

Cobalt-catalyzed amination of 1,3-cyclohexanediol and 2,4-pentanediol in supercritical ammonia

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The one-step procedure of amination of bifunctional secondary alcohols to diamines has been investigated in a continuous fixed-bed reactor. Application of supercritical NH_3 as a solvent and reactant suppressed catalyst deactivation and improved selectivities to amino alcohol intermediates, whereas selectivities to diamines remained poor (8–10%). The main reason for the low diamine selectivity of 1,3-dihydroxy compounds is water elimination leading to undesired monofunctional products via α, β -unsaturated alcohol, ketone or amine intermediates. This side reaction does not occur with 1,4-dihydroxy compounds which afford high aminol and diamine selectivities under similar conditions. Amination of secondary diols with ammonia was found to be faster, but less selective than that of the corresponding primary 1,3-propanediol.

Keywords: amination, supercritical ammonia, cobalt–iron catalyst, 1,3-cyclohexanediol, 2,4-pentanediol

1. Introduction

Heterogeneously catalyzed amination of alcohols is an economically important pathway for the manufacture of various aliphatic and aromatic amines [1–7] (scheme 1, pathway 1–5). However, yields and selectivities are rather low in the synthesis of aliphatic diamines from the corresponding diols and ammonia, and only alternative routes are applied for the production of these important intermediates.

Recent studies from our group [8–11] have shown that supercritical (sc) ammonia can be advantageously used as a solvent and reactant in the amination of simple alkanediols to diamines. The amination selectivity increases remarkably in the narrow pressure range of subcritical–supercritical transition of the medium. The selectivity improvement is attributed to the higher concentration of ammonia on the catalyst surface which favors the amination with ammonia and suppresses undesired elimination and dimerization type side reactions. For the amination of a series of diols, unsupported Co stabilized with 5 wt% Fe was found to be an efficient catalyst. An important feature of this catalyst is the absence of strong acidic or basic sites, as indicated by NH_3 and CO_2 chemisorption measurements [9].

These studies revealed that the yield is strongly dependent on the diol structure. Substitution of the H atoms at the α -C atom by methyl groups in 1,3-propanediol increases the diamine yield because the elimination of water affording a reactive allylic alcohol intermediate becomes impossible [8,9].

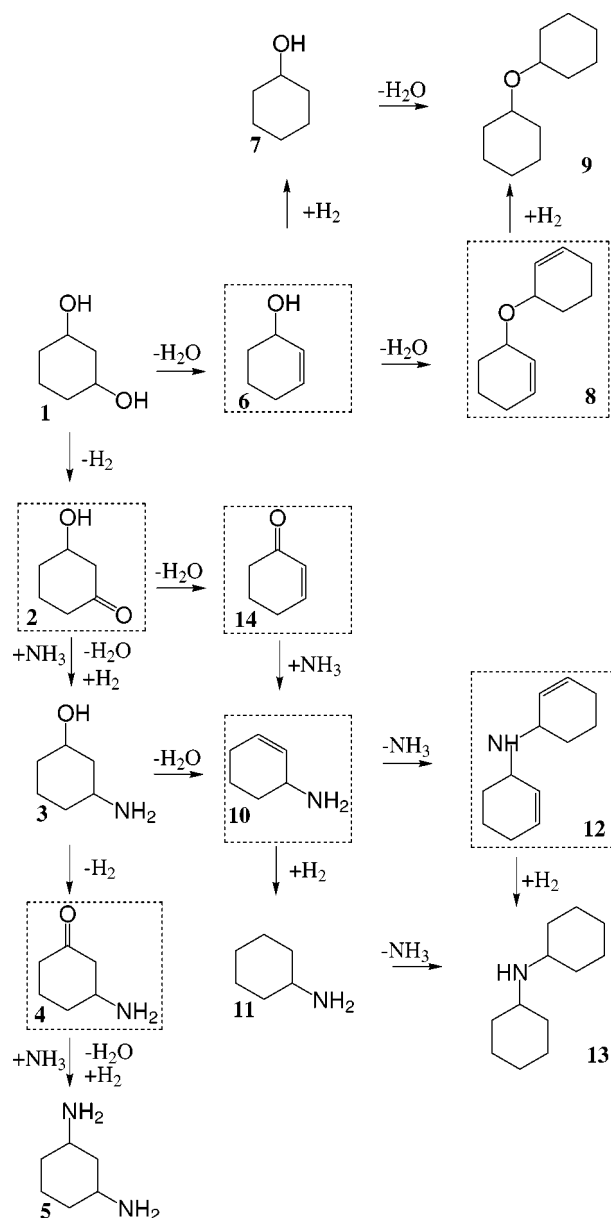
The highest yield (67%) was achieved in the amination of 1,4-cyclohexanediol to 1,4-diaminocyclohexane in sc NH_3 , and the amount of by-products (beside the useful aminoalcohol intermediate) was less than 5% [10]. It is not yet clear whether the outstanding amination selectivity has to be attributed to (i) the change from 1,3 to 1,4 positions of the OH functions which allows only the formation of the homoallylic alcohol by-product, or (ii) the higher reactivity of secondary alcohols in amination reactions compared to that of primary alcohols [12,13]. In order to clarify the role of reactant structure, we extended our studies to the amination of 1,3-cyclohexanediol and 2,4-pentanediol in sc NH_3 , using the same Co–Fe catalyst [9,10] and similar reaction conditions.

2. Experimental

1,3-cyclohexanediol (98%, Aldrich), 2,4-pentanediol (99%, Fluka), ammonia (99.998%, Pan-Gas), hydrogen (99.999%, Pan-Gas) and nitrogen (99.995%, Pan-Gas) were used without further purification.

The Co–Fe catalyst was prepared by coprecipitation [9]. Aqueous solutions of cobalt nitrate and iron nitrate, and ammonium carbonate were mixed at room temperature and the pH was adjusted to 7. The precipitate was filtered off, washed carefully with water, dried at 120 °C in vacuum and calcined at 400 °C for 4 h. Before the experiments, the catalyst was activated in the reactor in hydrogen (30 ml min^{−1}) for 4 h at 330 °C. Characterization of the catalyst by N_2 physisorption, XRD, XPS, TPR, ICP-AES, NH_3 chemisorption and DRIFT spectroscopic measurements is described elsewhere [9].

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Scheme 1. Amination of 1,3-cyclohexanediol to 1,3-cyclohexyldiamine via 3-amino-cyclohexanol. Intermediates in dashed boxes were not identified.

Amination experiments were carried out isothermally in a tubular flow reactor with an inner diameter of 13 mm and 38 ml volume. The reactor was loaded with crushed and sieved catalyst particles of 150–400 μm . The solutions of 1,3-cyclohexanediol in ammonia, or liquid ammonia and 2,4-pentanediol was dosed to the reactor by ISCO D500 syringe pumps. The pressure in the reaction system was set by a TESCOM back pressure regulator. Details of the reaction conditions are indicated in the figure caption. The liquid product was separated from the gas and analyzed by an HP5890 gas chromatograph (HP 1701 column, FID detector). Calibration factors of peak areas for products in the amination of cyclohexanediol were based on factors obtained from products 1 and 3. The products were identified by GC-MS analysis.

3. Results

Preliminary experiments indicated that even a rather high ammonia/alcohol molar ratio of 30–60 could not eliminate dimerization and oligomerization of the intermediate and product amines. Hydrogen in low concentration ($\text{NH}_3/\text{H}_2 = 60/1$) was applied to prevent the undesired dehydrogenation reactions (formation of nitriles and carbonaceous deposit). A comparatively short contact time ($5.55 \text{ g h mol}^{-1}$) was chosen in order to reduce the contribution of consecutive side reactions.

The reactant diols and the product amines are highly soluble in liquid ammonia at room temperature. It was shown for 1,3-propanediol [9] that the dilute reaction mixture formed a homogeneous fluid at or above the critical pressure (114.8 bar) and temperature (132.4°C) of ammonia.

Amination of 2,4-pentanediol was carried out in the temperature range $165\text{--}210^\circ\text{C}$ and pressure range 53–142 bar. Selectivities to diamine were around 10% at best (see table 1) but these values decreased further after 3–4 h time-on-stream. It is likely that the unstable performance of the Co-Fe catalyst is due to oligomer formation and site blocking. In comparison, no catalyst deactivation was observed with the same catalyst even after several days in the amination of 1,3-propanediol under otherwise similar conditions [9].

When the amination of 1,3-cyclohexanediol was carried out at 135 bar and in the temperature range $170\text{--}200^\circ\text{C}$, lower temperatures led to lower diol conversion, higher aminol selectivity and less side products. Accordingly, catalyst stability and the influence of pressure was investigated at 170°C . As it is illustrated in figure 1, the performance of the 95 wt% Co–5 wt% Fe catalyst varied significantly with the total pressure. At medium pressures (e.g., 53 bar, figure 1(a)), in the presence of liquid and gas (vapor) phases, catalyst deactivation occurred rapidly and steady-state conditions could not be reached within 8 h. In addition, the amination selectivity was poor, at best (3.5 h) only 16% to the amino alcohol intermediate and 5% to diamine (table 1). Working in scNH₃ (e.g., at 135 bar, figure 1(b)) the performance of the bimetallic catalyst stabilized within a few hours and the selectivity to aminol increased above 30% (table 1).

Scheme 1 lists some products of the amination of 1,3-cyclohexanediol identified by GC-MS. The middle pathway represents the target reaction from the diol (1) via the aminol (3) to the diamine (5). The intermediate carbonyl compounds (2 and 4) formed by dehydrogenation could not be detected, but it is assumed that their formation represents the rate-determining steps [2,14]. Note that intermediates of the transformation of the carbonyl compound to amine via NH₃ addition, water elimination and hydrogenation [2,6] are not shown in the scheme. Major side reactions are the dehydration of 1 to an allylic alcohol 6 or the trimeric cyclic ether. The reactive allylic alcohol is rapidly converted to cyclohexanol (7) and an ether (8, 9).

Table 1
Amination of various diols: the best selectivities achieved at medium conversions under different conditions.^a

Reactant diol	Catalyst	τ^b	p (bar)	T (°C)	Conv. (%)	S_{aminol} (%)	S_{diamine} (%)	S_{cum}^c (%)
2,4-pentanediol	Co-Fe	11.1	135	180	53	31	10	41
2,4-pentanediol	Co-Fe	11.1	135	186	85	13	9	22
1,3-cyclohexanediol	Co-Fe	5.55	135	170	56	39	8	47
1,3-cyclohexanediol	Co-Fe	5.55	106	170	21	12	4	16
1,3-cyclohexanediol	Co-Fe	5.55	53	170	79	16	5	17
1,3-propanediol ^d	Ni	11.1	135	189	59	–	–	26
1,3-propanediol ^e	Co-Fe	16.6	135	195	84	30	18	48
2,2-dimethylpropane-1,3-diol ^d	Ni	11.1	135	195	40	32	53	85
2,2-dimethylpropane-1,3-diol ^d	Ni	11.1	135	210	75	7	70	77
1,4-cyclohexanediol ^f	Co-Fe	11.1	135	165	76	42	55	97

^a Molar ratio in the feed: diol/H₂/NH₃ = 1/2/60.

^b Space time (g h mol⁻¹).

^c Cumulative selectivity.

^d From [11].

^e From [8].

^f From [10].

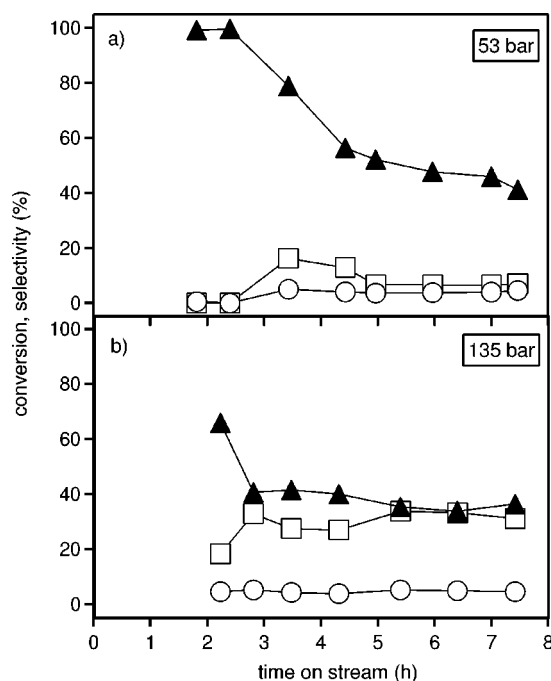


Figure 1. Effect of pressure and time-on-stream on the performance of a 95 wt% Co-5 wt% Fe catalyst in the amination of 1,3-cyclohexanediol. Conditions: 53 bar (a) or 135 bar (b), 170 °C, space time 5.55 g h mol⁻¹, molar ratio of alcohol/H₂/NH₃ = 1/2/60. (▲) Conversion, (□) selectivity to aminol, (○) selectivity to diamine.

via dehydration. Similarly, the key intermediate aminoalcohol (**3**) can afford cyclohexyl- and dicyclohexylamine (**11**, **12**, **13**) by dehydration and hydrogenation reactions. Alternatively these by-products can be formed via a conjugated unsaturated carbonyl compound (**14**). The selectivities to the undesired products **7** and **11** were considerably smaller under supercritical conditions (135 bar) than at medium pressure (53 bar). Note that dimerization and oligomerization of the bifunctional reactant and products **1**–**5** are not shown in scheme 1. Only one of them, a trimeric cyclic ether formed from **1** was identified by GC-MS. The amount

of each by-product varied in a broad range (1–20%), depending on the reaction conditions and time-on-stream.

4. Discussion

The diamine selectivities obtained in the amination of 2,4-pentanediol and 1,3-cyclohexanediol are very low. This observation corroborates the former reports that direct amination of diols to diamines is difficult and stepwise amination is more promising [15–17].

Higher pressures are favorable for the amination of 1,3-cyclohexanediol (figure 1). The cumulative selectivity to aminol and diamine is higher, and stabilization of the catalyst is achieved more readily, likely due to suppressed blocking of active sites by oligomers. At pressures far below the critical pressure ($P_c(\text{NH}_3) = 113.5$ bar), the reaction mixture consists of two phases: a liquid phase rich in non-volatile alkanediol and products, and a gas phase containing predominantly ammonia and hydrogen. Supercritical NH₃ is an excellent solvent for amines and alcohols due to extended hydrogen bonding [18]. In the near critical and supercritical region the reaction mixture forms a single homogeneous phase with significantly enhanced mass transport due to the elimination of phase transfer resistance, and to the higher diffusion coefficients and lower viscosity, compared to the situation in the liquid phase. Chemical equilibria and kinetics may also change substantially with pressure, but this effect on every particular reaction is very complex [19–22].

We assume that the concentration of ammonia at the catalyst surface in the presence of the homogeneous supercritical phase is higher than at subcritical conditions, which favors the desired reactions **1** → **5** and suppresses oligomerization and elimination (degradation) type side reactions (scheme 1).

The best cumulative selectivities to aminol and diamine, achieved in the amination of the secondary alcohols 2,4-

pentanediol and 1,3-cyclohexanediol, are 41 and 47%, respectively. When neglecting the poor stability of the Co–Fe catalyst in the former reaction, this selectivity range is comparable to the best value (48%) achieved in the amination of the primary alcohol 1,3-propanediol, under similar conditions (table 1). The secondary alcohols are significantly more reactive, as indicated by the lower reaction temperature required to achieve comparable conversions. However, this structural difference favors the side reactions even more and the final diamine selectivities are only 8–10%, about half of that achieved in the amination of 1,3-propanediol (18%). Consequently, the outstanding selectivities obtained in the amination of 1,4-cyclohexanediol (table 1) should be attributed to the 1,4 position of the OH groups, rather than the higher reactivity of secondary alcohols.

5. Conclusions

Direct amination of 2,4-pentanediol and 1,3-cyclohexanediol over a 95% Co–5% Fe catalyst revealed that applying scNH_3 as a solvent and reactant can minimize catalyst deactivation by suppressing dimerization and oligomerization type side reactions, and improve significantly the selectivity to the intermediate amino alcohol. A comparison of the amination of various linear and cyclic, primary and secondary dihydroxy compounds in scNH_3 [8–11] suggests that good diamine selectivities can be obtained in a one-step procedure only when dehydration of the diol or one of the intermediates is unfavorable or even impossible.

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