

Reductive amination of 1,6-hexanediol with Ru/Al₂O₃ catalyst in supercritical ammonia

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Hexamethylenediamine (HMDA) is an important reagent for the synthesis of Nylon-6,6, and it is usually produced by the hydrogenation of adiponitrile using a toxic reagent of hydrocyanic acid. Herein, we developed an environmental friendly route to produce HMDA via catalytic reductive amination of 1,6-hexanediol (HDO) in the presence of hydrogen. The activities of several heterogeneous metal catalysts such as supported Ni, Co, Ru, Pt, Pd catalysts were screened for the present reaction in supercritical ammonia without any additives. Among the catalysts examined, Ru/Al₂O₃ presented a high catalytic activity and highest selectivity for the desired product of HMDA. The high performance of Ru/Al₂O₃ was discussed based on the Ru dispersion and the surface properties like the acid-basicity. In addition, the reaction parameters such as reaction temperature, time, H₂ and NH₃ pressure were examined, and the reaction processes were discussed in detail.

1,6-hexanediol, hexamethylenediamine, supercritical ammonia, reductive amination, Ru/Al₂O₃

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1 Introduction

Hexamethylenediamine (HMDA) is one of the important chemicals and has a wide application in the chemical industry, such as in the synthesis of Nylon-6,6. The production of HMDA increases with an average annual rate of 1.9% in the world, and it would keep such an increasing rate until 2020 [1]. The commercial process for HMDA manufacture is usually the hydrogenation of adiponitrile (ADN) in ammonia over cobalt or iron catalysts (e.g., DuPont process) [1]. And ADN is mainly produced by the hydrocyanation of butadi-

ene, in which a toxic hydrocyanic acid is used. Therefore, to develop a green and environmental benign process for production of HMDA is of significant mission. Aliphatic and aromatic amines can be produced from the reductive amination of their corresponding alcohols [2–6], in which the reagents used are low-toxic and environmental benign. In addition, it was reported recently that 1,6-hexanediol (HDO) can be obtained from biomass via hydrogenolysis of 5-(hydroxymethyl) furfural [7,8]. Thus, the reductive amination of HDO should be a promising and competitive process for the production of HMDA.

Since the reductive amination of alcohol to produce primary amine was reported by Milstein [9] using a Ru PNP pincer complex, the reductive amination has attracted at-

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tention of researchers and some achievements have been obtained in the transformation of mono-alcohols to amines. However, the direct reductive amination of aliphatic diols to the corresponding diamines was little studied because it is more difficult for that the intermediates formed with two functional groups are more active and easily to transform to by-products through oligomerization and cyclization etc. [10,11]. For example, in the reductive amination of 1,3-propanediol over heterogeneous Co-Fe catalyst, the optimal selectivity of 1,3-diaminopropane was 34% at a conversion of 95% [12,13], and the selectivity was less than 20% at a conversion of 59% over the Ni/SiO₂ catalyst [14]. In addition, 2,4-diaminopentane was produced with only a 9% selectivity at the conversion of 85% in the reductive amination of 2,4-pentanediol over Co-Fe catalyst [15]. With the same Co-Fe catalyst, 1,4-cyclohexanediamine was produced with a 55% selectivity at a conversion of 76% in the reductive amination of 1,4-cyclohexanediol [16], which is much lower than the results obtained with homogenous Ru complexes that the selectivity of 71% (95% conversion), 78% (99% conversion), 100% (100% conversion) was obtained with Ru(CO)ClH(PPh₃)₃/Xantphos [17], Ru(CO)ClH(DPEphos)(PPh₃) [18], and Ru₃(CO)₁₂/acridine-based diphosphine [19], respectively. The reductive amination of biogenic isohexides with homogenous Ru catalysts produced diamine derivatives in a high selectivity of 95% [17,19], but a quite low selectivity of 20% was obtained over a heterogeneous catalyst of Ru/C [20]. For the amination of HDO, HMDA was produced with a yield of 81% with homogenous Ru-acridine catalyst [21], but, in contrast, the heterogeneous catalysts gave much lower yields as 10%–15% with Ni [22] and 24.8% with Co-Cu [23]. Therefore, it is still a great challenge to develop efficient heterogeneous catalyst in the reductive amination of HDO to HMDA.

In the present work, the authors screened several heterogeneous catalysts of the supported Ni, Co, Ru, Pt, Pd catalysts for the reductive amination of HDO in supercritical NH₃. The relationship between the catalytic performance and the surface properties of catalysts such as the metal dispersion, the acid/base properties was examined. The influence of reaction temperature, time, H₂ and NH₃ pressure were examined, and the reaction processes were discussed in detail.

2 Experimental

2.1 Materials

5 wt% M/Al₂O₃ (M=Ru, Pd, Pt) catalysts were purchased from Wako Pure Chemical Industries (Japan); Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O and MgO were purchased from Sinopharm Chemical Reagent (China); RuCl₃·3H₂O and SiO₂ from Sigma-Aldrich (USA); 1,6-hexanediol (HDO) from Aladdin (USA); hexamethylenediamine

(HMDA), hexamethyleneimine (HMI) and 6-amino-1-hexanol (AHO) were purchased from Tokyo Chemical Industry (Japan); acetonitrile, *tert*-butanol and Nb₂O₅ were purchased from Beijing Chemical Works (China); NH₃ from Dalian Special Gases (China). All the chemical reagents were used as received.

2.2 Catalyst preparation

25 wt% M/Al₂O₃ (M=Co, Ni) catalysts were prepared by the co-precipitation method. Nb₂O₅, SiO₂ and MgO supported Ru (5 wt%) were prepared by the impregnation method. The support materials of Nb₂O₅, SiO₂ and MgO were calcined in air at 500 °C for 3 h and cooled down to room temperature. The co-precipitation and impregnation samples were dried at 60 °C overnight and calcinated in air at 500 °C for 4 h. Before used in the reductive amination, the calcined catalysts were reduced in H₂ flow at the desired temperature for 2 h according to the H₂-temperature-programmed reduction (H₂-TPR) results. The reduction temperature determined was 550 °C for Ni/Al₂O₃, 650 °C for Co/Al₂O₃, and 200 °C for Ru/Nb₂O₅, Ru/SiO₂, Ru/MgO.

2.3 Catalyst characterization

Powder X-ray diffraction (XRD) analysis was made on a Bruker D8 Advance X-ray diffractometer (Germany) with a Cu K α source ($\lambda=0.154\text{nm}$) in a 2θ range of 10°–80° with a scan speed of 2°/min. Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-2010 instrument (Japan) operated at an accelerating voltage of 200 kV. H₂-TPR and CO₂ temperature-programmed desorption (CO₂-TPD) profiles were obtained on a Micromeritics Autochem II 2920 chemisorption instrument (USA). The instrument was calibrated by nano CuO. Before H₂-TPR run, 50 mg catalyst was loaded in an U-quartz tube and pretreated with ultra-pure argon at 120 °C for 30 min. After cooling to room temperature, the sample cell was heated from room temperature to 800 °C with a rate of 10 °C/min in H₂/Ar mixture gas. For CO₂-TPD test, 100 mg catalyst was pre-reduced in H₂/Ar mixture gas at desired temperature for 1 h. After the catalyst was cooled to room temperature, the adsorption was conducted by flushing the sample with CO₂/He mixture gas for 30 min. Hydrogen chemisorption was estimated based on the H₂-TPD results, and H₂-TPD was carried out at a temperature range of 25–800 °C with a heating rate of 10 °C/min under flowing of He.

The total acidity of catalyst was measured by means of potentiometric titration [24,25]. In a typical process, the catalyst (0.05 g) was suspended in acetonitrile and agitated for 3 h. Then, the suspension was titrated with 0.1 mol/L *n*-butylamine in acetonitrile at 0.05 mL/min. The electrode potential variation was measured with an automatic potentiometric titrator containing dual electrodes.

2.4 Activity measurement

HDO (5 mmol), catalyst (50 mg), and *tert*-butanol (5 mL) were loaded into a 50 mL stainless steel reactor. The reactor was flushed with H₂ for three times and then pressurized with 1 MPa H₂ at room temperature. After being heated to the desired temperature, NH₃ was introduced into the reactor with a high-pressure liquid pump (Hangzhou Zhijiang Petrochemical Equipment, China) to the desired pressure. The reaction was conducted while stirring the reaction mixture with a magnetic stirrer (1200 r/min). After reaction, the reactor was cooled and depressurized carefully and the residual NH₃ was removed by water. The products were identified by gas chromatograph-mass spectrometer (GC-MS; Agilent 5975/6890N, USA; HP-5 capillary column) and electrospray ionization mass spectrometry (ESI-MS). The products were quantitatively analyzed by GC (Shimadzu GC-2010, Japan; Rtx-50 capillary column) using *n*-octanol as an internal standard. The conversion was calculated by moles of HDO consumed divided by initial moles of HDO used and the selectivity was determined by moles of product *i* divided by total moles of products obtained.

3 Results and discussion

3.1 Catalytic performances and catalyst characterization

The catalytic activities of several supported metal catalysts such as Co, Ni, Pt, Pd and Ru supported on Al₂O₃ were examined and compared for the reductive amination of HDO in Table 1. Co/Al₂O₃ and Ni/Al₂O₃ catalysts showed the lowest reaction rate (entries 1, 2). Pt/Al₂O₃ and Pd/Al₂O₃ gave a relatively larger reaction rate, but the selectivity to HMDA was lower than 30% over these catalysts (entries 3, 4). Among the Al₂O₃-supported catalysts examined, Ru/Al₂O₃ gave the best selectivity to HMDA (38.4%) with a reaction rate of 90 h⁻¹ (entry 5). Then, Ru was selected as the catalytic

metal species, other different materials were examined as supports for Ru, including basic (MgO), amphoteric (Al₂O₃), and acidic (SiO₂, Nb₂O₅) oxides. It was found that Ru/Al₂O₃ gave the better selectivity to HMDA (38.4%), which was larger than those with Ru/Nb₂O₅ (31.3%) (entry 6), Ru/SiO₂ (17.2%), Ru/MgO (17.65%) (entries 7, 8), and Ru/MgO (14.2%) (entry 9).

For the supported Ru catalysts, the difference of their catalytic performances was discussed based on Ru particle dispersion and the properties of catalysis surface by XRD, hydrogen chemisorption, CO₂-TPD and potentiometric titration. The XRD results obtained are shown in Figure 1. The patterns of the supported Ru catalysts did not show difference to their supports, no diffraction pattern of Ru ($2\theta = 44.0^\circ$) was detected because that the Ru particle was very small. The surface properties of catalysts such as the particle size, specific surface area (SA_{Ru}) and the dispersion of Ru nanoparticles were examined by hydrogen chemisorption and the results are summarized in Table 2. The Ru nanoparticle size exposed on the surface of catalysts is at a range of 3.6–13.2 nm. The Ru/Al₂O₃ showed the largest reaction rate (Table 1, entry 5) and the smallest Ru particle size (Table 2, entry 3), but its turnover frequency (TOF) was lower than that over Ru/Nb₂O₅ which had the largest Ru particle size. These results show that the catalytic performance not only depends on the particle size of Ru but also on the other factors. In addition, the acid-base properties of catalysts were examined by titration and the results are shown in Table 2. The initial electrode potential (*E*_i) is suggested to indicate the maximum strength of acid sites, and the acid strength was classified according to the following scale: *E*_i > 100 mV (very strong acid sites), 100 mV > *E*_i > 0 mV (strong acid sites), 0 > *E*_i > -100 mV (weak acid sites) and *E*_i < -100 mV (very weak acid sites) [24,25]. The results of potentiometric titration *E*_i are listed in Table 2. Based on this classification, the acidity of catalysts is in an order of Ru/Nb₂O₅ > Ru/SiO₂ > Ru/Al₂O₃ > Ru/MgO (Figure S1, Supporting Information online).

Table 1 Reductive amination of 1,6-hexanediol over various catalysts ^{a)}

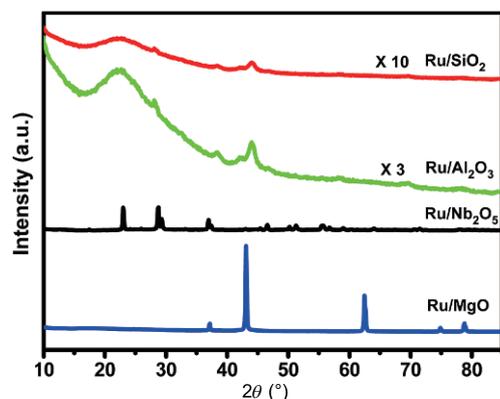
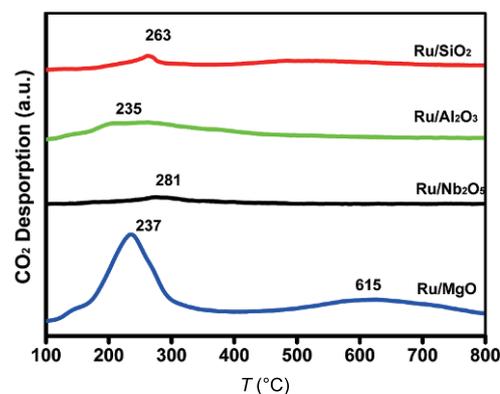
Entry	Catalyst	Conv. (%)	Selectivity (%)				Rate ^{c)} (h ⁻¹)
			AHO	HMDA	HMI	Others ^{b)}	
1	Co/Al ₂ O ₃	100	6.5	35.8	45.9	11.8	8
2	Ni/Al ₂ O ₃	100	6.5	21.2	66.5	5.8	8
3	Pt/Al ₂ O ₃	100	6.3	21.5	48.7	23.5	126
4	Pd/Al ₂ O ₃	100	11.8	29.8	50.2	8.2	67
5	Ru/Al ₂ O ₃	100	–	38.4	31.9	29.7	90 ^{d)}
6	Ru/Nb ₂ O ₅	100	19.1	31.3	23.0	26.6	61
7	Ru/SiO ₂	71.5	63.0	17.2	6.6	13.2	33
8	Ru/MgO	70.2	68.8	17.6	7.5	6.1	31
9 ^{e)}	Ru/MgO	98.9	3.2	14.2	51.0	31.6	33

a) Reaction conditions: 50 mg catalyst, 5 mmol 1,6-hexanediol, 5 mL *tert*-butanol, 1 MPa H₂, 15 MPa NH₃, 220 °C, 6 h; b) by-products of dimer and trimer; c) reaction rate was calculated by the mole of hydroxyl consumed divided the moles of total amount of Ru used and the reaction time; d) 4.5 h; e) 100 mg catalyst.

Table 2 The results and properties of supported Ru catalysts

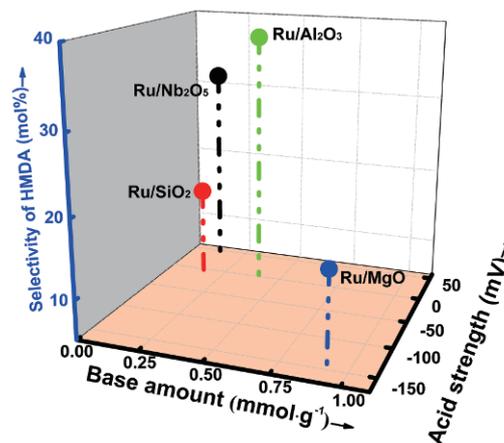
Entry	Catalyst	Particle size (nm)	SA _{Ru} ^{a)} (m ² /g)	Dispersion ^{a)} (%)	E _i ^{b)} (mV)	Amount of basic site ^{c)} (mmol/g)	TOF ^{d)} (h ⁻¹)
1	Ru/Nb ₂ O ₅	13.2	36.9	10.1	46.5	0.13	603
2	Ru/SiO ₂	6.5	75.6	20.7	-15.8	0.18	159
3	Ru/Al ₂ O ₃	3.6	135.3	37.1	-19.6	0.44	242
4	Ru/MgO	10.2	47.6	13.0	-161.6	0.94	239

a) Ru metal-specific surface area (SA_{Ru}) and dispersion were calculated based on the amount of hydrogen chemisorption; b) initial electrode potential of the suspension of catalysts in acetonitrile as shown in Figure S1; c) amount of surface basic site (mmol/g) determined by CO₂-TPD; d) turnover frequency, which was estimated as the overall rate of -OH conversion normalized by the number of active Ru sites over the specified time. The number of active sites was calculated by (the Ru dispersion) × (the total number of Ru atoms).

**Figure 1** XRD patterns of supported Ru catalysts (color online).**Figure 2** CO₂-TPD profiles of supported Ru catalysts (color online).

Furthermore, the basicity of the Ru catalysts was examined by CO₂-TPD, as shown in Figure 2. The supported Ru catalysts exhibited different CO₂ desorption peaks at a temperature range of 200–850 °C, corresponding to the medium to strong basic sites. The total amount of desorbed CO₂ (area of the peak) was significantly larger for Ru/MgO, indicating that Ru/MgO contains much larger amount of basic sites compared to Ru/Nb₂O₅, Ru/SiO₂ and Ru/Al₂O₃. The basicity of catalysts examined is in an order of Ru/MgO > Ru/Al₂O₃ > Ru/SiO₂ > Ru/Nb₂O₅ as seen in Table 2.

For the heterogeneous catalysis, the reaction is performed on the surface of catalyst, it contains three steps of adsorption, surface reaction and desorption, therefore the surface property of support is as the same important as the active metal species in the catalysis, which will influence the adsorption type of substrate and the reaction rate and product selectivity. Herein, the relation between the surface acid-basicity of catalysts and the selectivity to HMDA were discussed and the results are plotted in Figure 3. It is clear that the acid-basicity of catalysts has a large effect on the catalytic performance, the Ru/Nb₂O₅ with strong acidity gave the higher selectivity to HMDA. The Ru/Al₂O₃ with medium acid-basicity gave the best selectivity to HMDA, and the Ru/MgO with the highest basicity gave the lowest selectivity to HMDA. It was reported that the acid sites are advantageous to the adsorption of HDO with hydroxyl group and alkaline NH₃ [26], which favor to the dehydrogenation of hydroxyl to aldehyde group and the subsequent reductive amination of aldehyde group to amine

**Figure 3** Selectivity of HMDA vs. base amount and acid strength over the supported Ru catalysts (color online).

over Ru nanoparticles. At the same time, the basic sites may prohibit the further transformation of HMDA to other by-products. In other words, both the acidic and basic sites on the surface of catalyst are necessary for the reductive amination of HDO to HMDA. Therefore, Ru/Al₂O₃ gave the highest selectivity to HMDA, and it was selected for the following studies.

3.2 Influence of reaction conditions

The reaction temperature, time, H₂ and NH₃ pressures were

tested for the present reductive amination of HDO. It was found that the temperature and reaction time were important factors, significantly influencing the reaction rate and product selectivity. The changes of conversion and selectivity with time at different temperatures are shown in Figure 4. With prolonging reaction time and raising temperature, the conversion of HDO increased and the selectivity to AHO decreased. At 210 and 220 °C, the selectivity to HMDA increased with extending reaction time until the complete conversion of HDO. At 230 °C, the reaction occurred very fast and the conversion reached 100% within 1.5 h, but the selectivity to HMDA decreased with further extending reaction time.

The effect of H₂ pressure was examined and the results are

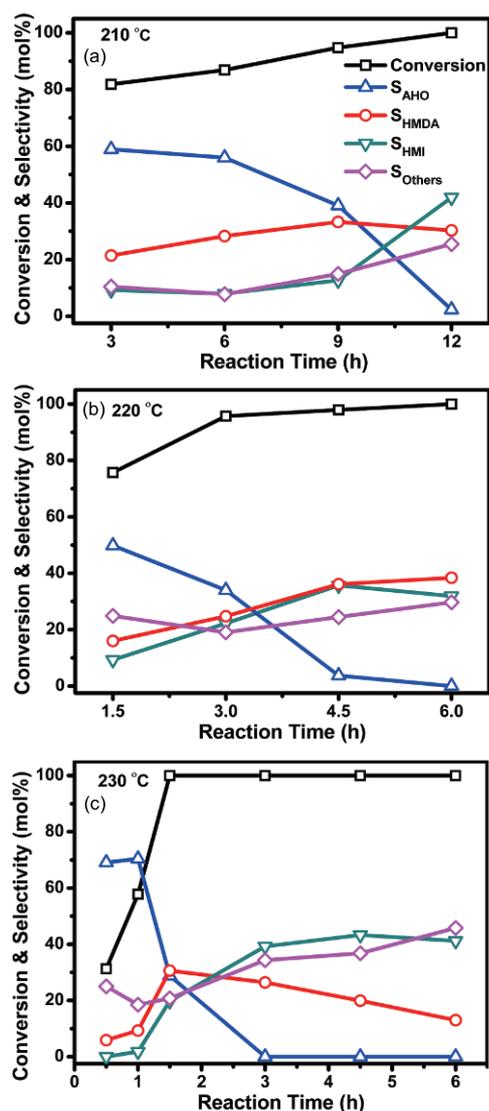


Figure 4 The changes of conversion and product selectivity with reaction time for the reductive amination of 1,6-hexanediol at different temperatures. (a) 210 °C; (b) 220 °C; (c) 230 °C. Reaction conditions: 50 mg Ru/Al₂O₃, 5 mmol 1,6-hexanediol, 5 mL *tert*-butanol, 1 MPa H₂, 15 MPa NH₃ (color online).

shown in Figure 5. From a stoichiometric point of view, no additional hydrogen was needed for the reductive amination because the consumption of H₂ in the hydrogenation of such intermediates as 6-imino-hexanol (**3**) and 6-imino-1-hexylamine (**6**) could be furnished by the H₂ produced from the dehydrogenation of HDO (**1**) and AHO (**4**). However, when the reaction was performed in the absence of H₂, the conversion of HDO was 75% and the selectivity to HMDA was only 15%. On the addition of 1 MPa H₂, the conversion of HDO reached to 100% and the selectivity to HMDA increased to 38.4%. The selectivity to HMDA decreased to 15% at a higher H₂ pressure of 2 MPa, because that HMI and by-products were largely produced. At the higher hydrogen partial pressure, more active sites would be occupied by hydrogen, restraining the adsorption of NH₃. Therefore the appropriate H₂ pressure is needed for obtaining high yield of HMDA.

The influence of NH₃ pressure is shown in Figure 6, the conversion of HDO reached 100% at a NH₃ pressure range of 3–15 MPa and the selectivity to HMDA increased from 2% to 38.4% with NH₃ pressure increasing up to 15 MPa. With further increasing pressure from 15 MPa to 22 MPa, the conversion and the selectivity decreased. NH₃ could affect the

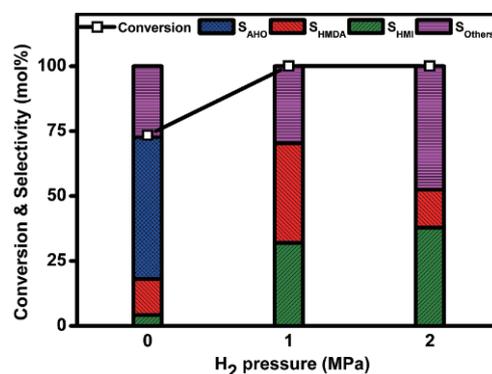


Figure 5 Influence of H₂ pressure on the reductive amination of 1,6-hexanediol. Reaction conditions: 50 mg Ru/Al₂O₃, 5 mmol 1,6-hexanediol, 5 mL *tert*-butanol, 15 MPa NH₃, 220 °C, 6 h (color online).

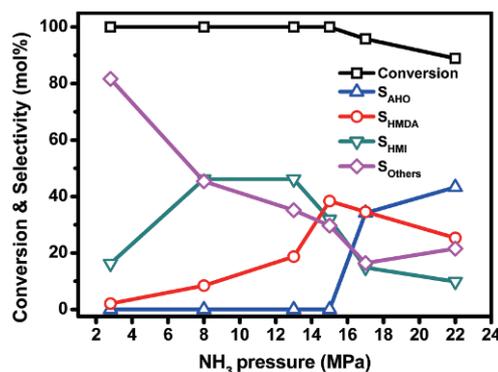


Figure 6 Influence of NH₃ pressure on the reductive amination of 1,6-hexanediol. Reaction conditions: 50 mg Ru/Al₂O₃, 5 mmol 1,6-hexanediol, 5 mL *tert*-butanol, 1 MPa H₂, 220 °C, 6 h (color online).

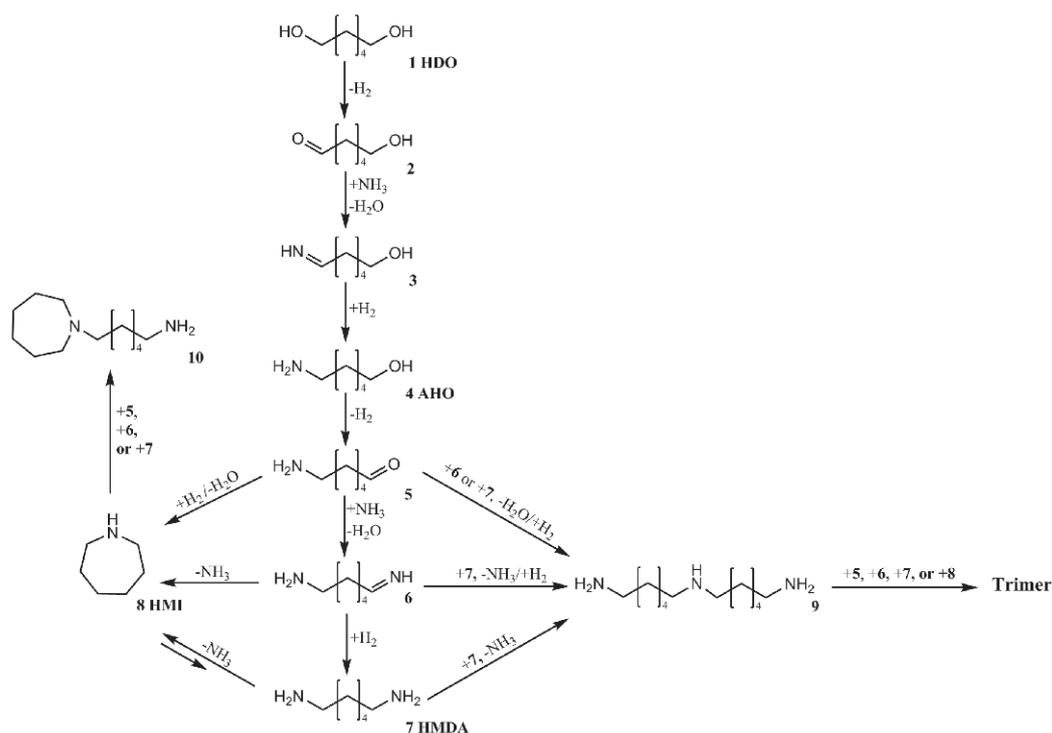
chemical equilibrium and reaction rate, when NH_3 pressure was raised up to above the critical point ($T_c=132.4^\circ\text{C}$, $P_c=11.48\text{MPa}$) [16], NH_3 expanded *tert*-butanol phase might be formed, which will improve the mass transport because of the elimination of the phase transfer resistance, as well as increase the diffusion coefficient and reduce the viscosity. Meanwhile, the concentration of NH_3 and H_2 in the reaction phase should be enhanced, and so the main reaction was accelerated relative to the side reactions such as cyclization, dimerization and oligomerization. Thus the selectivity to HMDA was improved significantly. The reduced reaction rate with further increasing NH_3 pressure after 15MPa could be explained by the dilution effect [27]. Even so, at the high pressure of 22MPa, the conversion of HDO could reach 100% when prolonged the reaction time to 12h and the selectivity of HMDA reached 34.5%.

3.3 Reaction pathways

For the present reductive amination of HDO, several products were identified and confirmed by GC-MS and ESI-MS (Figure S2 and Figure S3), Scheme 1 shows a possible reaction pathways proposed according to the product distribution during the reaction (Figure 4). Because of two hydroxyl groups ($-\text{OH}$) in the molecule of HDO, it could be transformed to an intermediate of 6-amino-1-hexanal (**5**) with an end functional group of aldehyde ($\text{C}=\text{O}$) and another end group of amine ($-\text{NH}_2$). 6-Amino-1-hexanal could be further aminated to enamine (**6**) with an end functional group of $\text{C}=\text{N}$ and another end group of amine ($-\text{NH}_2$). Both two

groups of $\text{C}=\text{O}$ and $\text{C}=\text{N}$ are very active and easily to react with intra- and/or inter- group of ($-\text{NH}_2$). So several products, such as 6-amino-1-hexanol (AHO, **4**), hexamethylenediamine (HMDA, **7**), and hexamethyleneimine (HMI, **8**), were majorly produced in the reductive amination of HDO. Besides, several by-products were also detected, which were dimer and trimer were produced via dimerization, cyclization and oligomerization.

In order to further discuss the reductive amination of HDO, additional reactions were conducted using such products as AHO, HMDA or HMI as starting substrates with $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst under the same reaction conditions. The results obtained are shown in Table 3. For the reaction of AHO, the conversion reached 100% in 6 h, and the selectivity of HMI and HMDA was 33.0% and 20.7%, respectively. A few by-products were produced from the dimerization and oligomerization of 6-amino-1-hexanol and/or HMDA. For the reaction of HMDA, its conversion was 86.9% and the selectivity to HMI was 53.6%. While, for the reaction of HMI, the conversion was 58.0% and the selectivity to HMDA was 14.7%. It is clear that HMDA can transfer to HMI and vice versa, but the cyclization reaction of HMDA to HMI was faster than the ring-opening reaction of HMI to HMDA. So, a high selectivity to HMDA was difficult to obtain in the reductive amination of HDO. However, the yield of HMDA obtained over $\text{Ru}/\text{Al}_2\text{O}_3$ was 38.4% herein, which is much larger than the reported results obtained with heterogeneous catalysts of the supported Ni (10%–15%) and Co-Cu (24.8%) catalysts [22,23].



Scheme 1 Possible reaction pathways for the reductive amination of 1,6-hexanediol.

Table 3 Results for the reaction of HDO, AHO, HMDA and HMI over Ru/Al₂O₃ under the reductive amination conditions^{a)}

Substrate	Conv. (%)	Selectivity (%)		
		HMI	HMDA	Others ^{b)}
HDO	100	31.9	38.4	29.7
AHO	100	33.0	20.7	46.3
HMDA	86.9	53.6	–	46.4
HMI	58.0	–	14.7	85.3

a) Reaction conditions: 50 mg catalyst, 5 mmol reactant, 5 mL *tert*-butanol, 1 MPa H₂, 15 MPa NH₃, 220 °C, 6 h; b) by-products of dimer (**9** and **10**) and trimer produced via dimerization, cyclization and oligomerization.

4 Conclusions

The reductive amination of HDO was studied over the supported Ni, Co, Ru, Pt, Pd catalysts in supercritical NH₃, among which Ru/Al₂O₃ presented the best catalytic performance. The higher reaction rate and product selectivity were obtained at an NH₃ pressure of 15 MPa (supercritical region), at which an expanded liquid phase was formed and the side reactions such as cyclization, dimerization and oligomerization were suppressed. It is confirmed that HMDA can transform to HMI and vice versa, but the cyclization reaction of HMDA to HMI was faster than the ring-opening reaction from HMI to HMDA. Under the optimum conditions, HMDA was produced with a yield of 38.4%, which is much better than the previous results obtained over the heterogeneous catalysts reported in the literature.

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Conflict of interest The authors declare that they have no conflict of interest.

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