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# Amination of diols and polyols to acyclic amines

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## Abstract

The heterogeneous catalytic transformations of bi- and polyfunctional alcohols to the corresponding linear and branched (but not cyclic) amines are reviewed. The aminating components are mainly ammonia, but also primary and secondary amines. The typical catalysts can be divided into two main groups: supported metal and multimetallic hydrogenation catalysts (e.g., Ni, Co, Cu and Ru on alumina or silica) and solid acids (e.g., H-Y and H-ZSM-5 zeolites, $SrHPO_4$, supported phosphoric acid). The reaction routes and mechanisms, and reaction conditions are discussed according to the different types of catalysts. Numerous examples are given illustrating the amination of (i) simple aliphatic diols to amino alcohols and diamines, (ii) amino alcohols to diamines and polyalkylenepolyamines, (iii) polyoxyalkylene diols and triols to the corresponding primary amines and (iv) polyhydroxy-carbonyl compounds (sugars) to polyhydroxyamines.

## 1. Introduction

The heterogeneously catalyzed amination of aliphatic alcohols, i.e., the reaction of an alcohol with ammonia, primary or secondary amine, is a well-known process for the synthesis of the corresponding primary, secondary and tertiary amines. The basics of alcohol amination were described by Sabatier and Mailhe [1,2] already at the beginning of this century. During the past decades, the reaction has been established as the industrially most important process for the manufacture of a variety of aliphatic and aromatic amines. Numerous examples can be found in reviews and books [3–19], though most of the original data have been published in patents, indicating the commercial value of the reaction.

In comparison to reports on amination of simple aliphatic alcohols, studies on the transformation of diols, triols and polyols to the corresponding acyclic di-, tri- and polyamines are scarce. This apparent contradiction is clearly not due to a missing interest in the products. Diamines and polyamines, especially ethylenediamine and its polyethylene polyamine homologues, find a broad range of commercial application [20,21]. The likely explanation for the limited scientific interest is that the amination of a simple (monofunctional) alcohol is already a rather complex process with several side reactions, and only the proper choice of the catalyst and reaction conditions can provide sufficiently high selectivity to the desired product. The difficulties are amplified when using a di- or polyfunctional alcohol reactant and in many cases the selectivity to the desired product is far below the economically acceptable level.

As an illustration, the most important processes for the manufacture of simple aliphatic diamines are collected in Table 1 [21–23]. Remarkably, no process starting from the relatively cheap diol is applied

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Table 1
Industrially applied processes for the manufacture of some primary aliphatic diamines (for more details, see Refs. [21–23])

| Diamine | Process | Comment |
|---|---|---|
| 1,2-Diaminoethane | (a) $Cl–(CH_2)_2–Cl+NH_3$ (aq.) | — |
| | (b) $H_2N–(CH_2)_2–OH+NH_3+H_2$ | Minor process yet |
| 1,3-Diaminopropane | $CH=CH–CN+NH_3$; $+H_2$ | Two-stage process |
| 1,4-Diaminobutane | (a) $THF+Cl_2$; $+NH_3$ | Two-stage process |
| | (b) $CH_2=CH–CH=CH_2+Cl_2$; $+NH_3$ | Two-stage process |
| 1,6-Diaminohexane | $NC–(CH_2)_4–CN+H_2$ | — |

commercially. The only example for alcohol amination is the transformation of monoethanolamine to ethylenediamine. Most of the diamines (and polyethylene polyamines) are traditionally manufactured from $\alpha,\omega$-alkylene dichlorides. A well-known disadvantage of the method is the corrosion caused by hydrogen chloride. The subsequent neutralization creates large amounts of aqueous sodium chloride and growing difficulties in its environmentally acceptable disposal. Considering the availability of reactants, the environmental and corrosion problems, the heterogeneously catalyzed amination of diols could be an attractive and economic alternative to some established processes.

From the point of view of selectivity, the easiest reaction is the amination of a diol or polyol with a secondary amine, as the product tertiary amine is relatively unreactive. (Not considering the cyclization reactions, which is out of the scope of this paper). On the other hand, the most demanding reaction type is the amination with ammonia to produce primary amines, as the product is considerably more reactive (basic) than ammonia. The topic of this review is the latter reaction, the amination of diols, triols and polyols to the corresponding primary amines. For a better understanding, the formation of amino alcohols and their transformation to diamines will also be discussed. As concerns the basic knowledge on the catalytic amination of aliphatic alcohols, the reader should consult with former reviews [3–7,9–11].

## 2. Catalysts, reaction routes and conditions

Two types of materials are suitable for the heterogeneously catalyzed amination of alcohols: hydrogenation–dehydrogenation catalysts, usually being supported metals, and solid acid catalysts, such as zeolites, phosphates and oxides. Accordingly, the reaction routes and conditions will be discussed in separate sections.

### 2.1. *Amination over metal catalysts*

The metal and supported metal catalysts, reported to be efficient in the amination of diols and polyols [25–58], are similar to those widely applied in the amination of simple aliphatic alcohols. No general rule concerning the choice of an active and selective catalyst can be found in the literature, which would be valid to a broad range of amination reactions. The frequently used active components are Ni, Co, Cu and Ru. Many catalysts described in patents or papers are multicomponent materials and contain some additive (e.g., Cr, Fe, Zn, Ir and Rh) for enhancing the activity, selectivity or long term stability. An example is shown in Table 2. Fe/alumina was found to be inactive in the transformation of ethanolamine to ethylenediamine, but incorporation of Fe improved the selectivity of Co and Ni catalysts.

Frequently used supports are alumina, silica and titania. A study of the amination of diethylene glycol with ammonia over supported Ni catalysts (Table 3) revealed a rather good correlation between the reaction rate and the specific Ni surface determined by oxygen chemisorption [59]. Seemingly, the role of support was to stabilize the dispersed metal and the reaction rate was independent of the acidity of the support.

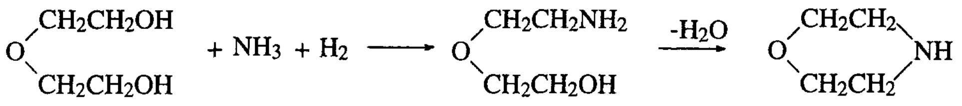
On the basis of the very few mechanistic studies available in the literature [48,59,60], Scheme 1 illustrates the key steps and the typical side reactions during the metal-catalyzed amination of $\alpha,\omega$-alkanediols **1** used as model reactions. For the sake of simplicity, the interactions of reactants, intermediates

Table 2
Comparison of metal catalysts in the amination of ethanolamine to ethylenediamine. Conditions: 7 g catalyst, 29 g ethanolamine, 37 g water, 81 g ammonia, 44 bar $H_2$, 150 bar total pressure, 225°C, autoclave (adapted from Ref. [31])

| Catalyst | Atomic (molar) ratio | Selectivity to ethylenediamine (%) | |
|---|---|---|---|
| | | At 40% conversion | At 60% conversion |
| Ni–Fe | 1:1 | 70 | 62 |
| Ni–Fe/$Al_2O_3$ | 0.9:0.1:1 | 61 | 55 |
| Ni–Fe/$Al_2O_3$ | 0.95:0.05:1 | 54 | 51 |
| Ni/$Al_2O_3$ | 1:1 | 54 | 52 |
| Raney Ni | — | 46 | 41 |
| Fe/$Al_2O_3$ | 1:1 | [a] | [a] |
| Ni–Co–Fe/$Al_2O_3$ | 1:1:1:3 | 65 | 60 |
| Co–Fe/$Al_2O_3$ | 1:1:2 | 69 | 62 |
| Ni–Co/$Al_2O_3$ | 1:1:2 | 51 | 50 |
| Co/$Al_2O_3$ | 1:1 | 50 | 48 |

[a] Inactive catalyst, no reaction occurred.

Table 3
Performance of various Ni catalysts in the amination of diethylene glycol, as shown below. Conditions: fixed bed reactor, 190°C, 1 bar, 0.5 g catalyst, diethylene glycol:$NH_3$:$H_2$=1:10:5 molar ratio (adapted from Ref. [59])

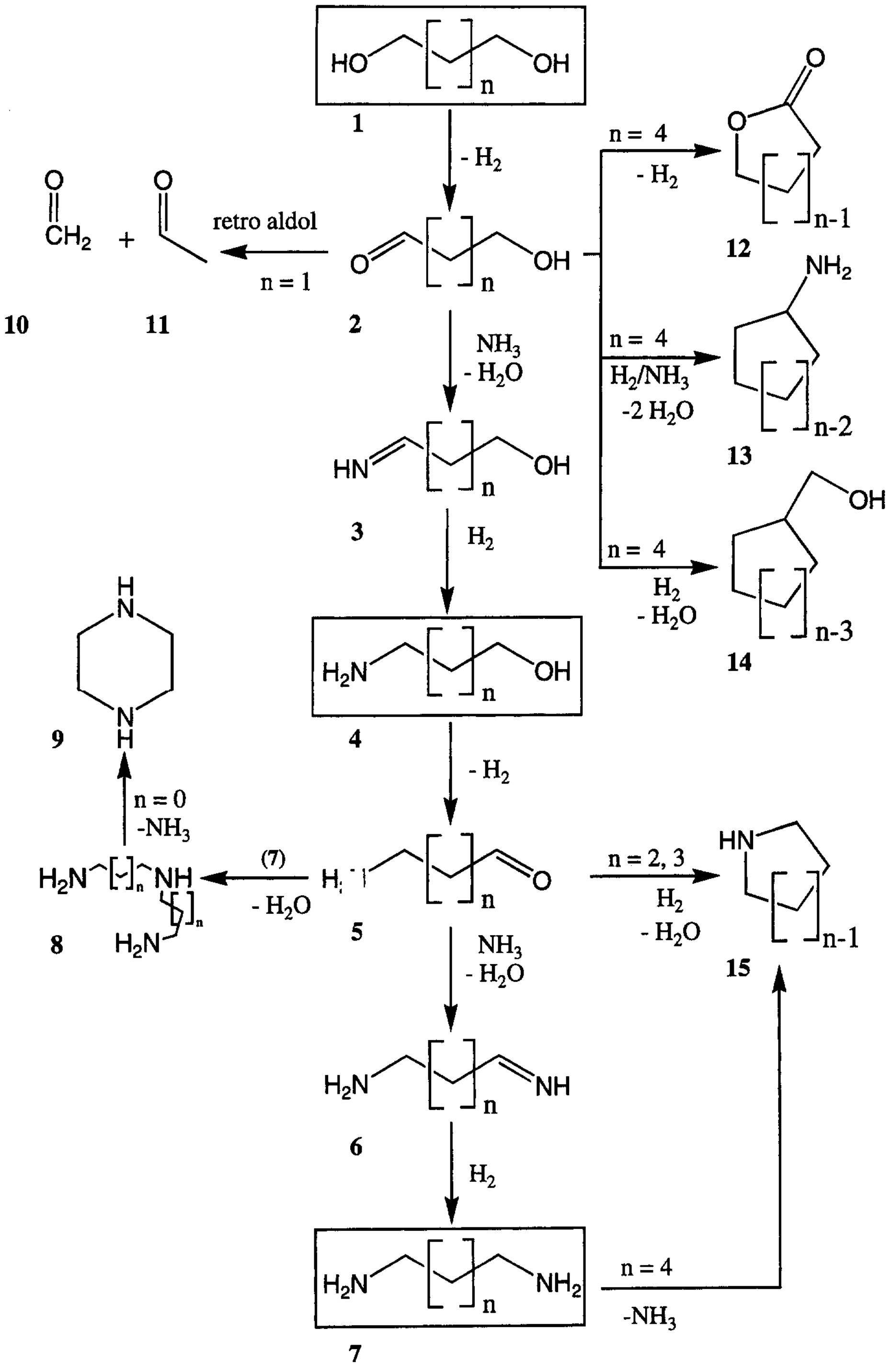


| Catalyst | Ni (wt%) | $S_{BET}$ ($m^2 g^{-1}$) | Chemisorbed $O_2$ ($ml\ g^{-1}$) | Rate constant[a] ($mmol\ h^{-1} g^{-1}$) |
|---|---|---|---|---|
| Ni/$SiO_2$ | 57 | 199 | 8.1 | 8.8 |
| Ni/$SiO_2$ | 38 | 142 | 7.2 | 7.6 |
| Ni/$SiO_2$ | 24 | 179 | 5.2 | 5.8 |
| Ni/$Al_2O_3$ | 52 | 123 | 4.0 | 4.7 |
| Ni/$V_2O_5$ | 57 | 121 | 3.5 | 2.7 |
| Ni/$TiO_2$ | 54 | 64 | 1.6 | 2.1 |
| Ni/$ZrO_2$ | 58 | 58 | 1.2 | 1.2 |
| Ni/ZnO | 52 | 88 | 1.2 | 1.1 |
| Ni/$Nb_2O_5$ | 52 | 46 | 0.2 | 0.6 |

[a] For the consumption of diethylene glycol.

and products with the catalyst surface are not specified. Also, here and in other schemes, simple arrows indicate the reaction route, though most of the transformations are equilibrium reactions. The equilibrium is indicated only to emphasize the importance of both directions.

The main reaction steps include the (i) dehydrogenation of one of the $-CH_2OH$ groups of **1** to a carbonyl group, (ii) condensation of the carbonyl group with ammonia, a primary or a secondary amine via a carbinolamine adduct to form an imine **3** (or enamine [7]), and (iii) hydrogenation to the monoaminated alcohol **4** (frequently termed as "aminol"). Basically, these steps are the same as those proposed for the amination of small and long chain aliphatic amines [6,7,61–63]. The second hydroxyl group of the diol reacts similarly forming compounds **5**–**7**. The key intermediates are the two adsorbed carbonyl compounds **2** and **5**; their formation and consumption can determine the overall rate and selectivity. The selectivity to the aminol **4** is usually good, but the diaminoalkane **7** is difficult to produce as a major


1
- H2
retro aldol
n = 1
10
11
2
NH3
- H2O
3
H2
4
- H2
5
NH3
- H2O
6
H2
7
n = 4
- H2
12
n = 4
H2/NH3
-2 H2O
13
n = 4
H2
- H2O
14
n = 2, 3
H2
- H2O
15
n = 4
-NH3
(7)
- H2O
8
n = 0
-NH3
9

Scheme 1.

product (on the other hand, some diamines can be prepared with good yield when starting from the aminol).

A multitude of side reactions are possible. Typical side reactions, which have already been evidenced in the amination of simple aliphatic alcohols, are the (i) disproportion of the amine to form secondary and tertiary amines, and ammonia [64], (ii) condensation or decarbonylation of the carbonyl compound intermediate and (iii) the formation of nitriles at high temperature and low hydrogen partial pressure [65]. Hydrocracking and hydrogenolysis of amines can also become dominant at high temperature [6].

With bifunctional alcohols the condensation and disproportionation reactions can result in "polyamines"; some of them with limited molecular mass are important products. One example is the formation of **8** from **5** and **7**. The undesired formation of oligomers and polymers is frequently reported and cannot be fully excluded, as most of the intermediates and products are bi- or multifunctional compounds.

Cyclization reactions represent another important class of side reactions. Some dominant routes to the formation of (hetero)cyclic products **9** and **12–15** are illustrated in Scheme 1 [46,48]. The structure of the alcohol, i.e., the distance of the functional groups determines the direction of the amination reaction. Short chain diols tend to dimerize to form stable cyclic compounds or produce oligomers, depending on the catalyst and reaction conditions. For example, 1,2-ethanediol (and ethanolamine) dimerize easily to piperazine **9** or form **8** and other polyamines of higher molecular mass. 1,6-Hexanediol tends to cyclization, forming five- or six-member rings such as **12–14** [48,51]. The self-condensation of $C_4$–$C_6$ aminol intermediates **4–15** via **5** or **7** has also been proposed [60]. On the basis of thermodynamic considerations, a similar reactivity of 1,4-butanediol and 1,5-pentanediol can also be expected though not yet evidenced. Low ammonia concentration favors the formation of cyclic products. Dehydrogenation of the cyclic products becomes dominant at high temperatures, leading to thermodynamically more stable aromatic compounds [66]. As the formation of 8–12 membered rings is energetically unfavorable, long chain diols ($>C_8$) tend to dimerize and oligomerize.

Fragmentation products by hydrogenolysis of the C–O and C–N bonds are typical of metal catalyzed amination reactions, especially at elevated temperature and pressure. With 1,3-diols an additional possibility is acid- or base-catalyzed reverse "retro" aldol reaction producing two carbonyl compounds from the intermediate $\beta$-hydroxy-aldehyde **2** [47].

The formation of primary amines from ammonia and alcohol is close to thermoneutral [10], whereas the further reactions to secondary and tertiary amines are slightly exothermic (each step by 7 kcal $mol^{-1}$). Thus, assuming that the contribution of entropy is minor, the conversion of primary amines to secondary and tertiary amines is thermodynamically favored. A similar behaviour can be expected based on kinetic considerations, due to the higher reactivity (nucleophilicity) of the primary amine, as compared to that of ammonia.

Consecutive reactions, diminishing the selectivity to primary amines, can be suppressed by applying high molar ratio of ammonia to diol (20:1 or even higher, e.g., Ref. [55]). A possible disadvantage of too large ammonia excess is the saturation of the catalyst surface by ammonia and a decrease of activity, as reported in some cases [39,43]. Similarly, moderate ammonia excess is recommended for the production of linear polyamines [9,39,79–81].

Although from a stoichiometric point of view hydrogen is not essential, its addition to the reaction mixture in amounts ranging from 0.1 to 2 mol per mol hydroxyl group is necessary when the amination is performed over metal catalysts, e.g., Ref. [55]. Saturated amines are formed predominantly in the presence of a sufficient amount of hydrogen, whereas imines, enamines and nitriles are favored in the absence of hydrogen [6,46]. Besides, hydrogen suppresses the simultaneously occurring disproportionation of amines and protects the catalyst from deactivation by incorporation of nitrogen and/or carbon into the metal lattice [28,67,68].

It was found in many cases that both batch reactors (autoclaves) and continuous flow systems (fixed bed reactors) are suitable for the amination of diols and polyols. The generally applied total pressure ranges between 50 and 300 bar, though it has been demonstrated that high pressure in a fixed bed reactor is not a prerequisite for obtaining good reaction rates and selectivities [46,48]. The reaction temperature necessary for achieving reasonable conversions is around 180–250°C. Under these conditions the ammonia–hydrogen mixture is in the supercritical state (for ammonia: $p_{crit}$=114 bar, $T_{crit}$=132°C [69]). Interestingly, no report has been published yet on the influence of sub- or supercritical medium on the rate and selectivity of an amination reaction.

Solvents (other than ammonia) are rarely applied. It was found [70] that in the amination of ethanolamine to a mixture of ethylenediamine and piperazine, addition of water increased the selectivity of a Ni–Cu–Cr-oxide catalyst to the cyclic product. Some contradictory observations on the influence of water will be discussed in the following sections.

In batch reactors the amount of metal catalyst is usually between 5 and 30 wt% related to the amount of alcohol. In continuous reactors the total amount of reactant feed varies in a broad range, usually between 0.5 and 10 g total feed per hour and gram catalyst (WHSV), e.g., Ref. [35].

## 2.2. Amination over solid acid catalysts

### 2.2.1. Reaction route over zeolites

Among the solid acid catalysts, zeolites are frequently used for the synthesis of small chain aliphatic diamines [71–77] or cyclic amines [78] from the corresponding amino alcohols. Y-zeolites, ZSM-5 and mordenites in their protonic form are the mostly employed molecular sieves. Only very few patents propose acidic oxides [79] or silicates [80,81] as efficient catalysts for the preparation of diamines or polyamines. Concerning the reaction conditions, the amination of diols over acid catalysts requires rather high temperature (250–450°C), as compared to the conditions applied with supported metal catalysts.

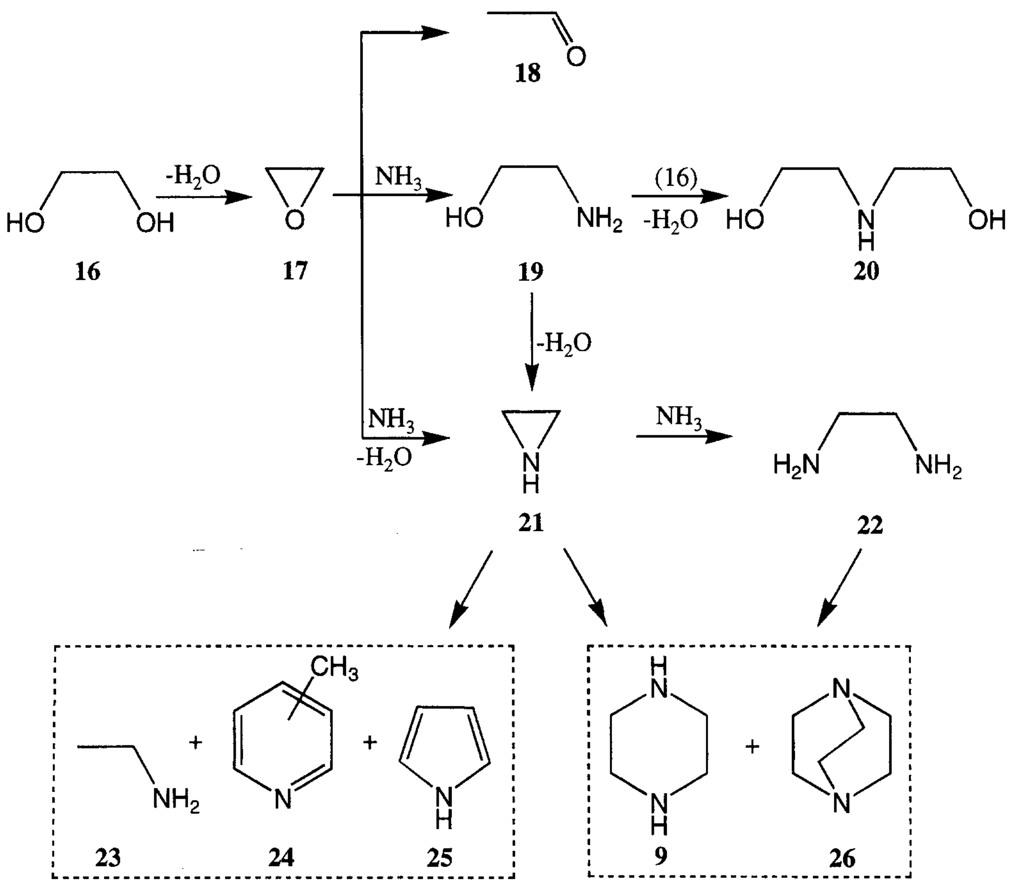
Despite the limited number of mechanistic studies it is clear that the Brønsted sites of zeolites play a key role in alcohol amination [71–75,82,83]. IR studies indicated that ammonia and amines are adsorbed on Brønsted sites and form ammonium species. The adsorption of the amine is much stronger than that of ammonia. Amino alcohols are adsorbed as ammonium-ions and not as oxonium-ions [73,74].

It has been proposed that the first step of the amination of monofunctional alcohols over zeolites (and acidic oxides) is the dehydration to an olefin or ether [3,10,18]. Using the example of the amination of ethylene glycol, Scheme 2 illustrates the key steps which have been proposed for the zeolite-catalyzed reaction, and also the rather broad range of products detected [74,76,77]. It is assumed that ethylene oxide is the intermediate after dehydration of the diol and ethyleneimine when using ethanolamine as the reactant. Typical product distributions observed over an iron-promoted natural zeolite are shown in Table 4 [77]. Ethylenediamine **22** was a minor product, independent of the reaction conditions or catalyst modification. Similar reaction steps and the formation of the corresponding epoxide and imine as key intermediates were proposed for the amination of 1,2-propanediol over H-ZSM-5 [76].

Ethylenediamine can be produced with good selectivity, when the reactant is ethanolamine, instead of ethylene glycol, as illustrated in Table 5 [74]. IR spectroscopic studies indicated that protonated ethyleneimine was the key intermediate and, interestingly, in some cases even the main product was ethyleneimine. The results also suggest that strong acidic sites in the limited size of the zeolite channels are favorable for the selective synthesis of ethylenediamine and for the suppression of the formation of bulky polyamines and heterocyclic compounds. There is no steric control when using macroporous silica–alumina, accordingly, self-condensation of ethanolamine to form cyclic and linear polyethyleneamines dominates over the reaction with the less nucleophilic ammonia [71].

An increase of the ammonia/ethanolamine molar ratio (up to 80) had a positive influence on the rate of ethanolamine conversion and the selectivity to ethylenediamine (Fig. 1). Recently, transient response experiments indicated that in methylamines synthesis over zeolites the rate determining step is the desorption of amines from the acidic sites, aided by adsorbing ammonia [82]. The rate enhancement observed in the presence of a large excess of ammonia in ethylenediamine synthesis can be explained similarly. The positive effect of high ammonia concentration on ethylenediamine selectivity is understandable from Scheme 2. A similar correlation between ammonia excess and ethylenediamine selectivity was observed when using silica–alumina catalysts [79].

On the basis of the observed product distribution, the possible reaction route in the zeolite-catalyzed amination of 1,4-butanediol **27** is depicted in Scheme 3. The main product is pyrrolidine **29**, independent of the reaction temperature (Table 6) [77] (note the same promoted zeolite catalyst and similar conditions were applied for ethylene glycol amination, as shown in



Scheme 2.

Table 4

Amination of ethylene glycol (**16**) over a natural aluminosilicate (gumbrin) promoted with 5 wt% ferric oxide. Product composition (according to Scheme 2): **9**, piperazine; **17**, ethylene oxide; **18**, acetaldehyde; **19**, ethanolamine; **22**, 1,2-diaminoethane; **24**, methyl pyridines; **25**, pyrrolidine. Conditions: fixed bed reactor, space velocity of glycol: 0.2 $h^{-1}$, glycol to $NH_3$ molar ratio=1:1 (adapted from Ref. [77])

| T (°C) | Products (wt%) | | Composition of the liquid product (wt%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Gas | Liquid | **9** | **16** | **17** | **18** | **19** | **22** | **24** | **25** | $NH_3$ |
| 300 | 7.8 | 92.2 | 1.6 | 82.4 | 4.7 | 2.0 | 3.7 | 0.3 | 1.8 | 2.3 | 1.2 |
| 325 | 12.6 | 87.4 | 1.2 | 80.0 | 5.7 | 1.6 | 3.5 | 0.5 | 2.1 | 3.8 | 1.5 |
| 350 | 17.0 | 83.0 | 1.1 | 76.6 | 7.0 | 1.5 | 3.4 | 0.7 | 2.1 | 6.5 | 1.1 |
| 375 | 23.7 | 76.3 | 1.0 | 75.3 | 6.6 | 1.2 | 3.1 | 0.7 | 2.3 | 8.9 | 0.9 |
| 400 | 28.8 | 71.2 | 1.0 | 73.6 | 6.6 | 1.2 | 2.8 | 0.9 | 2.5 | 10.7 | 0.7 |

Table 4). The first dehydration step can provide either tetrahydrofuran **28** or 3-buten-1-ol **30**. Tetrahydrofuran is rapidly aminated to the main product pyrrolidine, but no amines derived from the amination of the olefin **30** could be detected. This explanation is in agreement with former observations, that tetrahydrofuran reacts smoothly at 350°C with ammonia over acidic zeolites (e.g., H-L and H-Y) forming pyrrolidine with over 90% selectivity [84–86]. On the other hand, the selective amination of olefins (via Markov-

Table 5
Amination of ethanolamine with ammonia and solid acid catalysts, according to Scheme 2. Conditions: fixed bed reactor, contact time: 200 g $h^{-1}$ $mol^{-1}$, 330°C, 1 bar, $NH_3$/alcohol molar ratio: 50 (adapted from Refs. [73,74])

| Catalyst | Pore size (nm) | Conversion (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|---|
| | | | 22[a] | 21[b] | Cyclic[c] | Others[d] |
| $SiO_2$–$Al_2O_3$ | — | 100 | 1 | 7 | 49 | 43 |
| H-Chabazite | 0.38 | 4 | 4 | 69 | 13 | 14 |
| H-Faujasite | 0.74 | 6 | 13 | 76 | 9 | 9 |
| H-Linde-type L | 0.71 | 15 | 23 | 32 | 21 | 21 |
| H-Mordenite | 0.70 | 42 | 81 | 7 | 9 | 3 |

[a] Ethylenediamine.
[b] Ethyleneimine.
[c] Mainly piperazine and derivatives, and 1,4-diazabicyclo-octane.
[d] Mainly polyamines.

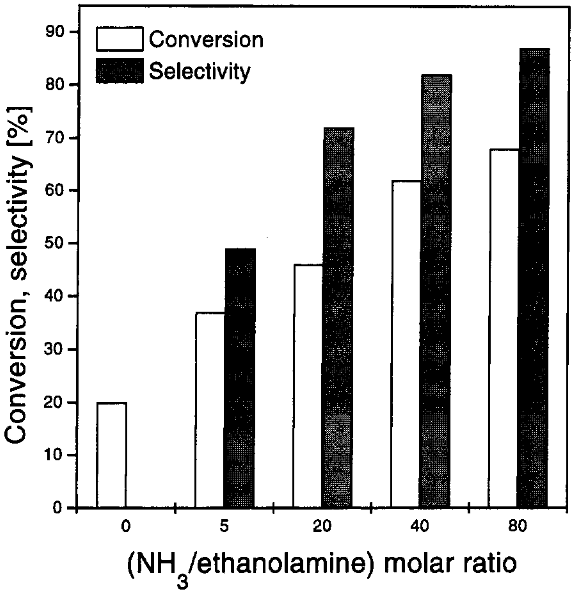


Fig. 1. Ethylenediamine synthesis from ethanolamine on EDTA-modified H-MOR zeolite (Si/Al=6.1) as a function of ammonia/ethanolamine molar ratio. Conditions: fixed bed reactor, 310°C, 1 bar total pressure, ethanolamine/$NH_3$/$H_2$ molar ratio=1:50:25 (adapted from Ref. [74]).

nikov addition of ammonia) is limited at low temperature by the insufficient activity of zeolites and by the thermodynamic equilibrium at temperatures above 300–350°C [9,87].

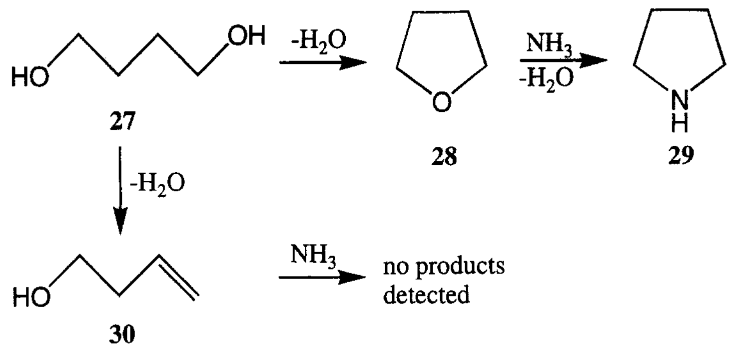
### 2.2.2. *Reaction route over phosphates*

Group I–IIIa and IIIb metal phosphates, such as $SrHPO_4$ and $LaHPO_4$, and also phosphoric acid treated alumina or titania gain increasing interest in catalytic amination reactions. They are suggested for the selective synthesis of mixed alkylamines [9,88] and acyclic polyalkylene polyamines [89–91]. The performance of some phosphate catalysts in the transformation of ethanolamine to ethylenediamine is illustrated in Table 7. $LaHPO_4$ was the most selective catalyst to ethylenediamine, but even in this case more than 50% of the products were cyclic amines and noncyclic tri- and polyamines.

Both autoclaves and fixed bed reactors (under pressure) have been used [89]. A vapor phase operation can be advantageous to minimize leaching problems.

It has been proposed [9,88] that the amination of alcohols over metal phosphate catalysts occurs via a "phosphate ester" mechanism. The alcohol is activated by a surface phosphate group and a phosphate ester is formed after elimination of a water molecule (Scheme 4). In the following nucleophilic substitution reaction the amine reactant replaces the surface phosphate, resulting in a new, alkylated amine and regenerating the surface active site.

Other possible routes could be excluded on the basis of experimental observations. Metal phosphates are relatively weak acids and their catalytic activity cannot be attributed to their acidic properties alone. Another probable mechanism would be the activation of the amine via a surface phosphoramide intermediate. A subsequent interaction with the alcohol reactant and hydrolysis of the amide would provide the alkylated amine and regenerate the active site. The formation of surface phosphoramides had been observed



Scheme 3.

Table 6
Amination of 1,4-butanediol **27** over a natural aluminosilicate (gumbrin) promoted with 5 wt% ferric oxide. Product composition according to Scheme 3. Conditions: fixed bed reactor, space velocity of diol: 0.2 $h^{-1}$, diol to $NH_3$ molar ratio=1:1 (adapted from Ref. [77])

| T (°C) | Products (wt%) | | Composition of the liquid product (wt%) | | | |
|---|---|---|---|---|---|---|
| | Gas | Liquid | **27**[a] | **28**[b] | **29**[c] | **30**[d] |
| 350 | 8.2 | 91.8 | 64.7 | 3.3 | 30.2 | 0.8 |
| 400 | 14.4 | 85.6 | 57.8 | 2.5 | 38.6 | 1.1 |
| 425 | 18.7 | 81.3 | 49.3 | 1.2 | 47.6 | 1.9 |
| 450 | 28.6 | 71.4 | 49.5 | 1.3 | 46.8 | 2.1 |

[a] 1,4-Butanediol.
[b] Tetrahydrofuran.
[c] Pyrrolidine.
[d] 3-Buten-1-ol.

when treating a phosphate catalyst with ammonia [92,93]. However, tertiary aminoalcohols are also reactive on phosphate catalysts and form cyclic amines. Since tertiary amines cannot form amides, this observation supports the phosphate ester mechanism of alcohol amination.

## 3. Examples on the amination of bi- and polyfunctional alcohols

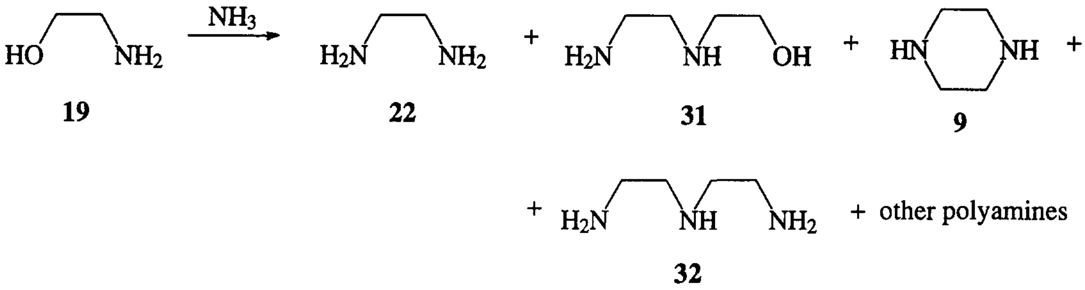
### 3.1. *Synthesis of ethylenediamine from ethylene glycol and ethanolamine*

Ethylene glycol is the simplest aliphatic diol which is produced in a large amount at a low price. Nevertheless, only a few patents are available on the amination of ethylene glycol to ethylenediamine [26,32,33,57,58]. At moderate conversions the selectivities to the ethanolamine intermediate are good, but the yields to ethylenediamine are usually moderate due to cyclization and dimerization reactions. A Co-oxide catalyst described in an early patent [58] seems to be an exception: this material provided 70% ethylenediamine yield at 90% glycol conversion, at 180°C and 300 bar. Other catalysts, such as Ni–Cu/alumina, Ni–Pd/silica or Ni–Re/alumina are less efficient [33,57].

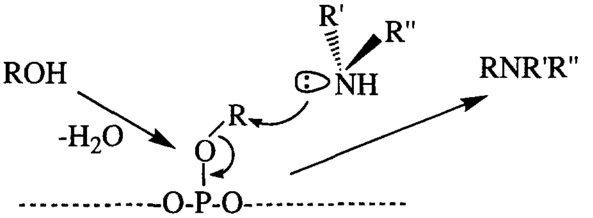
No further development of this process or recent reports on more promising catalysts for ethylene glycol amination have appeared, indicating the lacking commercial interest. As it was discussed in Section 1, ethylene glycol is not the raw material for the commercialized process, rather ethylene oxide is aminated directly to ethanolamine and then in a separate step to ethylenediamine [21–24,94]. Accordingly, only the ethanolamine→ethylenediamine transformation will be discussed below.

The usual reaction temperature is around 200°C. The selectivity to ethylenediamine is high at low

Table 7
Amination of ethanolamine **19** with ammonia over metal phosphate catalysts, as shown below. Conditions: batch reactor, 300°C, 130 bar, $NH_3$/ethanolamine molar ratio=2:1, 63.3 g ethanolamine, 35.5 g $NH_3$ (adapted from Ref. [90])



| Catalyst (wt%) | Time (h) | Conversion (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|---|
| | | | **22** | **31** | **32** | **9** |
| $LaHPO_4$ (19.3) | 2 | 53 | 34.8 | 7.5 | 9.1 | 7.0 |
| $LaHPO_4$ (18.5) | 4 | 50 | 49.2 | 26.5 | 10.2 | 5.0 |
| $NdHPO_4$ (19.3) | 2 | 68 | 12.3 | 9.8 | 11.5 | 9.9 |
| $YHPO_4$ (15.7) | 2 | 67 | 14.8 | 2.8 | 12.4 | 6.9 |
| $GdHPO_4$ (20.3) | 2 | 70 | 13.9 | 6.2 | 7.4 | 5.2 |
| $PrHPO_4$ (19.2) | 2 | 80 | 18.4 | 3.6 | 9.9 | 6.3 |



Scheme 4.

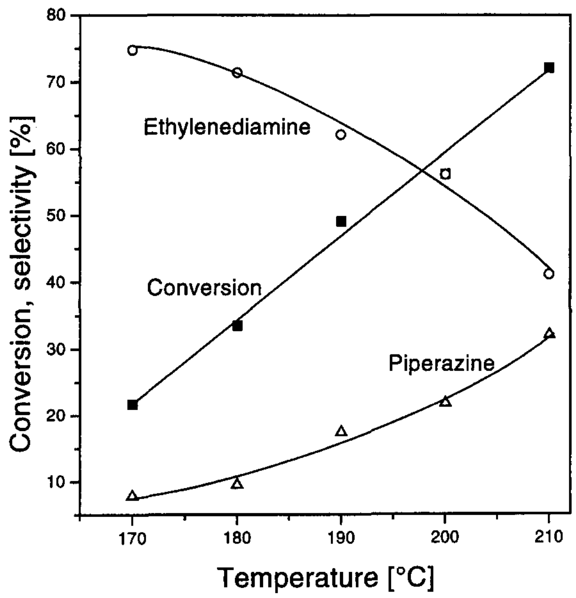


Fig. 2. Influence of temperature on product selectivity in the amination of ethanolamine over a Ni–Cu–Cr catalyst. Conditions: fixed bed reactor, 172 bar, feed: 4.9–5.5 g/(h ml cat.), $NH_3$/ethanolamine molar ratio: 5.3–6.3, 8.7–10.6 ml $H_2$/g reactant (adapted from Ref. [36]).

temperature, but the activity of metal catalysts is rather low at 150–170°C. At higher temperature cyclization reactions and (above 250°C) fragmentation of the alcohol and/or the amine become dominant [45]. An example demonstrating the product distribution in the interesting temperature range is shown in Fig. 2 [36]. The influence of increasing reaction time on the conversion and product distribution is similar to that of temperature. The formation of piperazine byproduct in consecutive amination reactions is favored by the long reaction time, as illustrated in Fig. 3 [31].

The crucial role of catalyst composition is thoroughly discussed in the patent literature [31,43,56]. For example, an increase of the metal content of a Ni/

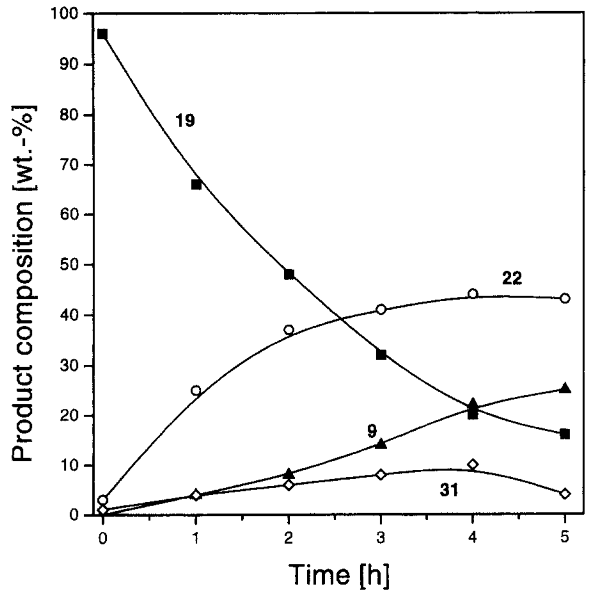


Fig. 3. Influence of reaction time on the product composition in the reaction of ethanolamine **19** with ammonia. Conditions: autoclave, Ni–Co–Fe/$Al_2O_3$ catalyst (24 wt%, related to **19**), **19**/$NH_3$ molar ratio: 1/10, 225°C, 150 bar. Numbers (according to scheme in Table 7): **9**, piperazine; **22**, ethylenediamine; **31**, aminoethylethanolamine (adapted from Ref. [31]).

alumina catalyst enhances the ethanolamine conversion and favors the formation of piperazine, as shown in Fig. 4 [56]. It is not clear, whether the higher selectivity to the cyclic product at high metal loading is due to the higher conversion or to the different size and morphology of the metal particles. Several promoters, such as iron, chromium and molybdenum, have been suggested to improve the ethylenediamine selectivity; for examples see Table 2.

As it was discussed in Section 2, the concentration of ammonia and hydrogen can strongly influence the reaction rate and selectivity over metal catalysts. High selectivity to ethylenediamine requires a large molar excess of ammonia, usually at least 10 mole per reacting hydroxyl group. Using a Ni catalyst, 130–170 bar ammonia pressure was suggested to afford 70–90% selectivity to ethylenediamine at 200°C [30]. Lower ammonia concentration favored the formation of polyethylenepolyamines and at 80 bar the selectivity to diamine was only 40%. The formation of di- and polyamines ("residue") can be significant even at low conversion, when the ammonia/alcohol ratio is not sufficiently high [32], as illustrated in Fig. 5.

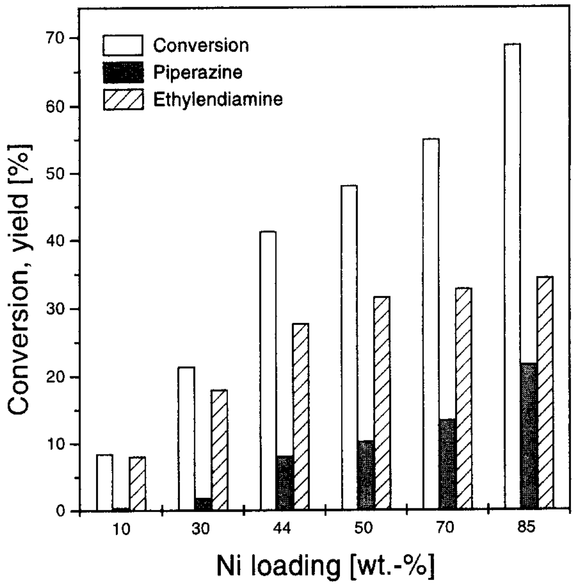


Fig. 4. Influence of the metal loading of Ni/alumina in the amination of ethanolamine with ammonia. Conditions: autoclave, $NH_3$/ethanolamine molar ratio: 10/1, approx. 0.5 bar $H_2$, 195°C, 146 bar total pressure, 8 h reaction time (adapted from Ref. [56]).

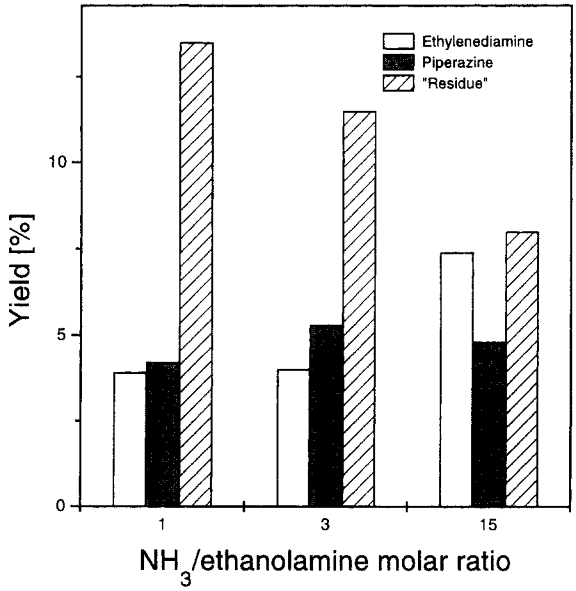


Fig. 5. Influence of $NH_3$/ethanolamine molar ratio on the product distribution at 20% ethanolamine conversion. Conditions: fixed bed reactor, Cu–Ni–Cr-oxide catalyst, 270°C, 186 bar (adapted from Ref. [32]).

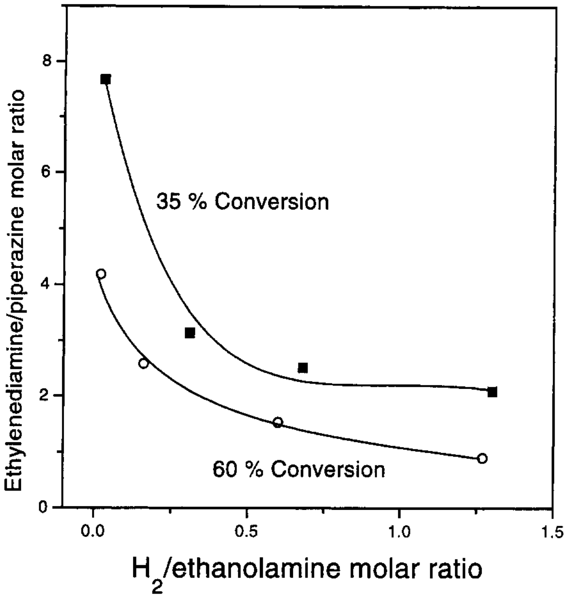


Fig. 6. Product composition as a function of hydrogen/ethanolamine molar ratio and ethanolamine conversion. Conditions: fixed bed reactor, Ni–Cu–Cr-oxide catalyst, liquid hourly space velocity 4.5 g/(h, ml$_{cat}$), NH$_3$/ethanolamine molar ratio: 6/1, 172 bar, no data for temperature (adapted from Ref. [35]).

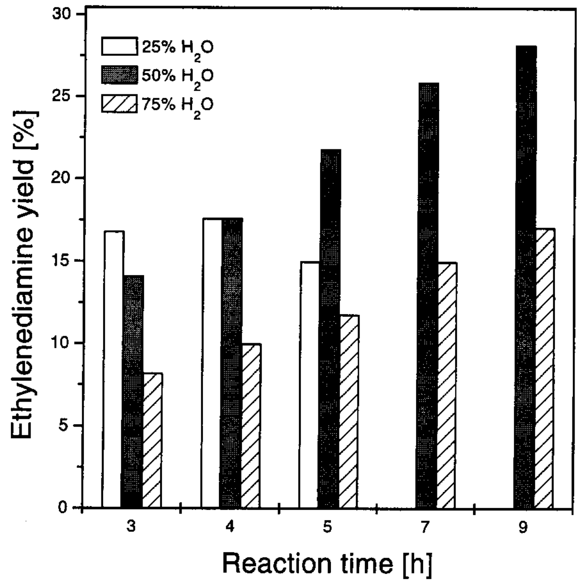


Fig. 7. Influence of the relative amount of water used as solvent in the ethanolamine→ethylenediamine transformation. Conditions: autoclave, 160°C; p(NH$_3$)=2 bar, p(H$_2$)=2 bar; Ni/alumina–silica catalyst (1 g/10 g ethanolamine), data for 25% water at 7 and 9 h are not available (adapted from Ref. [93]).

Beside the well-known effects of hydrogen on the selectivity and catalyst lifetime in the amination of small and long chain aliphatic alcohols, the relative amount of hydrogen can control the ratio between cyclic and linear amines in the amination of bifunctional alcohols. The usual hydrogen concentration is around 0.1–2 moles per mole hydroxyl group, e.g., Refs. [28,55]. The continuous amination of ethanolamine over a multimetallic catalyst is shown in Fig. 6 as an example. An increase of the hydrogen/ethanolamine molar ratio from 0.02 to 1.3 resulted in a decrease of the ethylenediamine/piperazine molar ratio by a factor of around 4 [35]. The application of low hydrogen concentration, which would be advantageous for obtaining good selectivity to the diamine, is limited by the low reaction rate due to catalyst deactivation [45].

All patents describing the amination of ethylene glycol or ethanolamine with ammonia mention the possibility of using solvents. Mainly water, dioxane, cyclohexane or tert-butanol have been proposed in order to moderate the activity (and improve the selectivity) of the catalyst, to minimize the self-condensation of ethanolamine or to increase the ammonia concentration in the liquid phase under low pressure conditions. Unfortunately, no unambiguous conclusions concerning the advantages of the presence of a solvent can be drawn from the literature. The majority of the reported processes were performed without any added solvent. Under medium and high pressure conditions ammonia, usually applied in high excess, acts as a solvent (liquid or supercritical fluid). A clear effect of added solvent is the lower reaction rate due to dilution of the reaction mixture [30,93]. A special case is the addition of water, which is formed also during reaction in stoichiometric amount. Water as a solvent can have either positive or negative influence on the diamine selectivity [24,38,57,93], as depicted in Fig. 7. Depending on the reaction time (conversion), higher initial water concentration in the reaction mixture improved or decreased the ethylenediamine yield over a supported Ni catalyst.

Interestingly, addition of piperazine to ethanolamine before the reaction improves the ethylenediamine selectivity [24]. The presence of 3–6% piperazine at the beginning of the amination reaction enhanced the ethylenediamine yield by 2–10% over a Ni/(alumina–silica) catalyst, and decreased the amount of linear and cyclic dimers. This observation offers a simple way to improve the diamine selectivity by recycling piperazine and shifting the equilibrium reaction responsible for its formation.

The synthesis of ethylenediamine from ethanolamine is catalyzed also by acidic zeolites [72–74], as discussed in Section 2.2.1. Good selectivities (up to 72% ethylenediamine) at almost complete conversion of ethanolamine were obtained after proper tuning of the acidic properties and the Si/Al ratio of mordenite. Dominant byproducts were piperazine, its *N*-alkylated derivatives and polyamines. The necessary reaction temperature was in the range of 300–330°C. Silica–alumina was more active but hardly selective to ethylenediamine.

Ethylenediamine is a reactive intermediate and its further transformation can provide a variety of linear and cyclic amines. It is therefore not astonishing that the ethylenediamine yield was found to be lower when using a pelletted catalyst instead of a powder, in a fixed bed reactor under otherwise identical conditions [24]. The negative effect of slow intraparticle diffusion can be minimized by using meso- or macroporous catalysts with relatively high outer surface area ("egg-shell" type catalyst).

### *3.2. Amination of ethylene glycol with amines*

In the amination of ethylene glycol with secondary amines relatively low amine/alcohol molar ratios (typically between 1 and 6) can be applied in this type of reactions [46,48]. An example is the Cu-catalyzed amination of ethylene glycol with dimethylamine in a continuous fixed bed reactor at atmospheric pressure [46]. Beside the amine/alcohol ratio, the hydrogen partial pressure had a crucial role in controlling the product distribution (Fig. 8). In the absence of hydrogen the dominant product was the enamine **35** (Scheme 5), but an increase of the molar hydrogen concentration up to 60% improved the total selectivity to "aminol" **33** and diamine **34** close to 80% (at over 90% conversion of glycol). The conversion was hardly dependent on the hydrogen/glycol or amine/glycol ratios. Addition of 25 wt% water to the reactant feed did not effect the reaction rate and diamine selectivity, but increased the fraction of aminol on the expense of enamine.

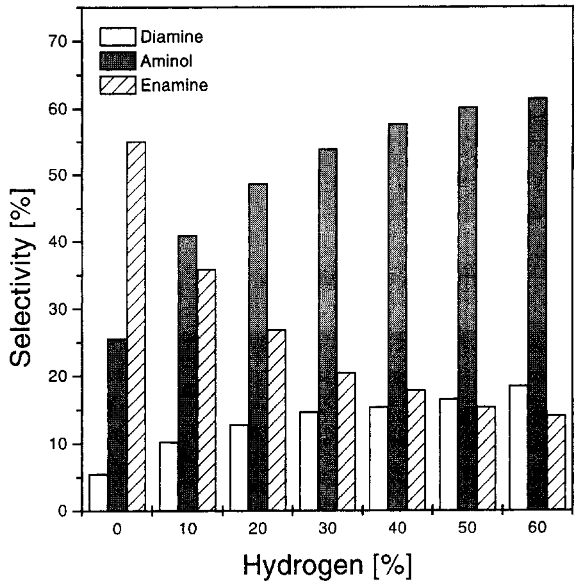
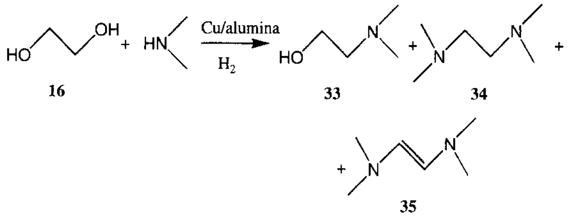


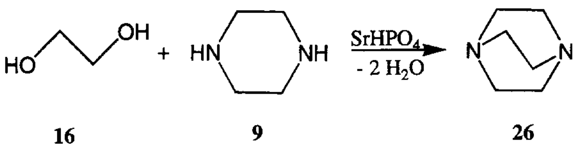
Fig. 8. Influence of relative hydrogen concentration on selectivity in the amination of ethylene glycol with dimethylamine, according to Scheme 5. Main products: 2-*N*,*N*-dimethylamino-ethanol (**33**, aminol), *N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminoethane (**34**, diamine) and *N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminoethene (**35**, enamine). Conditions: fixed bed reactor, Cu/alumina, 230°C, 1 bar total pressure, ethylene glycol: 0.1 bar, dimethylamine: 0.3 bar, diluent: nitrogen, conversion almost 100% (adapted from Ref. [46]).



Scheme 5.

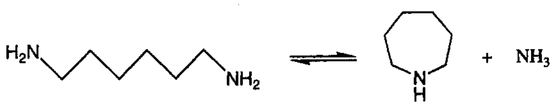
Even better selectivities to aminol and diamine (53% and 31%, respectively) were obtained in the same reaction over a $SrHPO_4$ catalyst [88], though the reaction conditions were more severe (275°C and 55 bar). $SrHPO_4$ showed outstanding selectivity, 97% at 71% conversion, in the amination of ethylene glycol with piperazine **9** to diazabicyclo[2,2,2] octane **26** at 350°C, as shown in Scheme 6.

An industrially important process, the synthesis of polyethylene polyamines by the amination of ethylene glycol or ethanolamine with ethylenediamine will be discussed in Section 3.5.



**16** **9** **26**

Scheme 6.

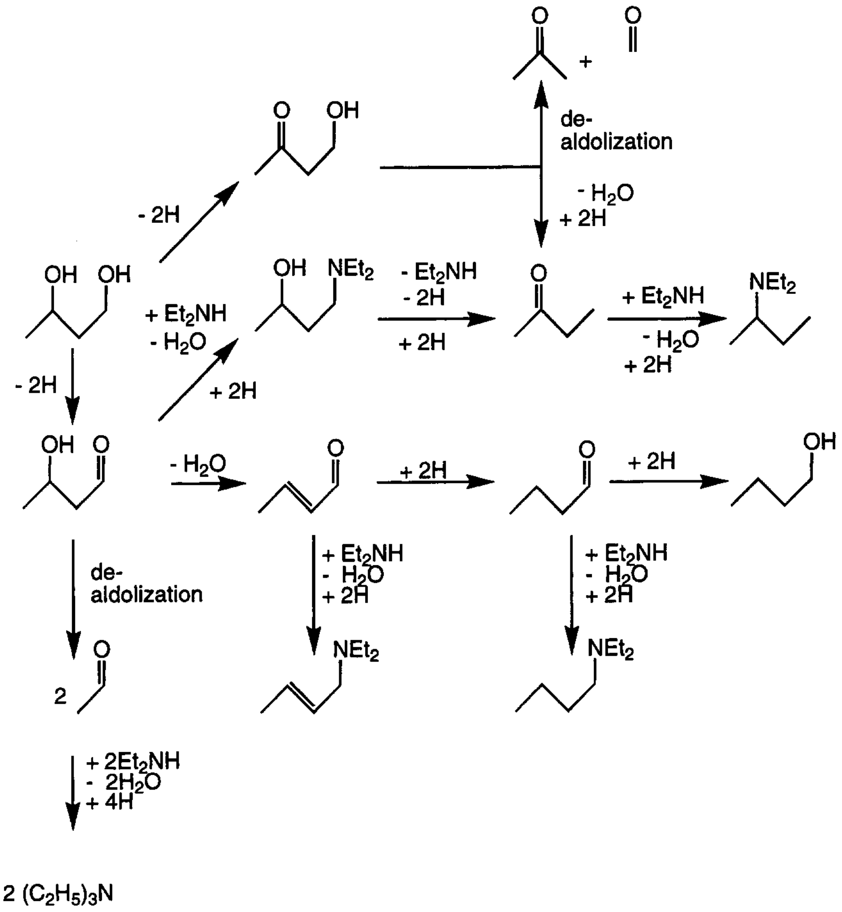


**36** **37**

Scheme 7.

### 3.3. Amination of higher aliphatic diols

Only a few examples are known in literature for the amination of higher aliphatic diols with ammonia. Moreover, these reactions are sometimes used only to demonstrate the application range of a new catalyst, without providing detailed information on the reaction route and product distribution. A typical example is the amination of 1,3-propanediol with ammonia, a reaction which was chosen to demonstrate the amination activity of a nickel–rhenium catalyst [33,34]. There are hardly any data available concerning the results of the reaction, except the conversion (45%) estimated on the basis of water formed. Other aliphatic bifunctional alcohols used for the production of primary diamines are 1,2-propanediol [58], 1,4-butanediol [95], 2,3-butanediol [31], 1,6-hexanediol



Scheme 8.

[28,48,51,52,58,96,97], 1,8-octanediol and 1,10-decanediol [52]. In all cases metal and supported metal hydrogenation catalysts were applied.

The selectivities to the half-aminated product "aminol" are usually good. For example, the reaction of 1,4-butanediol with ammonia afforded 73% selectivity to 4-amino-1-butanol at 47% conversion [125]. The reaction was performed in an autoclave at 210°C and 47 bar, and the Raney Ni catalyst was pretreated with aqueous $Na_2SO_3$ to suppress the side reactions. Conversely, pyrrolidine was the main product over zeolite-based catalysts at 350–450°C [77].

The amination of 1,6-hexanediol with ammonia is the most interesting reaction for industrial application, because 1,6-diaminohexane is used in large scale for polyamide production. The reaction is complicated by the simultaneous formation of hexamethyleneimine **37** via disproportionation reaction, as shown in Scheme 7 [51], or in a cyclization reaction from the aminol intermediate. For example, a Co–Ni–Cu/alumina catalyst converted an 80% aqueous solution of 1,6-hexanediol and ammonia to a mixture of imine (49%) and diamine (23%), at 220°C and 300 bar [28]. The process was more selective in dioxane as a solvent: Raney Ni provided 67% diamine and 33% hexamethyleneimine selectivities at 58% conversion. The reaction conditions used are common in metal-catalyzed amination of alcohols: 200°C and 138 bar total pressure in a batch reactor, and an ammonia/alcohol molar ratio of 20. Partial recycling of the hexamethyleneimine byproduct enhanced the diamine selectivity to 100% at 38% conversion, i.e., no additional imine was formed.

A comparison of the amination of 1,6-hexanediol and ethylene glycol with dimethylamine indicates a significant influence of the distance between the reacting OH groups [46,48]. Both reactions were performed in a continuous fixed bed reactor at atmospheric pressure over an alumina-supported Cu catalyst. The diamine from ethylene glycol (**34**, Scheme 5) is formed with 20% selectivity at best, at 250°C and high hydrogen concentration. The maximum selectivity to the diamine (*N,N,N′,N′*-tetramethyl-1,6-diaminohexane) in the amination of 1,6-hexanediol was 65% at 230°C, and the influence of hydrogen concentration was minor. Besides, in the amination of ethylene glycol the rather stable enamine **35** was a major product (Fig. 8), whereas enamine formation was negligible in the amination of 1,6-hexanediol.

Interestingly, no diamine among the products could be identified in the amination of 1,3-butanediol with diethylamine over a $CuO–Cr_2O_3–ZnO$ catalyst [47]. The major product was 2-butanone, its amount ranging between 38% and 60% as a function of temperature (170–250°C), amine/diol molar ratio (1–4) and space velocity (0.15–6 $cm^3\ h^{-1}\ g^{-1}$). Other important products were acetone (5–10%), triethylamine (8–23%) and *N,N*-diethyl-1-butylamine (3–14%). The reaction network, proposed on the basis of the product distribution, is depicted in Scheme 8. An important feature is the dealdolization of the $\beta$-hydroxy-carbo-

Table 8

Partial amination of 1,2-butanediol over supported Co, Ni and Pt catalysts. Conditions: autoclave, 10 g catalyst, 3 mol 1,2-butanediol, 6 mol ammonia, 180°C, 50 atm initial hydrogen pressure (adapted from Ref. [106])

| Catalyst | Atomic ratio of metals | Conversion (%) | Selectivity to 2-amino-1-butanol (%) | Molar ratio of aminated (sec.OH/prim.OH) |
|---|---|---|---|---|
| Co/MgO | 95/5 | 22 | 60 | 5.3 |
| Co/BaO | 95/5 | 21 | 70 | 4.7 |
| $Co/Fe_2O_3$ | 90/10 | 26 | 93 | 13.6 |
| $Co/ZrO_2$ | 95/5 | 67 | 56 | 8.6 |
| $Co/La_2O_3$ | 95/5 | 68 | 79 | 10.3 |
| $Co/ThO_2$ | 99/1 | 65 | 92 | 20 |
| $Co/ThO_2–Fe_2O_3$ | 97/1/2 | 64 | 86 | 14.5 |
| $Ni/Fe_2O_3$ | 80/20 | 20 | 43 | 14.4 |
| $Ni/ThO_2$ | 99/1 | 19 | 53 | 24.3 |
| $Ni/La_2O_3$ | 95/5 | 41 | 91 | 18.5 |
| Pt/C | 5/95 | 48 | 7.7 | 2.1 |

nyl compound intermediates formed by dehydrogenation of the diol reactant. Dealdolization is catalyzed by diethylamine, a well-known effect of *N*-bases in the field of homogenous aldol condensation and de-aldolization reactions [98]. The high reactivity of $\beta$-hydroxylamines (possible half-aminated intermediates of $\beta$-diols), was also demonstrated for a wide range of molecules [99]. For example, *N,N*-dimethyl-1-amino-3-butanol was almost quantitatively transformed to 2-butanone at 200°C over a $Cu-ZnO-Cr_2O_3$ catalyst.

A special case is the amination of aliphatic diols, which contain both primary and secondary hydroxyl groups [100]. The secondary hydroxyl group is more reactive and usually selectively convertible to an amino group with ammonia over supported Co and Ni catalysts, as shown in Table 8. The catalyst support had a substantial influence on the reaction rate (conversion) and selectivity. Excellent selectivities at moderate conversions could be achieved at or below 200°C. The activation of the primary hydroxyl group at higher temperatures enhanced the rate of side reactions and diminished the overall amination selectivity [100].

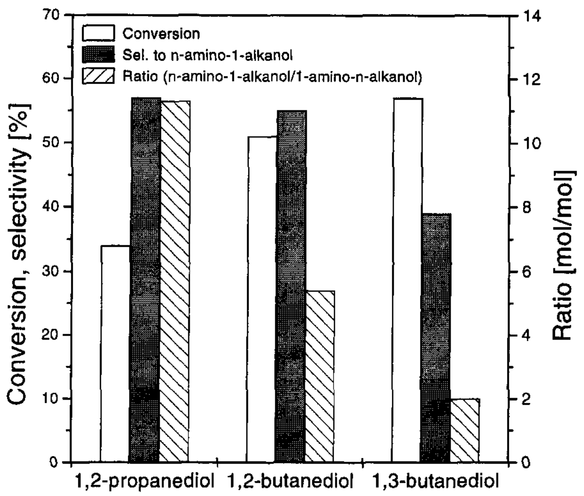
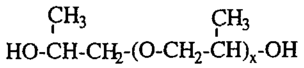
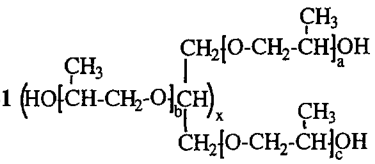
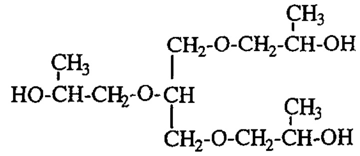


Fig. 9. Selective transformation of the secondary hydroxyl group in the amination of some 1,2- and 1,3-diols to *n*-amino-1-alkanols (*n*=2 or 3) over a Co catalyst. Conditions: autoclave, diol/ammonia molar ratio: 1/20, 180°C, $p(H_2)=50$ atm (adapted from Ref. [100]).

Table 9
Structures of polyoxyalkylene glycols used for the amination

| Polyoxyalkylene glycol compound | x | M [g/mol] | Ref. |
|---|---|---|---|
| **38** $HO-CH_2-CH_2-(O-CH_2-CH_2)_x-OH$ | 3-170 | > 230 | 104 |
| **39**  $HO-\overset{CH_3}{CH}-CH_2-(O-CH_2-\overset{CH_3}{CH})_x-OH$ | 33-85 | 230-500 | 105 |
| **40** $HO-CH_2CH_2-CH_2-CH_2-(O-(CH_2)_4)_x-OH$ | 1-50 | 162-4000 | 102 |
| **41**  $\left(HO[\overset{CH_3}{CH}-CH_2-O]_b\overset{CH_2[O-CH_2-\overset{CH_3}{CH}]_a OH}{\underset{CH_2[O-CH_2-\overset{CH_3}{CH}]_c OH}{CH}}\right)_x$ | 1-5 | > 230 | 104 |
| **42**  $HO-\overset{CH_3}{CH}-CH_2-O-\overset{CH_2-O-CH_2-\overset{CH_3}{CH}-OH}{\underset{CH_2-O-CH_2-\overset{CH_3}{CH}-OH}{CH}}$ | - | - | 110 |

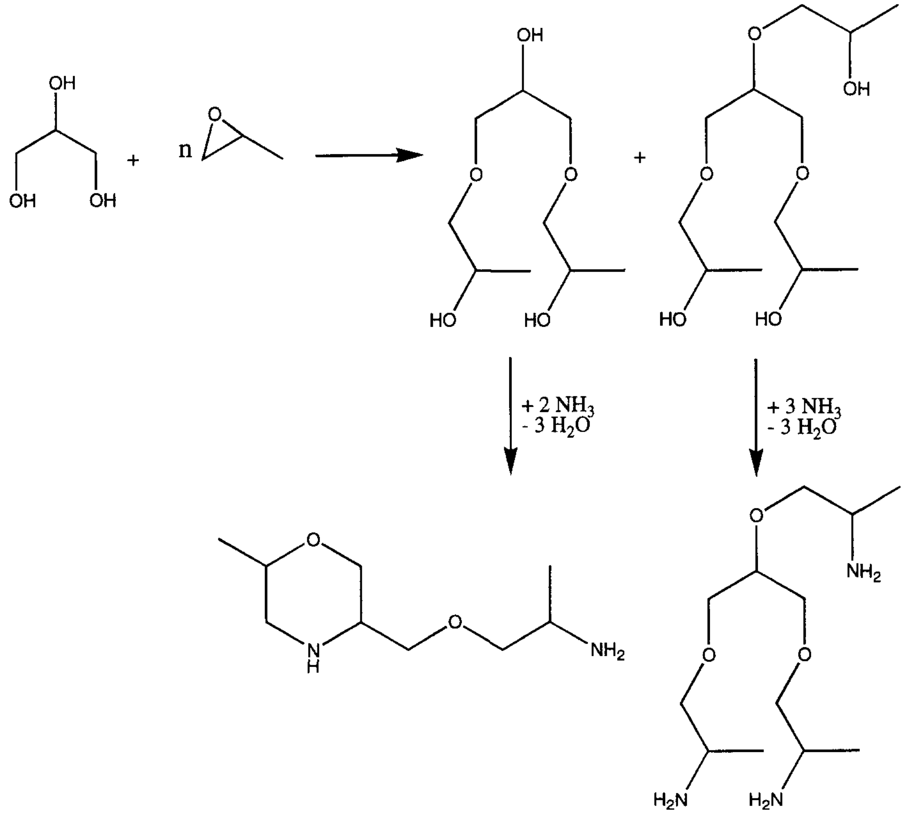
a+b+c=7–170.

The regioselectivity of the amination reaction depends also on the structure of the diol [100]. The most selective amination of the secondary hydroxyl group was achieved in the amination of 1,2-alkanediols (Fig. 9). Higher reactivity of the secondary OH group can be explained by the easy formation of the $\alpha$-hydroxyketone intermediate, which is thermodynamically more favored than the formation of the $\alpha$-hydroxyaldehyde. Competitive amination of 1- and 2-butanol over a $Co/La_2O_3$ catalyst showed hardly any difference in reactivity and selectivity to the corresponding amines, indicating the crucial importance of the vicinal hydroxyl groups in the regioselective amination of diols.

### 3.4. *Amination of polyoxyalkylene diols and triols with ammonia*

Polyoxyalkylene glycols and triols may possess a linear or branched structure with a usual molecular mass of 200–8000. Linear polyoxyalkylene diols are synthesized by the polymerization of terminal epoxides, such as ethylene oxide or propylene oxide (**38** and **39** in Table 9) or by polymerizing tetrahydrofuran **40** [42,101–109,124]. The polymer contains primary or secondary OH groups, depending on the monomer structure. Branched oligomers and polymers, such as compounds **41** and **42**, are obtained in the presence of an initiator, e.g., glycerol [104–112]. The latter reaction is nonselective, resulting in a mixture of polyoxyalkylene triols with different side chain sizes. The amination of such oligomeric and polymeric triols with ammonia includes also undesired cyclization reactions [110], as illustrated in Scheme 9.

The preferred catalyst is Ni, frequently Raney Ni [103–112]. A drawback of Raney Ni is the deactivation by water formed during the amination reaction. Various promoters, including Fe, Ru, Cu, Cr, Mo and Co, have been proposed to improve the selectivity and



Scheme 9.

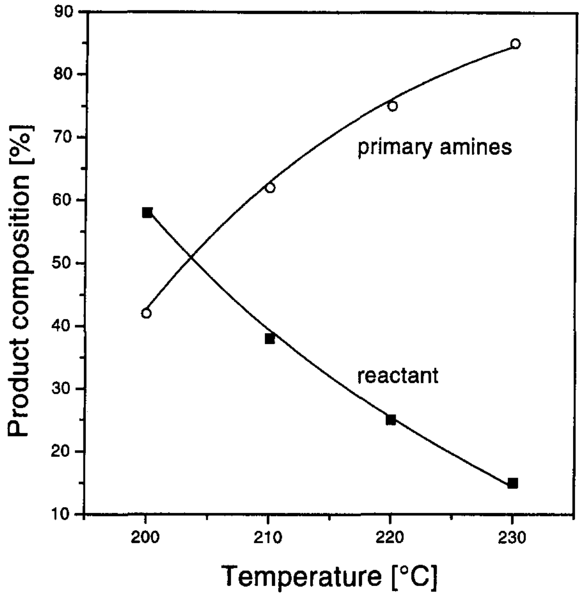


Fig. 10. Influence of temperature on the selective amination to primary amines of a polypropylene polyol containing three terminal hydroxyl groups (average molecular mass: 5000). Conditions: fixed bed reactor, Raney nickel nuggets, 145 bar, space velocity: 1.53–1.62 g/(h ml cat.), $NH_3$/OH groups molar ratio: 67 (mean value), $H_2$/OH groups molar ratio: 3.4 (mean value) (adapted from Ref. [104]).

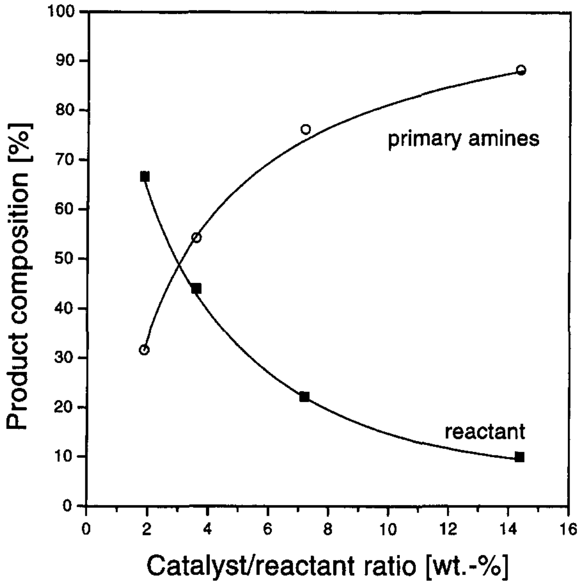


Fig. 11. Influence of catalyst/reactant weight ratio on the product composition in the amination of a polypropylene polyol containing three terminal hydroxyl groups (average molecular mass: 5000) over a Raney nickel catalyst containing 1% Mo promoter. Conditions: autoclave, 118 bar (mean value), 220°C, 7.2 wt% ammonia, 20 min reaction time, 99% selectivity to primary amines (adapted from Ref. [104]).

lifetime. Mesoporous structure of the support (e.g., alumina) is important in the amination of bulky reactants [105].

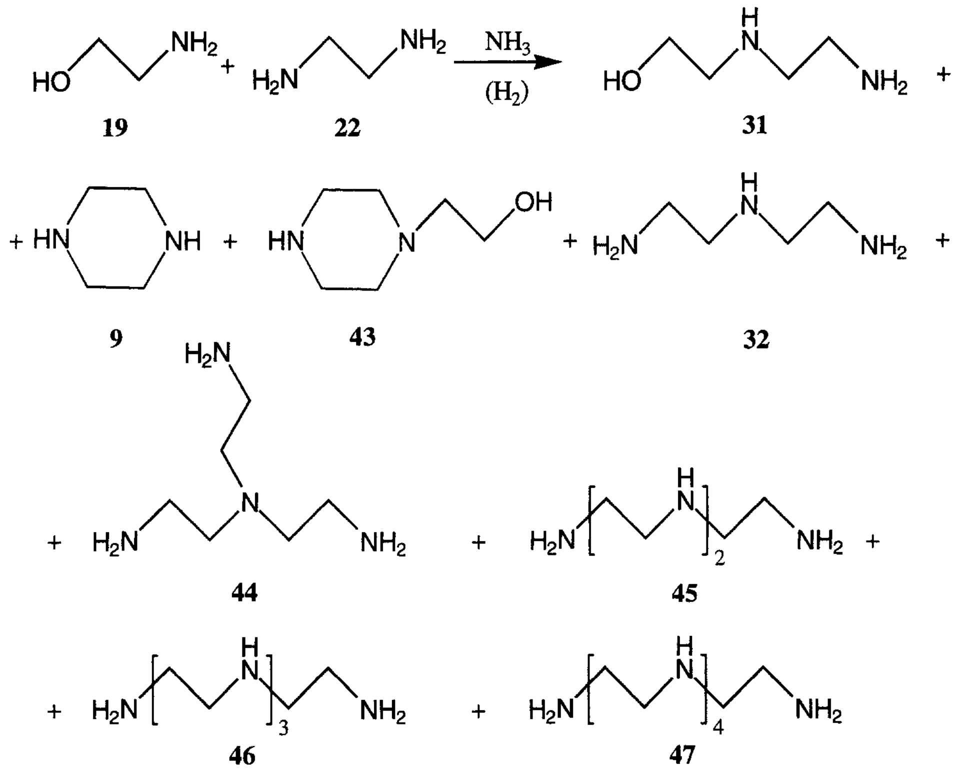
The available information concerning the product composition is rather limited. The conversion is usually estimated from the amount of water formed, and the selectivity by the ratio of primary and secondary amines. On the basis of this indirect analysis, the amination of polyoxyalkylene diols and triols to the corresponding primary amines provides distinctly better selectivities and yields than those reported for the amination of small chain aliphatic diols. A typical side reaction is the hydrogenolysis of the less reactive primary OH groups, which deteriorates the product quality [106]. Fig. 10 illustrates the good yields obtained in the amination of a polyoxypropylene triol with the general formula of **42** in Table 9. With increasing temperature (and conversion), the yield of primary amine approached 85% [104]. Even better results were obtained by enhancing the loading of a Mo-promoted Raney nickel catalyst, as depicted in Fig. 11. Interestingly, the selectivity to primary amines was hardly affected by the conversion, at least on the basis of the indirect analysis.

The amination with ammonia of polyoxyalkylene glycols containing primary hydroxyl groups is slow and incomplete [111,112]. Due to the big difference in their reactivity, secondary OH groups can be selectively aminated in the presence of primary alcohols [100], as discussed in Section 3.3.

For some special applications only a partial amination of polyols is required. For example, some polyoxyalkylene triols with a molecular mass of 300–1700 are used after partial amination with ammonia for the production of polyurethane foams. The degree of amination can be controlled by the reaction time (or residence time in the catalyst bed) [107].

### 3.5. *Synthesis of polyalkylene polyamines*

The industrially produced polyalkylene polyamines are mainly the oligomers of ethylenediamine. The major ethyleneamines are diethylenetriamine **32**, triethylenetetramine **45**, tetraethylenepentamine **46**



Scheme 10.

and pentaethylenehexamine **47**, as shown in Scheme 10. Polyalkylene polyamines arise normally as byproducts in each amination process starting from bifunctional alcohols. Beside these oligomers, branched chain homologues (e.g., **44**) and cyclic products (mainly piperazine **9** and its alkylated derivatives, e.g., **43**) are also formed. In contrast to piperazine, the oligomers are regarded as valuable products, especially diethylenetriamine.

For the production of polyalkylene polyamines, both metal catalysts [39,113–117] and solid acids, mainly phosphates [9,79–81,88–91,118] are employed. The supported phosphoric acid type catalysts are not truly heterogeneous and vapor phase operation is necessary to minimize the phosphate leaching [126–128].

The reactants are ethanolamine or ethylene oxide [117], and ammonia. Piperazine (up to 10 wt%) can be added before reaction to minimize its formation during amination [39]. Similarly, diaminoethane can also be recycled [39,119]. In general, a molar ratio of diaminoethane to ethanolamine from 0.1 to 0.25, of ammonia to ethanolamine from 5 to 10 and hydrogen in the range of 1–30 mol% of the total feed are used for metal catalysts. A typical product composition of such a process, using a Ni–Re–B catalyst, is shown in Fig. 12. The conversion was increased by applying higher temperatures. The most striking effect of high conversion (temperature) is the rapidly enhancing fraction of piperazine, mainly on the expense of ethylenediamine **22**.

The reaction over acid catalysts is usually carried out at higher temperatures (250–400°C). Still, as Fig. 13 illustrates, selectivities up to 70% to diethylenetriamine **32** and around 20% to triethylenetetramine **45** were achieved over a phosphated titania catalyst. The formation of undesired cyclic products **9** and **43** was remarkably low. Note that titania without phosphoric acid showed no detectable selectivity. In other cases temperatures below 270°C were suggested to obtain the required product composition over phosphate type catalysts [126].

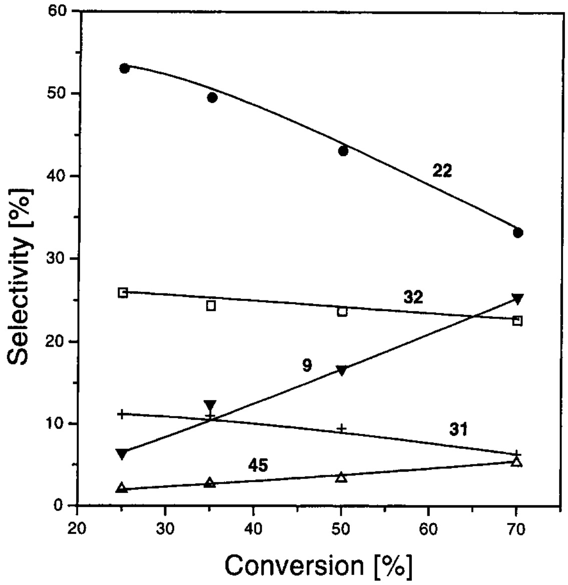


Fig. 12. Amination selectivity in the reaction of ethanolamine **19** with a mixture of ammonia and ethylenediamine **22**, according to Scheme 10. Conversion was increased at constant space velocity by increasing the temperature from 167°C to 190°C. Conditions: fixed bed reactor, Ni–Re–B catalyst; 150 bar, $NH_3$/**19** molar ratio=7. Space velocities: **19**, 12.4 mmol/(h, $g_{cat}$); **22**, 2.25 mmol/(h, $g_{cat}$). Main products: **9**, piperazine; **31**, *N*-(2-aminoethyl)ethanolamine; **32**, diethylenetriamine; **45**, triethylenetetraamine (adapted from Ref. [39]).

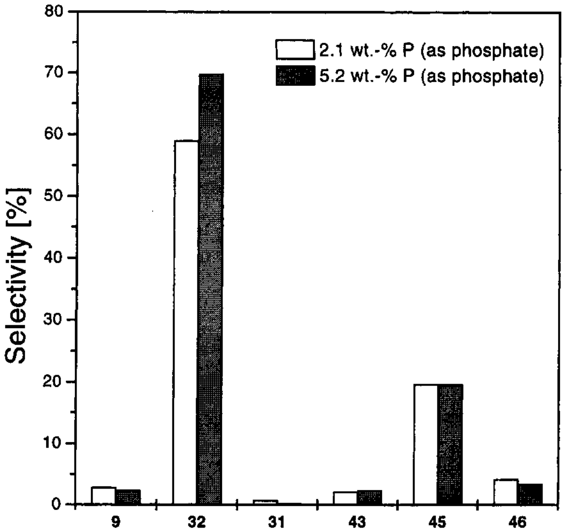


Fig. 13. Polyethylenepolyamine products from the reaction of ethylenediamine **22** and ethanolamine **19** over phosphated titania catalysts (characterized by the P content), according to Scheme 10. Conditions: fixed bed reactor, 70–140 bar (not specified), 325°C, **22**/**19** molar ratio: 2, 65% conversion of **19**. Main products: **9**, piperazine; **32**, diethylenetriamine; **45**, triethylenetetramine; **46**, tetraethylene-pentamine; **31**, *N*-(2-aminoethyl)ethanolamine; **43**, *N*-(hydroxyethyl)-piperazine (adapted from Ref. [118]).

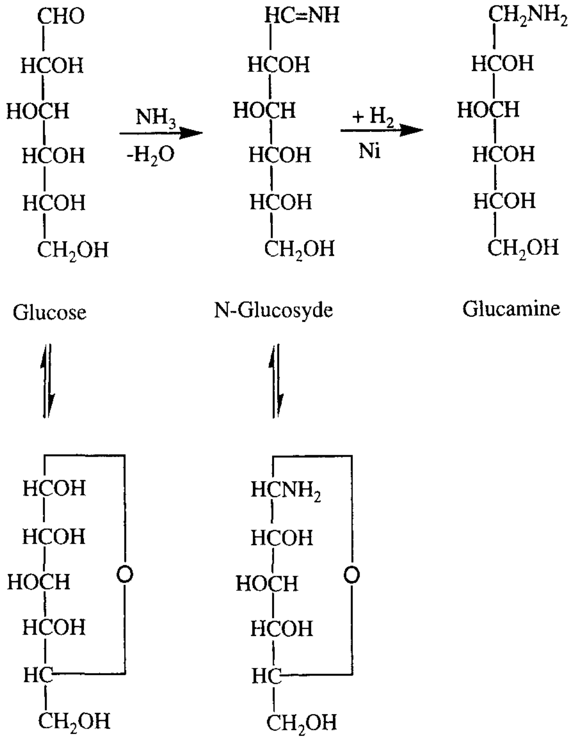
3-Amino-1-propanol and 1,3-diaminopropane were also used for the synthesis of polyalkylene polyamines [113–115]. Contrary to diaminoethane oligomers, the polypropylene polyamines are almost free of cyclic, branched and deaminated products [113,114]. By increasing the hydrogen pressure, the conversion decreased and the formation of dipropyltriamine dimer was favored, whereas at higher temperatures the yield of dimer was lower. Oligomers of higher molecular mass could be decomposed to the valuable dimers and trimers [113,114].

### 3.6. *Amination of sugars*

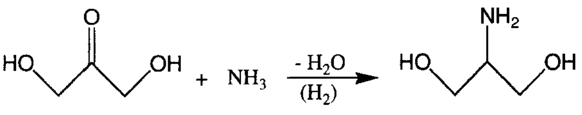
The reaction of sugars with ammonia belongs only formally to the amination of polyols. In fact, none of the OH groups is transferred to an amino group under the mild conditions applied, rather the carbonyl group of an aldose or ketose is aminated selectively to form, e.g., glucamine [120] or isomaltamine [121]. Simple monosaccharides, such as glucose, are converted with liquid ammonia to the *N*-glucoside (imine), followed by hydrogenation to the amine (glutamine [120]) over a metal catalyst, usually Ni, as depicted in Scheme 11.

The reaction runs smoothly at 50–100°C and 120 bar [122]. The *N*-glucoside intermediate is labile, especially in the presence of water, and susceptible to caramelization (Millard reaction). Therefore, a high hydrogenation rate is required to shorten the lifetime of imine. On the other hand, the more severe conditions are applied for hydrogenation, the higher is the tendency to form fragmentation products such as ethanolamine and diaminoethane. Still, under optimized conditions about 90% selectivities to the desired primary polyhydroxy-amines were obtained in the amination of monosaccharides [120]. The proposed continuous process allows even the use of water as solvent without formation of secondary amines.

Amination with ammonia of polysaccharides is less selective. For the quantitative preparation of such amino-sugars, hydrazine was found to be a better aminating agent [121], though it is too expensive



Scheme 11.



48

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Scheme 12.

for industrial applications. In the amination of palatinose the first reaction step, the condensation with hydrazine, was very slow (17 h at 20°C) but the subsequent hydrogenation over Raney Ni at 50°C and 150 bar was fast and efficient [123]. The yield to "isomaltamine" (sweetener, equimolar mixture of two stereoisomers) was 97%, as compared to 79% with ammonia as aminating agent. In the amination of other dissacharides the yields to the corresponding monoaminoglycosyl-hexitols was lower, in the range of 17–63%. Possible side reactions are isomerization, retro-aldol reaction, $\beta$-elimination, Heyns- and Amadoni-rearrangement, or Millard-reaction [123].

A similar reaction is the synthesis of serinol **49** from dihydroxyacetone **48**, according to Scheme 12 [129–131]. This pharmaceutical intermediate can be prepared over Raney Ni or supported noble metal catalysts at 50–90°C and 6–100 bar, in the presence of ammonia and hydrogen. Yields up to 99% were reported when the condensation step was completed before starting the catalytic hydrogenation.

## 4. Conclusions

The amination of di- and polyfunctional alcohols to the corresponding primary, secondary and tertiary amines can be performed under conditions similar to those applied in the amination of simple aliphatic alcohols. Both reactions are catalyzed by metal hydrogenation–dehydrogenation type catalysts and by solid acids (mainly zeolites and phosphates). The main difference resides in the complexity of the reactions: many more side reactions are possible in the amination of diols and triols, as compared to that of monofunctional alcohols. Accordingly, the proper tuning of reaction parameters and catalyst composition, and the development of an economic process for the synthesis of diamines and triamines are rather demanding. So far, there are not too many reactions reported in which the selectivities to the desired amines are sufficiently high, and good yields are even less frequent.

However, the industrial importance of di- and polyamines and the need for relatively cheap, noncorrosive and environmentally friendly processes for their manufacture create a strong driving force fostering further research in this field.

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