalytic Systems for MEA Reductive Amination in Batch Processes[a]

catalysts	T (°C)	p (atm)	n_{NH3}/n_{MEA}	time (h)	conv. (%)	sel. (%)	yield (%)	ref
Ni/Co/Fe/Al₂O₃	200	150	10.1	5	60	62	37.2	17
Cu/Co/Re/Al₂O₃	175	24.7	10	6	57	7[b]	–	52
Ni−Ru−Re	250	70.7	9.7	8	19.2	81.4	15.6	53
Ni−Pt−Y/Al₂O₃	180	20[c]	6.5	8	34.8	65.3	22.7	54

[a]Conv.: conversion of MEA. Sel.: selectivity to EDA. −: the information was not found in the literature. [b]n_{EDA}/n_{PIP}. [c]H₂.

3.1.1.1. Bi- and Polymetallic Catalysts. In general, bi- and polymetallic catalysts facilitate the catalytic processes due to the synergy between different metals. For instance, Johansson et al. demonstrated a supported amination catalyst consisting Fe with either Ni, Co, or mixtures for the reductive amination of aliphatic alcohols and aminoalcohols. With regard to EDA synthesis, up to 62% EDA selectivity was obtained with 60% conversion of MEA at 200 °C over a preferred Ni/Co/Fe/Al₂O₃ catalyst.[17]

3.1.1.2. Support Effect. The performance of a catalyst is closely related to the surface properties of the carrier, such as surface area, pore size, and pore volume. These surface properties would affect the adsorption/desorption equilibrium of reactants, thereby affecting the conversion and selectivity.[67] King found that both activity and selectivity were improved only by using transitional Al₂O₃ in a Ni-Re-based reductive amination catalyst.[68] Bartley investigated different supports of Ni−Re catalysts and found that SiO₂−Al₂O₃ with surface areas of 50−200 m²/g and pore volumes of 0.5−1.0 mL/g helps improve the EDA selectivity.[59] The introduction of SiO₂ modulates the quantity of the surface Lewis acid and base sites of the Al₂O₃ support, which would affect the adsorption and desorption of amines and contribute to better catalytic performance.

The acid−base properties of the support also play an essential role in determining EDA selectivity, since they can control the adsorption behavior of amines by pre- and post-treatment methods. Köll et al. pretreated the carrier using an aqueous HCl solution, which significantly improved the activity and selectivity of the MEA amination reaction.[37] However, most metal oxides are unstable in strong acids, which will reduce the mechanical strength and shorten the lifetime of catalyst. Ding and his co-workers reduced the possibility of imine polymerization by ammonifying the carrier, giving a 56.6% MEA conversion with 81.2% EDA selectivity over the ammonified Ni−Re−B/Al₂O₃.[69]

3.1.1.3. Promoting Effect. In order to improve the activity, selectivity, or catalyst lifetime of the catalyst, various promoters were introduced into the catalysts. Chang et al. added one or more of La, Ca, Mg, Li, Cr Fe, Cs, and Rh into a catalyst comprising Ru, Co, Cu, B, and/or Ni for the MEA amination reaction.[56] Likewise, Köll et al. disclosed an effective catalyst with Ni and Co as dual active components and Ru as a

Table 4. Summary of Representative Catalytic Systems for MEA Reductive Amination in Continuous Flow Processes[a]

catalysts	T (°C)	p (atm)	n_{NH3}/n_{MEA}	con. (%)	sel. (%)	yield (%)	ref
Ni−Cu−Cr	100−400	30−400	6	56.2	9.9[b]	−	18
Ni−Cr/diatomite	115	35	1.33	52	19[b]	−	19
Ni−Re/γ/θ-Al$_2$O$_3$	180	128	10	72.7	53.4$_{wt}$	−	55
Ni/Co/Cu/Ru/Re/B/T-869	185	170	25	60.5	69.84	−	56
Ni−Re/Al$_2$O$_3$	175	175	10	50.4	82.1	−	57
Ni−Re/SiO$_2$	170	80	10	85.7	51.5	−	58
Ni−Re−B/SiO$_2$	160	−	10−12	39.1	80.1$_{wt}$	−	59
NaRhNi/Al$_2$O$_3$	215	190	25.5	32.2	98.4	31.7	60
Co/Ni/Cu/P$_2$O$_5$/Al$_2$O$_3$	160	300	5.6	54	82	−	61
Co/Cr/P$_2$O$_5$/Al$_2$O$_3$	160	300	4.2	−	−	38	62
Ni−Re−B	166.8	155.5	7	25	53.1	−	63
NiCoCuReK/TiO$_2$	200	80	5	72.3	77.2	−	64
Ni−Re−B/Al$_2$O$_3$	155	100[c]	10	69.5	80.2	−	65
Ni−Re−B/Al$_2$O$_3$	155	180	10	42.6	85.4	−	66

[a]Conv.: conversion of MEA. Sel.: selectivity to EDA. −: the information was not found in the literature. wt: mass fraction. [b]n_{EDA}/n_{PIP}. [c]H$_2$.
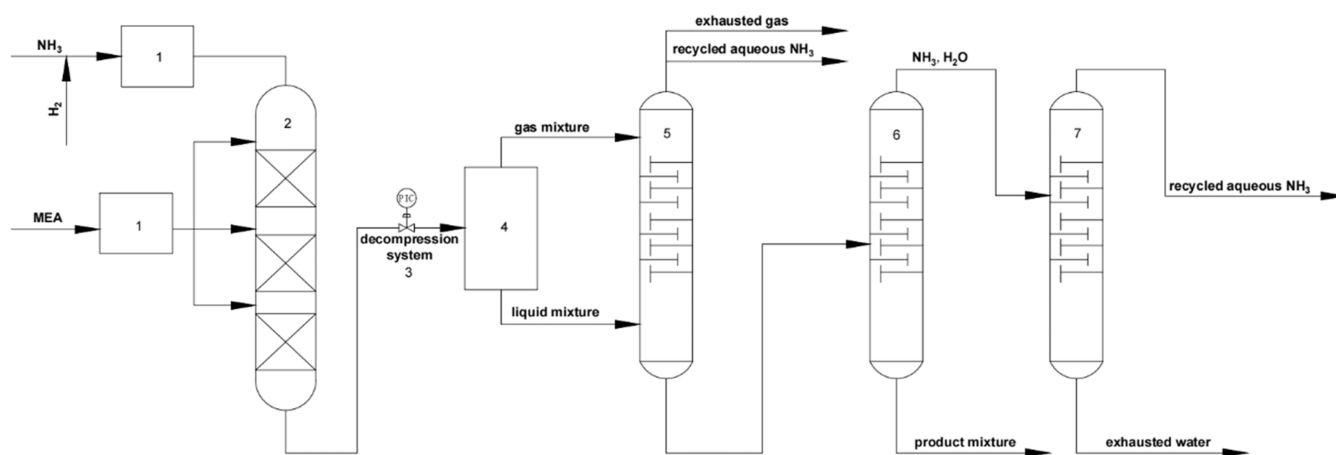

Figure 4. Schematic diagram of the apparatus: 1, heater; 2, reactor; 3, valve; 4, gas separator; 5−7, distillation column.

promoter for MEA amination, delivering an MEA conversion of >50% with >70% EDA selectivity under a pressure of 5.5 MPa at 200 °C.[37,38,70,71] The results of the comparative experiments revealed that the addition of Ru in the catalyst is beneficial to improve the EDA yield. In addition, the yields of cyclic byproducts decrease at higher H$_2$ concentrations, while lower H$_2$ concentrations have little effect. Remarkably, Bai provided a simple but effective strategy for doping Fe to disperse Cu and Cr on the surface of the Cu−Cr−Fe/Al$_2$O$_3$ catalyst, which not only improves the catalytic activity and EDA selectivity but also suppresses the sintering of Cu and further extends the catalyst lifetime.[72]

Re is a common promoter in reductive amination catalysts, which could not only improve the conversion of MEA but also enhance the selectivity of EDA.[52,53,57,58,68,73] Ding and co-workers found that Re species in Ni−Re-mediated catalysts prefer to atomically disperse on the surface of NiO, which effectively suppresses the sintering process of Ni^0 particles during the reaction.[73] The influence of particle sizes on a Ni−Re/SiO$_2$ catalyst was investigated. The catalyst with smallest Ni particle size (4.5 nm) exhibited the highest MEA conversion due to the high dispersion and abundant surface sites of Ni. On the other hand, the growth of the Ni particle enhanced the proportion of terrace Ni sites and the electron density of surface Ni sites. This is beneficial to the desorption of intermediates, facilitating the amination between MEA and

NH$_3$ to form EDA.[58,74] Therefore, the balance of minimizing size enhanced activity and increasing size enhanced selectivity is decisive in affording a high yield of EDA.

Subsequently, Union Carbide Corporation innovated a Ni−Re catalyst with the addition of B, giving an enhanced EDA selectivity of 80 wt % in 39% MEA conversion over a Ni−Re−B/SiO$_2$ catalyst at 160 °C.[59] Significant progress has been made by utilizing a gas−liquid−solid three-phase amination reactor (Figure 4).[65,66] Under this efficient process, 42.6% one-way conversion of MEA with up to 85.4% selectivity of EDA was obtained over a Ni−Re−B/Al$_2$O$_3$ catalyst. Unfortunately, the leaching of B is inevitable, resulting in product contamination and separation difficulties.

3.2. Condensation Amination Route. *3.2.1. Catalysts for the Condensation Amination Route.* Similar to the EG condensation amination reaction process, researchers mainly focused on solid acids like phosphoric acid, tungstic acid, and heteropolyacid in the early stage.[75] However, the poor EDA selectivity caused by the irregular pore structures of the solid acids seriously limited their application in MEA amination. Therefore, increased attention has been paid to zeolites or modified zeolites with high acid density and special micro-porous structures for MEA condensation amination to achieve the goal of shape-selective catalysis. The research mainly focuses on the regulation and control of surface acidity and pore structure. The modification methods of zeolites mainly

Table 5. Summary of Typical Catalytic Systems for MEA Condensation Amination in Continuous Flow Processes[a]

catalysts	T (°C)	p (atm)	n_{NH_3}/n_{MEA}	LHSV (h^{-1})	con. (%)	sel. (%)	yield (%)	ref
H-EDTA-MOR	330	1	50	—	96	72	—	76
Nb/Fe-MOR	330	40	20	0.18	65	68	—	77
1.0AT-Cal	280	40	12	4.58	52.8	93.6	—	78
H-BMOR	390	20	30	0.4	90.2	—	64.3	79
Ce-MOR	340	20	40	0.4	50.5	80.1	—	80
Fe/M-MOR(H)	310	40	12.5	4.58	52.8	93.6	—	81

[a]Con.: conversion of MEA. Sel.: selectivity to EDA. —: the information was not found in the literature.

include metal ion incorporation, partial dealumination, and pore size engineering. A list of typical catalytic systems for condensation amination of MEA to EDA in a continuous flow reactor are shown in Table 5.

3.2.1.1. Effect of catalyst acidity. The condensation amination of MEA is an acid-catalyzed reaction, and the type, strength, amount, and distribution of the acids are vital for the catalytic performance. Segawa developed a series of mordenite (MOR) catalysts for the vapor-phase MEA amination reaction.[41,76,82] The as-received H-MOR enabled a MEA conversion of 58% with an EDA selectivity of 76% at 603 K with a NH$_3$/MEA molar ratio of 50 under normal pressure.[41] The results of the comparative experiments suggested that the MOR channels retard the formation of bulkier PIP derivatives and polyamines, promoting the selectivity of EDA, and the reaction for the formation of EDA requires the stronger acidic sites. In order to clarify the correlation between the Brønsted acid amount and EDA yield, the reaction was observed over a HCl dealuminated MOR (H-HCl-MOR).[82] Since the increase in Brønsted acid increases the number of protonated EIs and facilitates the formation of EDA, both the acid amount and EDA yield increase sharply at the beginning of the dealumination. However, further acidity increment will lead to the deactivation due to framework collapse and loss of acid sites by dealumination (Figure 5).
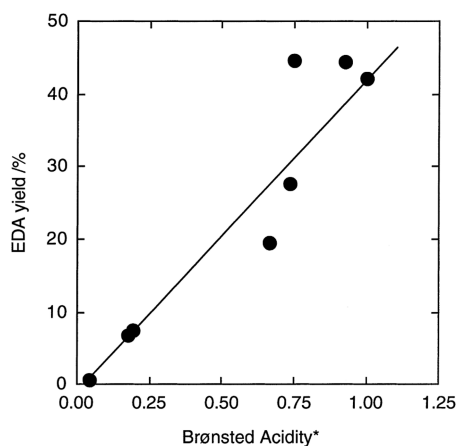

Figure 5. Relationship between Brønsted acid amount and EDA yield of H-HCl-MOR. Reproduced with permission from ref 82. Copyright 2000 Elsevier B.V.

Impressively, the authors reported that a moderately dealuminated H-MOR catalyst treated with EDTA (H-EDTA-MOR) exhibits an EDA yield of 69.1% compared to that 44.6% over the H-HCl-MOR catalyst due to the decrease in acid strength, giving relatively easier desorption of the protonated EI intermediate from the catalyst surface to form EDA.[76] This

result was also confirmed by Zhao, who investigated MEA condensation amination over alkali (NaOH) treated MOR. The result suggested that the strong Brønsted acid sites would hinder the desorption of the alkaline reactants and products from the acid sites, significantly increasing the chance of further side reactions.[78] Therefore, zeolites with adjustable acidic/basic sites would be desirable to boost the catalytic performance of the condensation amination reaction.

In order to achieve the appropriate acidity, considerable effort has been made to modify zeolites with metals like Fe, Cu, Zn, and La.[77–80,82–89] In 2008, Zhao and his colleagues reported a Cu- and Zn-modified MOR catalyst (Cu/Zn-H-HCl-MOR) with 56% conversion of MEA with a 67% selectivity of EDA. The enhanced catalytic performance was attributed to the increased amount of Brønsted acid sites and the improved adsorption ability from Cu. Regrettably, the dehydrogenation reaction is prone to occur on metal-loaded zeolites, leading to the formation of byproducts like pyrazines.[90,91]

3.2.1.2. Effect of Pore Size. The pore structure of the amination catalyst has a significant impact on the catalytic performance due to shape selectivity. Deeba and his co-workers reported that zeolites with pore channels ranging from 5 to 7 Å in diameter significantly improve the EDA yield. The intracrystalline mesopores are sufficiently large to facilitate the quick diffusion of NH$_3$, MEA, and EDA, whereas the generation of linear, branched, and cyclic polymeric amines is retarded.[92,93] Yang investigated the effects of the crystallinity degree and crystal size of H-MOR zeolites and found that the sample with better crystalline phases enhances the EDA yield due to its more regular pore channels and more pronounced shape selectivity.[84]

Although zeolites are desirable to improve catalytic selectivity, the characteristics of shape-selective catalysis result in limited mass transfer for similar-sized reactants, leading to a decrease in catalytic efficiency. Further, the limited diffusion inside the pores would hinder the product spill from the pore channels, causing further side reactions. Groen et al. proposed an approach of manufacturing hierarchically structured micro- and mesoporous zeolites to solve this problem.[94] The micropores serve as microreactors for shape selective catalysis, while the mesopores serve as channels for diffusion to decrease the probability of secondary reactions and thereby increase the product selectivity. Zhao showed that alkali treatment produces more opening mesopores on the H-MOR catalyst and effectively accelerates the diffusion rate.[78] The alkali-treated H-MOR exhibits an MEA conversion of 52.8% with 93.6% EDA selectivity, which is the highest selectivity reported in the literature so far. Recently, an Fe-modified hierarchical MOR catalyst was fabricated with a high EDA selectivity, which was ascribed to the increased Brønsted acid sites from the extra-framework octahedral Fe species.[81]

4. SUMMARY AND OUTLOOK

Herein, we summarized the progress in the green, efficient, and cost-effective synthesis of EDA by direct or indirect amination of EG. A series of catalysts such as metal hydrogenation—dehydrogenation catalysts, solid acids, and ionic liquids have been extensively explored.

Despite the significant advances achieved in the past few decades, most of the existing catalytic systems for EDA synthesis, especially from EG, are far from large-scale industrialization. A series of grand challenges remain to be addressed. First, the current catalysts for the selective synthesis of EDA from EG and MEA demonstrate significantly lower activity. Thus, it is urgent to develop more effective catalytic systems to achieve the highly efficient conversion of EG. This includes exploring advanced catalysts such as supported metal nanoparticles, metal—organic frameworks (MOFs), and single-atom catalysts tailored for efficient EDA production. Second, the major challenges for the selective amination of EG/MEA are the highly complex products and their difficult separation. Hence, determining how to break the thermodynamic equilibrium and improve the selectivity of EDA will be vital for researchers in the future. Dynamic regulation of reaction conditions and the development of catalysts for the selective adsorption of $-NH_2$ and $-OH$ would contribute to higher EDA selectivity. Third, detailed mechanistic and structure—performance relationship investigations by in situ characterizations and theoretical calculations will provide insights into reaction mechanisms and catalyst—substrate interactions. This would be beneficial for the rational design of high-performance catalysts. Additionally, organic amines pose health risks upon prolonged exposure, and it is essential to prioritize safety in the handling and use of EDA and related amines. Strengthening security-related guidelines and implementing appropriate safety measures will be crucial for ensuring safe operation. Finally, it is challenging to scale up catalytic processes from lab-scale to industrial-scale, which might lead to reduced efficiency and increased environmental impact at large scales. Factors such as mass transfer limitations, heat and mass distribution, and reactor design become more pronounced and complex when transitioning from lab to plant. Therefore, the reaction conditions need to be optimized to ensure optimal performance under the increased operating conditions. Moreover, the environmental impact of scaling up catalytic processes must be considered, including energy consumption, waste generation and greenhouse gas emissions.

We sincerely hope that this Review can help researchers in the fields of organic synthesis, catalysis, and medicinal and biological chemistry and play a positive role in the green catalytic synthesis of EDA.

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