

Nickel-catalyzed amination of 1,3-propanediols differently substituted at C2-position: influence of reactant structure on diamine production

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Abstract

The heterogeneously catalyzed amination of 2,2'-dimethyl-1,3-propanediol, 2-methyl-1,3-propanediol and 1,3-propanediol over a commercial silica supported Ni catalyst has been studied in a continuous fixed-bed reactor using supercritical ammonia at 135 bar in the temperature range 180–235°C. The amination of 2,2'-dimethyl-1,3-propanediol afforded as main products the corresponding diamine (70%) and the amino alcohol (7%) resulting in a cumulative selectivity of 77% at 75% conversion. The application of supercritical ammonia and an ammonia excess favoured the desired reactions. At temperatures > 210°C the amination selectivity decreased due to the formation of *iso*-butylamine. The amination of the structurally related 2-methyl-1,3-propanediol and 1,3-propanediol under similar reaction conditions afforded much lower amination selectivities (< 20%) mainly due to degradation products formed by water elimination. Direct elimination of water is not possible for 2,2'-dimethyl-1,3-propanediol. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The metal-catalyzed amination of aliphatic alcohols provides an economically interesting pathway to a multitude of amines [1–4]. However, the yields and selectivities are usually rather low in the synthesis of aliphatic diamines from the corresponding diols and ammonia.

The metal-catalyzed synthesis of aliphatic amines from the corresponding alcohols includes the dehydrogenation of the alcohol to a

carbonyl compound; the condensation with ammonia to form an imine or enamine, and the hydrogenation to the amine [5,6]. Each intermediate and the product amine can take part in various side reactions, such as condensation, decarbonylation, disproportionation and hydrolysis [7–10]. The synthesis of a diamine from the corresponding diol requires the repetition of all three steps which increases the by-product formation. In addition, the bifunctional intermediates have the tendency to undergo oligomerization reactions [4,11,12]. A further difficulty is that the intermediate and product amines are significantly more reactive than ammonia.

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We have found recently that the application of supercritical ammonia (scNH_3) as a solvent and reactant affords remarkable selectivity improvement in the amination of 1,3-propanediol, compared to the subcritical pressure procedure [13]. Here we extend the studies on amination with scNH_3 to structurally related 1,3-propanediols. The nickel-catalyzed amination of 2,2'-dimethyl-1,3-propanediol, 2-methyl-1,3-propanediol and 1,3-propanediol is compared. The aim is to gain a better understanding of the relationship between the structure of the reactant diol and the amination selectivity.

2. Experimental

A commercial silica-supported nickel catalyst (Ni-6458, Engelhard) containing 56 wt.% nickel was used. The catalyst was supplied from the manufacturer in a reduced and stabilized form. Before the experiments, the catalyst was activated in hydrogen flowing at 30 ml min^{-1} for 4 h at 250°C .

The following reactant purities were quoted by the manufacturer: 1,3-propanediol > 98% (Fluka), 2-methyl-1,3-propanediol > 99% (Aldrich), 2,2-dimethyl-1,3-propanediol > 98% (Fluka), ammonia 99.98% (Pan-Gas), hydrogen 99.999% (Pan-Gas) and nitrogen 99.995% (Pan-Gas).

The specific surface area (S_{BET}), mean cylindrical pore diameter ($\langle d_p \rangle$) and specific pore volume ($V_{\text{p(N}_2)}$) of the catalyst were determined by nitrogen physisorption at 77 K using a Micromeritics ASAP 2000 apparatus. Before measurements, the catalyst sample was degassed for 10 h at 150°C . The surface area was calculated in the relative pressure range of 0.05 to 0.2, assuming a cross section area of 0.162 nm^2 for the nitrogen molecule. The mean cylindrical pore diameter was determined using the equation $\langle d_p \rangle = 4V_{\text{p(N}_2)}/S_{\text{BET}}$. The mean pore diameter was calculated by the Barrett–Joyner–Halenda method [14].

X-ray diffraction patterns were measured on a Siemens D5000 powder X-ray diffractometer using CuK_α radiation (35 mA, 35 mV, Ni-filter). The diffractograms were compared to JCPDS data files [15] for catalyst phase identification. The mean nickel crystallite size was estimated using the Scherrer equation [16].

Adsorption of ammonia was studied applying the pulse thermal analysis (PTA) technique on a Netzsch thermal analyser STA 409 coupled with a quadrupole mass spectrometer QMG 420 (Balzers). Ammonia pulses were injected by a valco dual external sample injection valve equipped with two 1 ml sample loops. After catalyst activation, ammonia pulses were injected at 50°C . The flow rate of the He carrier gas was 50 ml min^{-1} . Details about the experimental setup and principle of the TPA method are reported elsewhere [17,18].

DRIFT-spectroscopic measurements of ammonia adsorption were performed on a Perkin–Elmer 2000 FT-IR-spectrometer. Preliminary, a potassium bromide background spectrum was recorded at 50°C (100 scans, 1 cm^{-1}). The catalyst was pretreated at 300°C for 1 h in an argon flow of 15 ml min^{-1} to remove physisorbed water. Subsequently, it was activated with hydrogen at 250°C , similarly as before catalytic tests. Then the background spectra of the samples were recorded in argon at temperature steps of 50°C from 50°C to 250°C . After cooling to 50°C , the catalyst was exposed to ammonia flowing at 50 ml min^{-1} (3600 ppm in Ar) for 20 min. Finally, the catalyst was heated and the spectra were recorded at 50°C to 250°C , in steps of 50°C .

The apparatus for catalytic tests consisted of the dosing system for liquid ammonia, the alcohol (two syringe pumps ISCO D500) and hydrogen (mass flow meter), a high pressure fixed-bed reactor and a gas–liquid separator. The reactor was constructed of an Inconel[®]-718 tubing of 13 mm inner diameter and 38 ml volume. The temperature in the reaction zone was measured by a thermocouple located in the center of the tube and was regulated by a PID cascade con-

troller. The total pressure in the reactor system was set by a Tescom back pressure regulator.

Standard reaction conditions were: 8.0 g catalyst; catalyst sieve fraction 0.14–0.4 mm; 210°C, total pressure = 135 bar, contact time = 40 000 gs mol^{-1} and molar ratio of the reactants $\text{R-OH}/\text{NH}_3/\text{H}_2 = 1/60/2$.

Conversion, yield and selectivity of the liquid products were determined by a gas chromatograph (HP-5890A, FID-Detector; HP-1701 column). The products were identified by GC-MS analysis.

3. Results

3.1. Catalyst properties

The commercial silica-supported Ni catalyst was characterized by nitrogen adsorption, XRD, and ammonia adsorption applying pulse thermal analysis and DRIFT-spectroscopic measurements. The results of the characterization are summarized in Table 1 and Fig. 1. The DRIFT-spectrum of ammonia adsorption (Fig. 1) shows strong adsorption bands due to Lewis acidic sites. Vibrations at 1240 cm^{-1} and 1610 cm^{-1} are ascribed to deformation modes ($\delta_s \text{NH}_3$, $\delta_{as} \text{NH}_3$) [19,20]. A multiplet was observed in the NH stretching region (3362 cm^{-1} , 3252 cm^{-1} , 3187 cm^{-1} , 3165 cm^{-1}) due to the asymmetric and symmetric $\nu \text{N-H}$ as well as to the first overtone of $2\delta_{as} \text{NH}_3$ [21]. Vibrational bands due to Brønsted sites were not observed. The adsorbed ammonia species could be totally removed from the surface by heating the sample to 250°C.

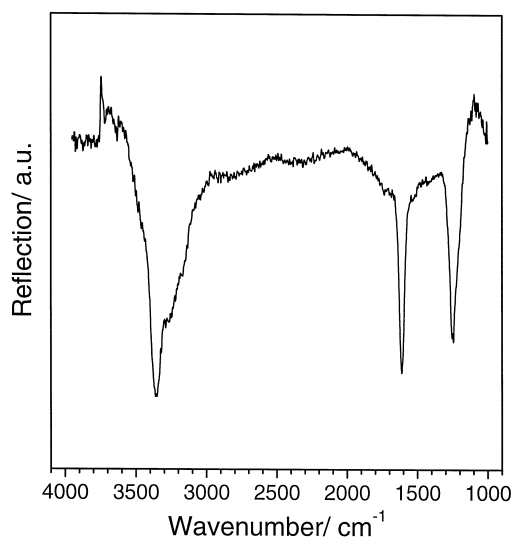


Fig. 1. DRIFT-spectrum of ammonia adsorbed on activated commercial Ni catalyst at 50°C; carrier gas: 50 ml min^{-1} Ar, difference spectrum obtained after subtraction of the background spectrum is shown.

3.2. Amination of 1,3-propanediols

To explore the influence of reactant structure on the product distribution aminations were performed with 1,3-propanediols differently substituted in C2 position: 2,2'-dimethyl-1,3-propanediol, 2-methyl-1,3-propanediol and 1,3-propanediol. The comparative catalytic tests were carried out in the temperature range 180–235°C at 135 bar using supercritical ammonia (critical data of ammonia: $T_c = 132.4^\circ\text{C}$, $P_c = 114.8 \text{ bar}$ [22]) as solvent and reactant. The existence of a single supercritical phase was confirmed by separate tests [13]. A small ratio of hydrogen in the feed (1–5 mol%) was sufficient to prevent the

Table 1
Properties of nickel catalyst (Engelhard, No-6458)

Catalyst	$S_{\text{BET}}^a / \text{m}^2 \text{ g}^{-1}$	$V_{\text{p},\text{N}_2}^b / \text{cm}^3 \text{ g}^{-1}$	$\langle d_p \rangle^c / \text{nm}$	$\Theta^d / \mu\text{mol g}^{-1}$	Nickel crystallite size / nm ^e
Ni-6458 E	180	0.17	4.9	418	5

^aBET specific surface area.

^bBJH cumulative desorption pore volume.

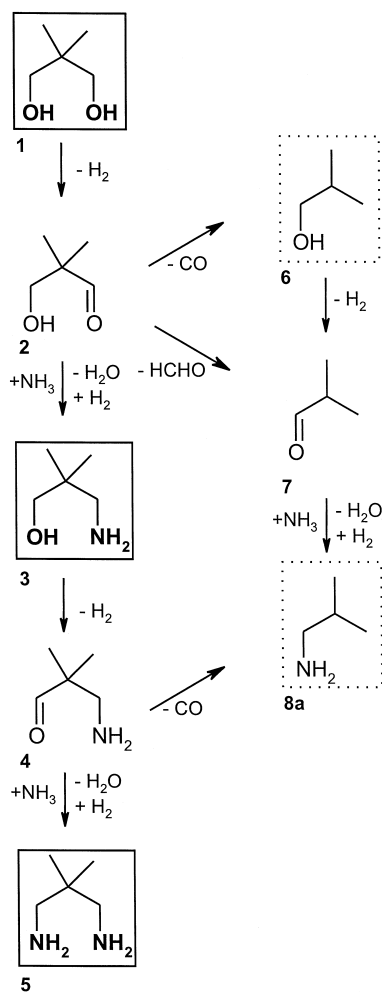
^cMean pore diameter $\langle d_p \rangle = 4V_{\text{p},\text{N}_2} / S_{\text{BET}}$.

^dAmount of chemisorbed ammonia at 50°C.

^eMean crystallite size determined by XRD line broadening of (111) and (200) reflection.

undesired dehydrogenation reactions and the formation of nitriles and carbonaceous deposit. But a rather high ammonia/alcohol molar ratio of 60 was necessary to minimize the condensation of the product amines with the aldehyde intermediate and to favour the reaction with the less reactive ammonia [23].

Reactions occurring during the amination of 2,2'-dimethyl-1,3-propanediol are summarized in Scheme 1. Fig. 2 shows the conversion of 2,2'-dimethyl-1,3-propanediol and the selectivity to corresponding amino alcohol (3), diamine



Scheme 1. Identified products and suggested reactions occurring during the nickel-catalyzed amination of 2,2'-dimethyl-1,3-propanediol with supercritical ammonia. Compounds identified are framed. The dashed line frames indicate detected by-products.

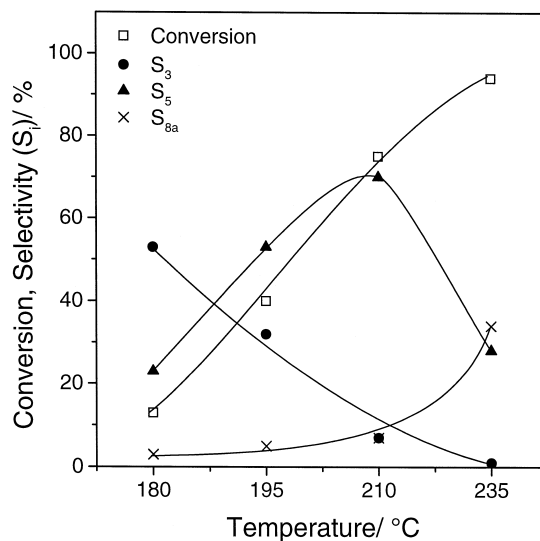


Fig. 2. Influence of temperature on conversion of 2,2'-dimethyl-1,3-propanediol (1) and selectivities to 2,2'-dimethyl-3-amino-1-propanol (S_3), 2,2'-dimethyl-1,3-diaminopropane (S_5) and *iso*-butylamine (S_{8a}). Superscripts denote products as given by numbers in Scheme 1. Standard conditions (see Section 2).

(5) and *iso*-butylamine (8a, by-product) as a function of temperature. The conversion increased from 13 to 94% in the range 180 to 235°C. With increasing temperature (conver-

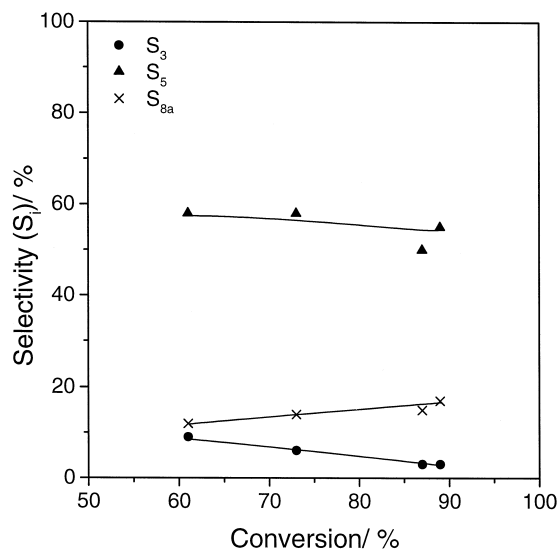


Fig. 3. Influence of conversion on selectivity to 2,2'-dimethyl-3-amino-1-propanol (S_3), 2,2'-dimethyl-1,3-diaminopropane (S_5) and *iso*-butylamine (S_{8a}). Superscripts denote products as given by numbers in Scheme 1. Conditions: contact time: 20000–80000 gs mol^{-1} ; 227°C, otherwise standard conditions (see Section 2).

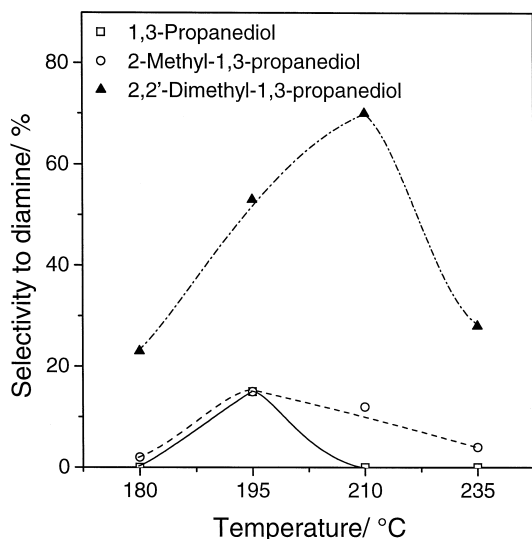


Fig. 4. Influence of temperature on diamine selectivity of the nickel-catalyzed amination of the different 1,3-propanediols. Standard conditions (see Section 2).

sion) the selectivity to amino alcohol dropped from 50% to almost zero at 235°C, whereas the diamine selectivity reached a maximum of 70% at 210°C (corresponding to 75% conversion). The loss of selectivity to the amino alcohol below 210°C is mainly due to the consecutive reaction of this intermediate to the diamine. At temperature above 210°C the selectivity to amino alcohol (**3**) and diamine (**5**) decreased, but the formation of *iso*-butylamine (**8a**) was noticeable favoured.

A change of conversion from 61 to 89%, induced by varying the contact time in the range

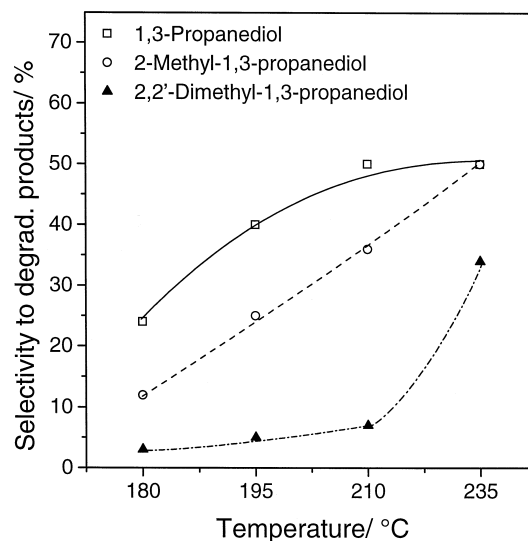


Fig. 5. Influence of temperature on diamine selectivity to degradation products (compare Schemes 1 and 2) formed during the amination of 2,2'-dimethyl-1,3-diaminopropane, 2-methyl-1,3-propanediol and 1,3-propanediol. Standard conditions (see Section 2).

20 000 to 80 000 gs mol^{-1} , hardly affected the selectivity to desired reaction products (Fig. 3). The selectivity to amino alcohol (**3**) and diamine (**5**) decreased about 3 to 6%, the *iso*-butylamine formation increased about 5% with higher conversion.

In contrast to the amination of 2,2'-dimethyl-1,3-propanediol, 2-methyl-1,3-propanediol and 1,3-propanediol amination (Fig. 4) afforded only low selectivity to the diamines (< 20%). The shift of the selectivity maximum to lower temperature indicates an increased reactivity of 2-

Table 2
Product distribution in amination of 1,3-propanediols

Reactant	Temp./°C	Conv./%	Selectivity S_i /%			
			3 + 5 ^a	Liquid ^b degr. prod.	Dimers	Gaseous ^c degr. prod.
2,2-Dimethyl-1,3-propanediol	204	59	83	6	< 2	ca. 9
2-Methyl-1,3-propanediol	204	59	21	32	< 2	ca. 45
1,3-Propanediol	189	59	26	35	< 2	ca. 37

Conditions: catalyst Ni (Engelhard, No-6458), 135 bar, 40 000 gs mol^{-1} , reactant molar ratio (R-OH/NH₃/H₂) = 1/60/2.

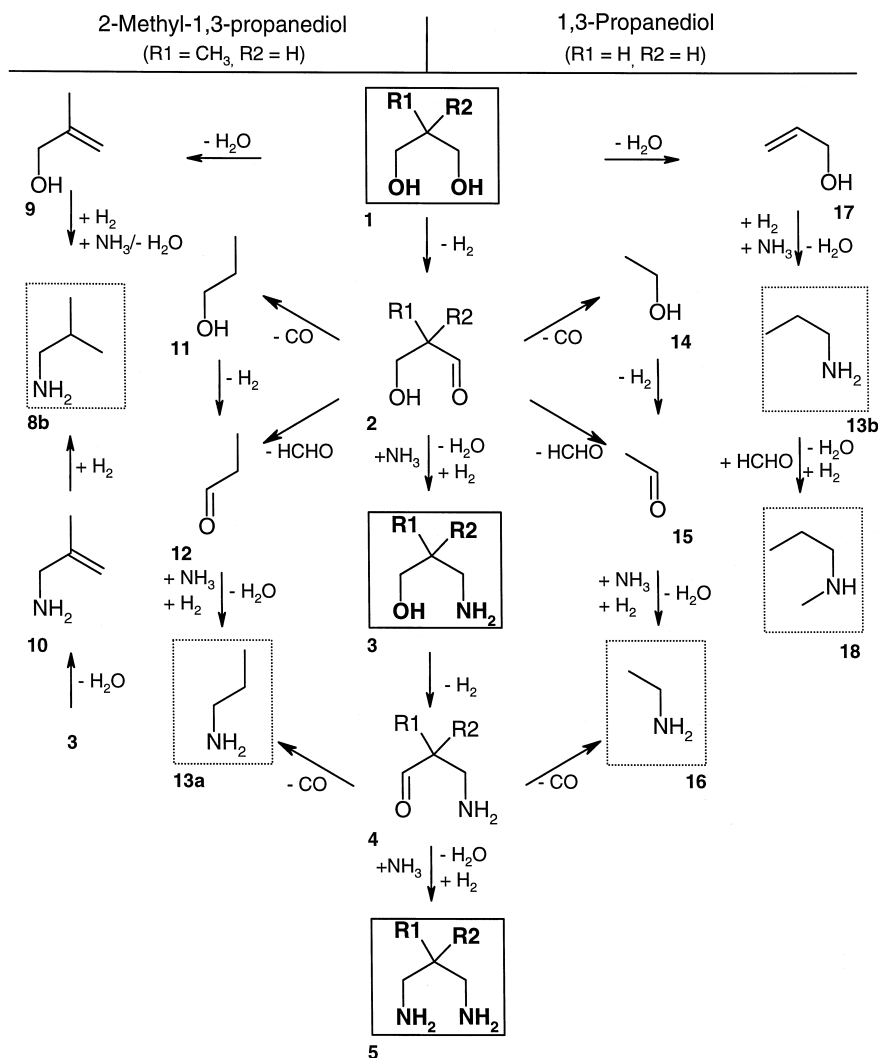
^aNumbers refer to those used to designate products in Scheme 1 and Scheme 2.

^bSelectivity to degradation products **6**, **8a**, **8b**, **13a**, **13b**, **16** and **18^a**.

^cSelectivity to gaseous degradation products.

methyl-1,3-propanediol, 1,3-propanediol and their consecutive products. A comparison of the product distribution (selectivities) obtained in the amination of the three different diols is shown in Table 2. At the same conversion of 59%, 2-methyl-1,3-propanediol and 1,3-propanediol indicate much stronger tendency to undergo degradation reactions. Interestingly, the amount of oligomers in the product mixtures was minor. The selectivity to degradation prod-

ucts determined in the liquid product mixture as a function of temperature is presented in Fig. 5. The diamine selectivity of the amination of 2,2'-dimethyl-1,3-propanediol shows a prominent maximum around 210°C. The decline at higher temperature is due to the degradation reactions. In contrast, 2-methyl-1,3-propanediol and 1,3-propanediol show only a weak maximum in diamine selectivity at lower temperature (ca. 180°C) due to strong degradation reactions.



Scheme 2. Identified products and suggested reactions occurring during the nickel-catalyzed amination of 2-methyl-1,3-propanediol (left) and 1,3-propanediol (right) with supercritical ammonia. Compounds identified are framed. The dashed line frames indicate the detected by-products.

A more detailed insight into the various reaction pathways affording undesired side products were obtained by GC-MS analysis of the reaction mixture. The various identified compounds in the product mixture are summarized in the Schemes 1 and 2.

4. Discussion

The origin of the strikingly different selectivity behaviour of 1,3-propanediols can be traced to their different tendency to undergo side reactions under amination conditions. Based on the analyzed products and intermediates the pathways presented in Schemes 1 and 2 are proposed.

The side reactions of the 2,2'-dimethyl-1,3-propanediol conversion produced mainly *iso*-butylamine (**8a**). Two reaction pathways for the production of **8a** are feasible. A base (or acid) catalyzed *retro*-aldol reaction of the β -hydroxy-aldehyde (**2**) or a *retro*-hydroformylation of **2** and/or **4**. The catalytic activity of amines in homogeneous aldol condensation and *retro*-aldol reaction has been known for long [24–26]. The *retro*-aldol reaction was recently found to be an important side reaction in the amination of 1,3-butanediol with dimethylamine [27]. Higher reaction temperature and the presence of an amine enhanced the *retro*-aldol reaction in the heterogeneous system. Accordingly, it is very likely that the product amines of the investigated reaction and the temperature above 200°C (Fig. 5) caused the formation of **8a**.

Iso-butylamine (**8a**) could also be a consecutive product from *iso*-butylalcohol (**6**), which was found in the liquid product mixture. Additionally, the gas chromatographic analysis of the gas phase revealed the formation of carbon monoxide. Both **6** and CO were probably produced by a decarbonylation (*retro*-hydroformylation) of **2**. The hydroformylation reaction of an alkene over metal catalysts is always accompanied by a strong parallel hydrogenation reac-

tion. Supported Ni mainly catalyzes the hydrogenation of the unsaturated bond (and not the hydroformylation) [28]. It is very likely that the release of CO and the strongly favoured alkene hydrogenation shifted the reaction equilibrium to **6**, which was aminated to the consecutive product **8a**.

A frequently observed side reaction of amines is the ammonia elimination reaction [27]. However, the products of this reaction, *neo*-pentanol or the corresponding amine *neo*-aminopentane were not detected in the reaction mixture.

The degradation products of 2-methyl-1,3-propanediol and 1,3-propanediol amination are shown in Scheme 2. 2-Methyl-1,3-propanediol degraded to *iso*-butylamine (**8b**) and aminopropane (**13a**), which were found in a mass ratio of 4:1. **13a** is again the product of the *retro*-aldol or *retro*-hydroformylation reaction. In contrast **8b**, the major by-product, was very likely generated by an elimination reaction. Possible reaction sequences are: (i) the elimination of water **1** \rightarrow **9** \rightarrow **8b**, **3** \rightarrow **10** \rightarrow **8b** and (ii) the elimination of ammonia from intermediate **3** to produce **8b**. Interestingly, the conversion of 1,3-propanediol over nickel showed the same types of side reactions as 2-methyl-1,3-propanediol: *retro*-aldol, *retro*-hydroformylation to produce aminoethane (**16**) and the elimination reaction, which produced the major by-product aminopropane (**13b**) via **17**. A direct elimination of water is not possible in the case of 2,2'-dimethyl-1,3-propanediol, because of a missing hydrogen at the C2-position. Accordingly, it is very likely that the rather high difference in selectivity to the diamine is due to dehydration of 2-methyl-1,3-propanediol and 1,3-propanediol, respectively. Dehydration of alcohols are catalyzed by acidic catalysts [29]. The amount of chemisorbed ammonia on the used nickel catalyst (Table 1) was approximately half of that adsorbed on an acidic zeolite (H-ZSM-S), which indicates considerable (Lewis) acidity of the catalyst [30]. Several side reactions are affected by the acidity of the support. This is corroborated by recent studies of

the cobalt-catalyzed amination of 1,3-propanediol [23].

5. Conclusions

The comparative study of the nickel-catalyzed amination of different 1,3-propanediols in supercritical ammonia indicated a strong dependence of the achievable diamine selectivity on the 1,3-propanediol structure. 2,2'-dimethyl-1,3-propanediol afforded a product mixture containing the corresponding diamine (53%) and amino alcohol (5%) as major products. Temperature above 210°C were found to be detrimental to diamine selectivity due to favoured formation of *iso*-butylamine, which was generated by *retro*-aldol and/or *retro*-formylation reactions. In contrast to the amination of 2,2'-dimethyl-1,3-propanediol, 2-methyl-1,3-propanediol and 1,3-propanediol afforded only low diamine and amino alcohol selectivity under similar reaction conditions. This behaviour could be traced to a higher tendency of these diols to undergo degradation reactions, particularly the direct elimination of water, which does not occur with 2,2'-dimethyl-1,3-propanediol, due to a missing hydrogen at the C2 position. Elimination of water is favoured on acidic catalysts.

Acknowledgements

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