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Synthesis of 1,2-propanediamine via reductive amination of isopropanolamine over Raney Ni under the promotion of K_2CO_3

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Abstract

Catalytic amination of isopropanolamine and ammonia to 1,2-propanediamine over Raney Ni with potassium carbonate as the additive was reported. Characterization of N_2 adsorption–desorption and XRD were performed to reveal the textural and structural properties of the catalysts. With the additive of potassium carbonate, the selectivity of 1,2-propanediamine was improved, while the side generation of 2,5-dimethylpiperazine was suppressed. The catalytic reaction parameters were optimized and the yield of 1,2-propanediamine reached 80% under the optimized reaction condition.

Keywords Isopropanolamine · 1,2-Propanediamine · Raney nickel · Potassium carbonate · Reductive amination

Introduction

Amines are basic and bulk chemical raw materials for production of pharmaceuticals, agrochemicals, polymers and dyes (Rossin and Peruzzini 2016; Choi et al. 2011; Suslov et al. 2017). There are various methods for synthesizing amines of which the most commonly used is through amination of alcohols and ammonia for the starting material is inexpensive and readily available (Lawrence 2004; Legnani et al. 2017; Subramanian et al. 2014; Bahadori et al. 2013; Crossley et al. 2016; Pera-Titus and Shi 2014; Liu et al. 2017a, b; Pelckmans et al. 2017). Moreover, the only by-product is water, and thus attracts much attention as green and atom-economical chemistry.

Primary diamine is one of the most important amines (Lawrence 2004; Zhao et al. 2015) which can be synthesized via reductive amination of bifunctional alcohol (diol and aminoalcohol). But amination of short-chain diol suffers low conversion and is always accompanied by other side reactions such as cracking, condensation, dehydration reaction. More so, the selectivity of the diamine is low owing to the generation of poly and cycle amine byproduct, which is attributed to the high activity of amine for the strong nucleophilicity. Therefore, synthesis of diamine with high selectivity by reductive amination of bifunctional alcohol is put forward higher requirements.

To search high-performance catalytic system, many attempts have been presented. It was reported (Imm et al. 2011; Pingen et al. 2013) that diamines can be synthesized by amination of diols with Ru catalyst under the cooperation of ligand and base in homogeneous process (Scheme 1, reaction 1). The conversion and selectivity were both over 95% for specific substrate alcohol. However, the amination of linear alky diols was not involved. Although Ru catalyst has high performance in the amination of cycle diols, the recovery and reuse of noble metal and ligand from these homogeneous catalytic systems were much more difficult. Comparatively, the catalysts in the heterogeneous catalytic reaction process are easily recovered and reused, in spite of most of them hardly achieved satisfactory activity and selectivity of primary diamines. Metal catalysts (Ru, Ni, Co, etc.) were employed in heterogeneous amination of bifunctional alcohol to diamine (Scheme 1, reaction 2). With the supported Ru catalyst, poor conversion (lower than 10%) was obtained for amination of propane-1,2- and -1,3-diol and butane-2,3-diol, while the cyclic amines were the main products for pentane-1,5-diol and hexane-1,6-diol (Niemeier et al. 2017). Li et al. (2017) reported that the

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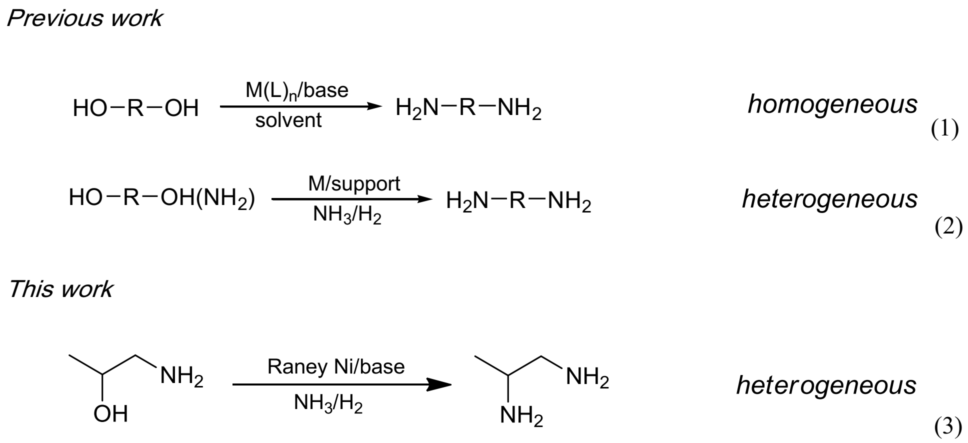
Scheme 1 Synthesis methodologies of diamine chemicals



hexane-1,6-diamine can be obtained with the Ru/Al_2O_3 catalyst by the amination of 1,6-hexanediol, while the selectivity of hexane-1,6-diamine was only 38%. Only aminoalcohols were obtained by amination of propane-1,2-diol over Rh–In catalyst (Takanashi et al. 2014). In this aspect, to reduce the cost, noble metal-free catalysts have been developed. For example, Co-modified H-ZSM-5 catalyst was prepared to investigate the reductive amination of ethanolamine to ethylenediamine, but selectivity was lower than 20% (Zhang et al. 2007). Co–Fe or Ni catalysts was studied for the amination of alky diols in supercritical ammonia (Fischer et al. 1999a, b, c, d; Jenzer et al. 1999). However, the selectivity of diamines was below 40% for amination of linear alky diols and selectivity was below 70% even for amination of α-substituted or cycle diols. Recently, Ma et al. (2018) reported reductive amination of monoethanolamine over Ni–Re catalyst and the conversion was less than 45% when the selectivity of ethylenediamine was about 80%. Therefore, it is necessary to explore the new convenient heterogeneous catalysts with high performance for preparation of diamines.

In previous work, we reported a direct reductive amination of 2-amino-2-methyl-1-propanol to produce 2-methyl-1,2-propyldiamine over Raney Ni catalyst (Wang et al. 2017). Inspired by the promotion of base in homogeneous catalytic system, herein, the direct amination of bifunctional secondary alcohol with ammonia to diamine over Raney Ni catalyst under the promoter of base was developed. The introduction of base, especially for K_2CO_3, can improve the selectivity of 1,2-propylenediamine by reductive amination of isopropanolamine (Scheme 1, reaction 3) (Scheme 1).

Experiment

Catalyst preparation

$PdCl_2(PPh_3)_2$, $Pd(OAc)_2$, $RhCl(PPh_3)_3$, $IrCl_3$, Pt/C and 5% Rh/C were from Kaida Chemical Engineering Co., Ltd., Shaanxi, China. Raney Co catalyst (RTH-6110) used in experiments was supplied by Dalian Tongyong Chemical Co., Ltd., Liaoning, China. Above catalysts were used without pre-treatment before experiments. The Ni–Al alloy powders (average particle size is 50 μm), containing about 50% Ni and 50% Al (w/w), were produced by Dalian Tongyong Chemical Co., Ltd., Liaoning, China.

Isopropanolamine (IPA, > 99%) used in experiment was purchased from Chengdu Kelong reagent Co., Ltd., Sichuan, China. Ammonia was purchased from Xinghua Chemical Industry Incorporated Co., Ltd, Shaanxi, China. The other analytical reagents such as $NaOCH_3$, Li_2CO_3, Na_2CO_3, K_2CO_3, KOH and NaOH were supplied by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Deionized water and high purity hydrogen were used in experiment.

Raney Ni catalyst was made by follow procedures: the Ni–Al alloy powders (termed as Ni–Al) were added to 30 wt% aqueous sodium hydroxide in a beaker immersed in thermostated water at 70 °C by batch carefully and kept at 80 °C for more than 5 h. The extracted catalysts were washed with deionized water until neutralized. The samples were finally washed with absolute ethanol for three times, and transferred to stoppered tubes for storage in absolute ethanol at room temperature. The resultant Raney Ni was designated as FR.

Catalyst characterization

The specific surface areas of the samples were obtained with a Micromeritics ASAP 2020 nitrogen adsorption instrument at 77 K. The samples were degassed under vacuum at 250 °C for 8 h. BET surface areas were determined by the Brunauer–Emmett–Teller (BET) method and total pore volume and average sizes were evaluated by the standard Barrett–Joyner–Halenda (BJH) methodc of the isotherm. XRD patterns of the samples were collected with an Empyrean, PANalytical X-ray diffractometer (Cu Kα, $\lambda = 0.15418$ nm).

The pattern for the structure refinement was taken in a 2θ range of 5–90° with a step width of 0.026°.

Catalyst test

The amination reactions were carried out in a 50-mL sealed autoclave. The catalysts, isopropanolamine, and bases were placed into the autoclave. Air in the autoclave was evacuated by pressurization–depressurization cycles with nitrogen and subsequently with hydrogen. Then, after vacuuming the autoclave, liquid ammonia was placed into the reactor. After that, the mixture was pressurized with hydrogen to specific pressure, and the stirring speed was set as 800 rpm. The autoclave was heated to 170 °C and kept for specific time before it was cooled to room temperature and depressed to atmospheric pressure. The mixture was filtrated and the catalyst was washed with water and ethanol for three times, respectively. The recycled Raney Ni collected from the reaction without the additive of K_2CO_3 was denoted as AR; recycled Raney Ni collected from the reaction with the additive of K_2CO_3 was denoted as KAR. The liquid mixture was analyzed by GC–MS (Agilent 6890N/5975B). To separate the reaction products, the temperature in the GC oven was kept at 323 K for 5 min, and then heated to 523 K with the ramp of 10 K/min. The liquid products were analyzed by a gas chromatograph (Shimadzu GC-2014C) with a capillary column (DB-35 30 m × 0.32 mm × 0.25 μm) equipped with a flame ionization detector (FID). The conversion of IPA and selectivity of 1,2-propylenediamine (PDA) for each experiment was defined as follows:

$$X = \frac{\text{mass amount of IPA reacted}}{\text{mass amount of IPA loaded}} \times 100\ \text{wt\%}$$

$$S = \frac{\text{mass amount of PDA}}{\text{mass amount of all products}} \times 100\ \text{wt\%}$$

The yield of PDA was calculated as defined:

$$Y = X \times S \times 100\%$$

Results and discussion

Catalyst screening

In the dehydrogenation and hydrogenation reaction, the nature of the active center metal is the most important parameter for the activity and the product distribution. Noble metals (Ru, Ir, Pd, et.) (Yang et al. 2017; Imm et al. 2011; Lafrance et al. 2012; Knoefel et al. 2017) and transition metals (Co, Ni, Cu) (Yue et al. 2017; Martinez-Asencio et al. 2011; Liu et al. 2017a, b; Takanashi et al. 2014) catalysts are known to be effective catalysts for reductive amination of alcohols in previous study. Therefore, various catalysts for the reductive amination of isopropanolamine with NH_3 were investigated to screen the catalyst, which is summarized in Table 1.

Table 1 Amination of isopropanolamine with ammonia over various catalysts

Entry	Cat./loading	Conv.%	Sel.%		Yield% (PDA)
			PDA	DMP	
1[a]	$PdCl_2(PPh_3)_2$/3 mol%	41.9	17.7	3.0	7.4
2[a]	$Pd(OAc)_2$/3 mol%	13.4	–	–	–
3[a]	$RhCl(PPh_3)_3$/3 mol%	83.2	20.9	16.6	17.4
4[a,b]	$IrCl_3$/3 mol%	23.7	–	–	–
5[a,c]	$Cu(NO_3)_2$/3 mol%	5.7	–	–	–
6[a,c]	$Ni(NO_3)_2$/3 mol%	14.3	–	–	–
7	Ru(5%)/C/10 wt%	5.1	42.4	4.9	2.2
8	Pd(5%)/C/10 wt%	17.1	34.6	14.6	5.9
9	Raney Ni/3 wt%	69.3	83.8	6.6	58.1
10	Raney Co/3 wt%	56.9	86.3	4.9	49.1

Reaction conditions: isopropanolamine (0.1 mol); ammonia (0.16 mol); initial hydrogen pressure 4 MPa; 170 °C; 15 h

[a] 0.04 mol IPA, 5 mL CH_3Ph

[b] 4 mol% PPh_3

[c] 6 mol%PPh_3

Under the investigated reaction conditions, homogeneous catalysts $Pd(OAc)_2$, $IrCl_3$, $Cu(NO_3)_2$ and $Ni(NO_3)_2$ showed low activity and no target product was detected (Table 1, entries 2, 4–6). $PdCl_2(PPh_3)_2$ showed 7.4% yield of PDA (Table 1, entries 1). $RhCl(PPh_3)_3$ turned out to be the most active homogeneous catalyst (80% conversion of IPA) but the yield of PDA was less than 20% as well as the low selectivity (Table 1, entries 3). For heterogeneous catalysts, Ru(5%)/C and Pd(5%)/C both gave very low yield of PDA (Table 1, entries 7, 8). Raney-type Ni and Co catalysts provided higher activity and selectivity. For example, the Raney Co gave PDA yield of 49.1% (Table 1, entries 10), while the Raney Ni catalyst exhibited higher activity than Raney Co catalyst, which gave 69.3% conversion and 58.1% yield of PDA (Table 1, entry 9). Therefore, Raney Ni was employed for further study.

The effect of base on the catalytic performance

The catalytic performance can be effectively improved when properly base was introduced into the homogeneous catalytic reaction of reductive amination of alcohol (Roundhill 1992). Once Raney Ni was discovered as the best catalyst in terms of activity and selectivity, the effect of the base was investigated on the activity and selectivity.

Table 2 Amination of isopropanolamine over Raney Ni with various bases

Entry	Base	Con%	Sel%		Yield% (PDA)
			PDA	DMP	
1	$NaOCH_3$	38.2	25.7	18.1	9.8
2	*t*-BuOK	28.5	7.9	7.9	2.3
3	NaOH	22.4	17.9	19.1	4.0
4	KOH	11.6	18.6	8.5	2.2
5	Li_2CO_3	42.9	86.5	5.7	37.1
6	Na_2CO_3	36.6	81.3	7.7	29.8
7	K_2CO_3	55.5	93.7	1.5	52.0
8	$(NH_4)_2CO_3$	3.7	17.1	–	0.6
9	KOAc	59.1	79.1	9.0	46.7

Reaction conditions: isopropanolamine (0.1 mol); ammonia (0.2 mol); Raney Ni (3 wt%); base loading (10 mol%); initial hydrogen pressure 4 MPa; 170 °C; 15 h.

When the bases were added into the reaction system, all activities were decreased. When the strong base such as sodium methoxide, potassium tert-butoxide was added, the selectivity of PDA was also declined as well as the yield (Table 2, entries 1 and 2). The activity decreased greatly and gave the yield of PDA less than 4.0% when hydroxide base was introduced (Table 2, entries 3 and 4). There was no significant change of the selectivity when lithium carbonate or sodium carbonate was added (Table 2 entries 5, 6). When potassium carbonate was added, the selectivity was enhanced, which reached up to 93.7% (Table 2, entry 7). Comparing with KOH, KOAc and $(NH_4)_2CO_3$, it was believed that the improvement of the selectivity was probably due to the synergistic effect of the potassium cation and carbonated anion. The lone pair electrons of the oxygen atom in the base of Table 2 can form the coordinate bond with the unfilled atomic d-orbital of Ni, which changed the electronic properties of Ni and their close neighborhood (Mink and Horváth 1998). Therefore, the activity was declined. It can be induced that different bases poisoned the catalyst with different levels due to the decrease of the activity by addition of base. The different cations also can be weakly absorbed on the Ni atoms which synergistically combined with the effect of the oxygen atom from the base. Consequently, the adsorption of substrates was changed and the selectivity was adjusted. Additionally, the carbonate salts may facilitate isolation of the surface primary amine species, which diminishes the formation of secondary amines. For the $(NH_4)_2CO_3$, the catalyst almost lost the activity. Besides the carbonate anion deactivated the catalyst, the ammonia released by $(NH_4)_2CO_3$ increased the chemisorption of ammonia on the Ni, which decreased the adsorption of the substrates (Du et al. 2006). Therefore, the activity decreased dramatically when $(NH_4)_2CO_3$ was added in the reaction system. Then, Raney Ni/K_2CO_3 was found to be an efficient catalytic system for reductive amination of isopropanolamine to produce PDA.

Structural characteristics of catalysts

Table 3 listed the BET surface area, total pore volume and average pore diameter of various catalysts determined by the BET analysis.

The Ni–Al alloy powder had the lowest BET surface area, total pore volume and the biggest average pore diameter, which was consistent with its nonporous and alloy powered property (Okamoto et al. 1980; Dellannay et al. 1982; Lei et al. 2001). The surface area and pore volume of the spent Raney Ni increased (Freel et al. 1969; Fouilloux et al. 1972), while the pore diameter decreased (Table 3, entry 2 and 3). When the K_2CO_3 was employed, the surface area and pore volume of Raney Ni increased more than that of the pure Ni catalyst, while the pore diameter became smaller (Table 3, entries 3 vs. 4). Addition of K_2CO_3 increased the surface area, pore volume and the amount of small pore of Raney Ni.

Figure 1 presents the XRD patterns of the samples. The peaks of Ni_2Al_3 and $NiAl_3$ were obviously visible for Ni–Al alloy powered (Lei et al. 2001; Robertson and Anderson 1971) and the Ni peaks could be found in all of the Raney Ni catalysts, which implied that all catalysts existed as crystalline phase completely. The XRD peaks at 2θ of 44.4°, 51.7° and 76.1° belonged to [1 1 1], [2 0 0] and [2 2 0] diffraction peaks of Ni^0 separately (Lu et al. 2015; Robertson

Table 3 Surface area, pore volume, average pore diameter, average crystallite size and relative crystallinity of the catalysts

Entry	Cat.	S_{BET} (m^2/g)	*V* (mL/g)	Average pore diameter (Å)	Average crystallite size (Å)[a]	Relative crystallinity (%)[b]
1	Ni–Al	0.9	0.003	142.0	426	–
2	FR	18.2	0.037	73.0	132	100.0
3	AR	60.6	0.102	57.3	114	64.9
4	KAR	78.8	0.152	47.0	145	83.7

[a] Calculated from the peaks at $2\theta = 44.4°$

[b] Calculated from the total areas of peaks at $2\theta = 44.4°$, 51.7° and 76.1°

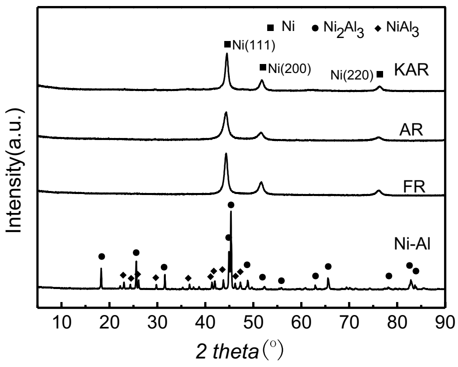


Fig. 1 XRD patterns of samples

and Anderson 1971). FR gave the high, narrow and intense XRD peaks. Peaks of AR were broad and weak, which illustrated that the crystalline of the catalysts have been damaged to some extent. XRD peak height of KAR was higher than that of AR, while the peaks width of KAR was narrower. Table 3 gave the average crystallite dimensions and relative crystallinity (assuming fresh Raney Ni was 100%) of the catalysts which were calculated according to the classical Scherrer relation (Robertson and Anderson 1971). The crystallite size of AR decreased from 132 to 114 Å after reaction and the relative crystallinity went down to 64.9% (Barnard et al. 2011). When K_2CO_3 was added into the reaction, the crystallite size of KAR sample became larger than that of FR and the relative crystallinity remained 83.7%, which indicated that addition of K_2CO_3 had protected the crystalline structure of Raney Ni in the reductive amination of isopropanolamine. In other words, the K_2CO_3 adsorbed on the surface of Ni particles and protected the crystallinity of Ni. These were consistent with the deactivation of the catalyst when K_2CO_3 was added.

Effect of K_2CO_3 on side reaction

It is widely accepted that reductive amination of alcohol with ammonia involved two steps: dehydrogenation and hydrogenation, as shown in Scheme 2.

The main reaction (solid line arrows) started with the dehydrogenation of IPA on Raney Ni to generate carbonyl compound **1** and one molecule of hydrogen (the dehydrogenation process). Then, compound **1** participated in two pathways. One was that compound **1** reacted with ammonia to give an imine **2**, which was then hydrogenated to PDA catalyzed by Raney Ni. Meanwhile, the Raney Ni catalyst was recycled (Scheme 2, left side). The other one was that the compound **1** was self-coupled to compound **3**, which was further hydrogenated to 2,5-dimethylpiperazine (DMP). This was the most important side reaction (Langdon et al. 1962).

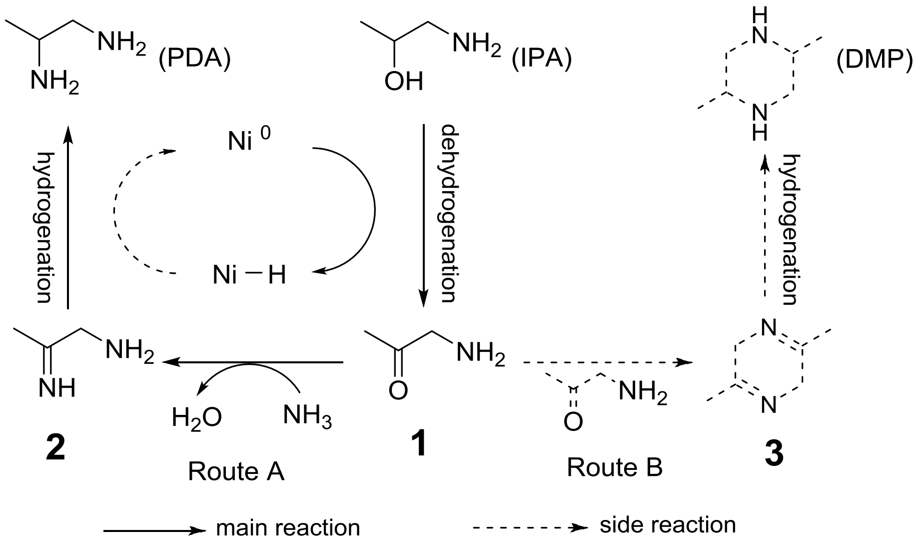
To further investigate the effect of K_2CO_3, the reaction was carried out without ammonia. Without ammonia, the reaction only processed in route B. The results exhibited high selectivities (> 80%) toward DMP with or without K_2CO_3. The conversion of IPA was 81.0% in the absence of K_2CO_3 (Table 4, entry 1), and decreased significantly to 33.6% using K_2CO_3 (Table 4, entries 1 vs. 2). Therefore, introduction of K_2CO_3 inhibited the side reaction to DMP, which contributed to the increase of the selectivity of PDA.

Table 4 Condensation of IPA over Raney Ni without NH_3 when K_2CO_3 was introduced or not

Entry	Base	Loading	Con%	S_{DMP}%
1	–	–	81.0	92.5
2	K_2CO_3	8 mol%	33.6	81.4

Reaction conditions: isopropanolamine (0.15 mol); Raney Ni (3 wt%); initial hydrogen pressure 4 MPa; 170 °C; 10 h

Scheme 2 Catalytic reductive amination of IPA to PDA and the side reaction



Effect of various reaction conditions

We further studied the effect of the amount of Raney Ni and K_2CO_3 loading on the catalytic performance. With 10 mol% K_2CO_3 added, the conversion of IPA increased along with the increase of Raney Ni loading (Table 5, entries 1–3). Moreover, the selectivity of PDA decreased with the increase of the Raney Ni loading, while DMP increased. When the amount of Raney Ni was 3 wt%, the activity decreased with the increasing of the K_2CO_3 loading (Table 5, entries 4–6). In addition, the selectivity of PDA increased, while DMP declined. These indicated that the K_2CO_3 could reduce the activity by poisoning the catalyst. However, the conversion of route B reaction decreased more than route A with the addition of K_2CO_3, the selectivity of PDA increased. Therefore, it could be concluded that the selectivity of PDA was improved with the sacrifice of the activity. When the Raney Ni loading was increased to 5 wt% (Table 5, entries 7 and 8), the changes of activity and selectivity of PDA catered to the above conclusion. The ratio of Raney Ni/K_2CO_3 has accountable effect on the conversion and PDA selectivity.

The effect of hydrogen pressure was studied in the range of 1–5 MPa. As shown in Fig. 2, IPA conversion decreased with the increasing hydrogen pressure; the value decreased from 80.0% at 2.0 MPa to 62.3% at 5.0 MPa. The selectivity of PDA slightly increased and then kept constant. These results demonstrated that the hydrogen pressure was considered to give rise to the gradual decrease in the number of working sites on the surface of catalyst. On the other hand, the reaction pressure reached 10.2 MPa when initial hydrogen pressure was 3.0 MPa, while the pressure was 9.0 MPa as initial hydrogen pressure was set to 2.0 MPa. The high pressure may promote NH_3 adsorption and accelerate the condensation reaction of intermediate **1** with NH_3 to some extent, minimizing dimerization of the intermediate **1** to produce DMP (Fischer et al. 1999a, b, c, d).

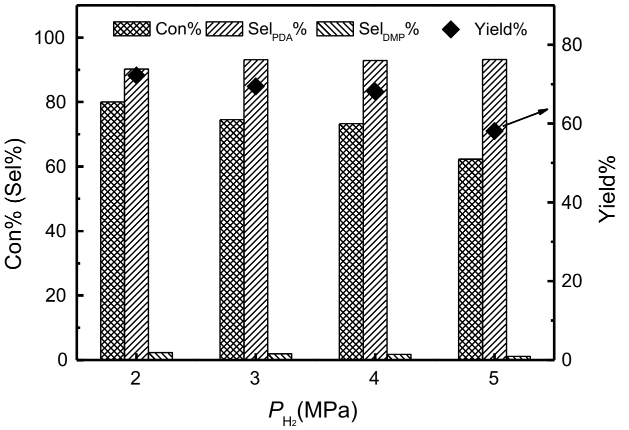


Fig. 2 Effect of initial hydrogen pressure. Reaction conditon: isopropanolamine (0.1 mol); ammonia (0.2 mol); Raney Ni (3 wt%); base loading (10 mol%); 170 °C; 15 h

The molar ratio of NH_3 to isopropanolamine was also investigated. With the increasing molar ratio of NH_3 to isopropanolamine from 1.2 to 4.0, the conversion passed through maxima at 3.0, whereas the selectivity of PDA kept increasing in the studied range (Fig. 3). When the ratio is lower than 4.0, the increase of the concentration of NH_3 accelerated the selectivity of route A, as main reaction, resulting in the increase of conversion. However, too much NH_3 would take more active sites by the chemisorptions. Consequently, the surface adsorption of the organic substrates was decreased, which led to decrease of conversion when the ratio is greater than 3.0.

As illustrated in Fig. 4, the reaction time was optimized. Obviously, the conversion increased with the extending reaction time. However, the selectivity of PDA was slightly decreased, while the selectivity of DMP increased. The yield of PDA could reach 80% when the reaction time prolonged to 30 h.

Table 5 Reductive amination of isopropanolamine on various conditions

Entry	Raney Ni loading (wt%)	K_2CO_3 loading (mol%)	Con%	Sel%		Yield% (PDA)
				PDA	DMP	
1	2	10	32.0	95.5	0.6	30.6
2	3	10	55.5	93.7	1.5	52.0
3	4	10	68.5	89.8	2.4	61.5
4	3	5	65.1	81.5	6.3	53.1
5	3	8	57.5	92.7	1.5	53.3
6	3	15	42.8	94.9	1.2	40.6
7	5	15	73.3	89.9	2.7	65.9
8	5	18	60.8	93.4	1.4	56.8

Reaction conditions: isopropanolamine (0.1 mol); ammonia (0.2 mol); initial hydrogen pressure 4 MPa; 170 °C; 15 h

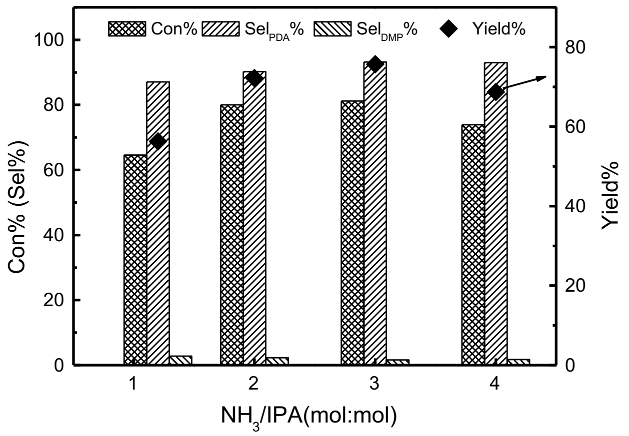


Fig. 3 Effect of mole ratio of NH_3 to isopropanolamine. Reaction conditon: Raney Ni (3 wt%); base loading (10 mol%); initial hydrogen pressure 4 MPa; 170 °C; 15 h

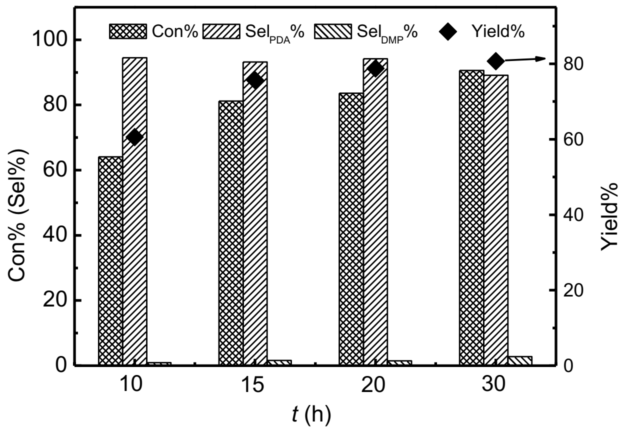


Fig. 4 Effect of reaction time. Reaction condition: isopropanolamine (0.1 mol); ammonia (0.2 mol); Raney Ni (3 wt%); base loading (10 mol%); initial hydrogen pressure 4 MPa; 170 °C; 15 h

Conclusion

In summary, K_2CO_3 was employed as the additive to improve the selectivity of 1,2-propanediamine in the reductive amination of isopropanolamine by ammonia over Raney Ni catalyst. Potassium carbonate can stabilize the crystalline structure of Raney Ni. With the addition of K_2CO_3, it gave different effects on the activity and the selectivity. K_2CO_3 can improve the selectivity of 1,2-propanediamine by preventing the conversion of isopropanolamine to 2,5-dimethylpiperazine with sacrificing of the activity. At the optimized conditions, the yield of 1,2-propanediamine can reached up to 80% with the selectivity of about 90%. This work extended our knowledge of heterogeneous reductive amination of bifunctional alcohol.

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