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Article

Heterogeneous Ru-Based Catalysts for One-Pot Synthesis of Primary Amines from Aldehydes and Ammonia

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Abstract: The direct reductive amination of carbonyl compounds with NH_3 and H_2 is an alternative route to produce primary amines in practical production. The search for efficient and selective catalysts has attracted great interest. In the present work, the reductive amination of heptaldehyde with NH_3 was investigated over a Ru-based catalyst. The product selectivities were found to be related with the supports of Ru. The alumina with spinel structure (γ-Al_2O_3, θ-Al_2O_3)-supported Ru catalysts exhibited selectivity favoring primary amines (94% yield) at 100% heptaldehyde conversion under optimal conditions. Purely basic (MgO, CaO) and relative acidic (Nb_2O_5, SnO_2, MCM-41, HZSM-5) supports showed relatively poor selectivity towards primary amines (0%–53% yield). The reductive amination mechanism was also proposed. The Schiff base *N*-[heptylene]heptyl-1-amine was a key intermediate. Ru/γ-Al_2O_3 was shown to be an excellent hydrogenolysis catalyst to selectively produce primary amine by amination and hydrogenolysis of *N*-[heptylene]heptyl-1-amine.

Keywords: heterogeneous catalyst; Ru; reductive amination; aldehyde; ammonia

1. Introduction

Primary amines are known to be key compounds in chemical industry and biology, which are important building blocks for production of many chemical products, such as polymers, solvents, dyes, surfactants, agrochemicals, and biologically-active compounds [1–4]. Due to their importance, much effort has been devoted to developing various approaches for the synthesis of primary amines, such as the alkylation of halides with NH_3 [5,6], the reduction of nitriles [7,8], hydrocyanation and reduction of alkenes [9], hydroamination of olefins [10,11], amination of alcohols [12–14], and the reductive amination of carbonyl compounds [15–17]. Among the methods, the reductive amination of carbonyl compounds with NH_3 was the most attractive and practical way of producing primary amines both in industry and academic laboratories. The overall transformation is highly atom-efficient and economic. However, one-pot amination of carbonyl compounds with NH_3 generally suffers from a main issue that the chemoselectivity is relatively poor, as the initially-generated amines are more nucleophilic than ammonia itself, thus often resulting in a mixture of products of primary, secondary, and tertiary amines [18]. Thus, the highly-selective synthesis of primary amines remains full of challenges.

In attempts to achieve high yield of aliphatic primary amines, much work has been performed in the last decades. Since the first catalyzed amination of aldehydes or ketones using NH_3 and H_2 with Ni catalyst was reported by Mignonac in 1919 [19], both homogeneous and heterogeneous catalysts were used for the direct reductive amination of carbonyl compounds [20–30]. For example, the reductive amination of aliphatic and aromatic ketones catalyzed by homogeneous Ir and Rh complexes was presented in the patent literature [20], but the selectivity of a primary amine was poor and the reaction conditions were strictly rigorous. Beller *et al.* reported the first example of a homogeneous Rh catalyst to catalyze reductive amination of aldehydes with NH_3 to afford primary amines. Although high selectivity and yield towards aromatic primary amines was achieved, high pressures and temperatures were required (135 °C, 65 bar H_2). Moreover, the yields of the aliphatic primary amines from aliphatic aldehydes were still poor under similar reaction condition [21]. Recently, homogeneous methods were reported to prepare primary amines from ketones with reductants such as ammonium formate [22,23], silane [24,25], $NaBH_4$ [26], the Hantzsch ester [27], $NaBH_3CN$ [28], nBu_3SnH [29], and $Zn(BH_4)_2$ [30] instead of hydrogen. Compared to these expensive and environmentally-problematic reducing agents, H_2 was a cleaner and more economic reducing agent in practical production.

For the practical application, the homogeneous catalytic system had the problems in the catalyst recovery and reuse. Heterogeneous catalysts could be separated easily after the reaction by simple filtration, which are more ideal for large-scale application. Up to now, most of the heterogeneous catalysts for the amination of carbonyl compounds with NH_3 and H_2 were reported in patent literatures, such as Ni, Co, and noble metal-based solid catalysts [31]. There were only a few papers about the reductive amination of aliphatic primary aldehydes or ketone with solid catalyst and seldom clarify its process [32–34]. For instance, Raney Ni was commonly applied to reductive amination of aldehydes with ammonia in the early literature, but it had several disadvantages including the requirement of high H_2 pressure (0.2–12.5 MPa) and low activity and selectivity of the final products [32]. Bodis and co-workers used carbon supported group VIII noble metal (Pt, Pd, Rh, and Ru) as catalysts for the reductive amination of butyraldehyde with NH_3. It was found that Rh and Ru catalysts were active and selective in the production of primary amine under 50 bar H_2 pressure, while Pt and Pd catalysts favored for the secondary amine formation [33]. MgO/Al_2O_3 supported Ru was applied to reductive amination of 2-butyl-2-ethyl-4-cyan-butyraldehyde [34]. The moderate yield of diamine was obtained, but high pressures and temperatures were also required. Thus, an environmentally-sustainable and cost effective process for the production of aliphatic primary amines by selective reductive amination of aliphatic aldehydes with NH_3 is of great fundamental, as well as practical, interest.

The Ru-based catalysts are the most active catalysts for the reductive amination of carbonyl compounds to the corresponding amines. However, few reports about the comparison study on the different types of catalyst supports were found. The catalytic amination process was also seldom to be clarified. In this work, we reported that supported Ru nanoparticles catalyst, synthesized from various cheap metal oxides as the supports, acted as effective heterogeneous catalysts for the selective synthesis of aliphatic primary amines directly from aliphatic aldehydes, NH_3 and H_2 under relatively mild conditions. The choice of a suitable support was found to play an important role in the determining the catalytic selectivity of Ru catalyst. The effects of reaction solvent and reaction temperature were discussed in detail. The reaction mechanism of reductive amination of aldehyde with NH_3 was also proposed.

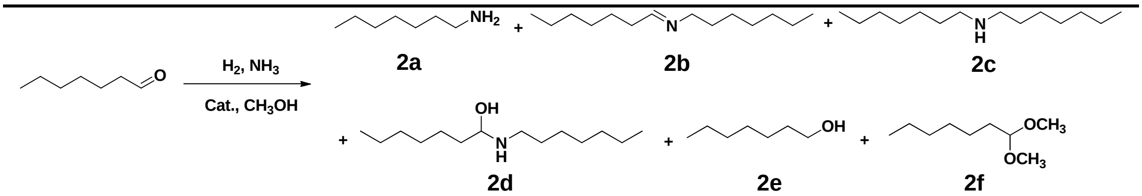
2. Results and Discussion

2.1. Influence of Support on the Catalytic Performance

In searching for an active catalyst for reductive amination of aldehydes, Ru was supported on various support materials (CaO, MgO, ZrO_2, CeO_2, Nb_2O_5, SnO_2, HZSM-5, MCM-41, α-Al_2O_3, θ-Al_2O_3, γ-Al_2O_3) by impregnation methods, followed by H_2 reduction at 500 °C. Reductive amination of heptaldehyde to 1-heptylamine **2a** with NH_3 and H_2 was chosen as a model reaction. The catalytic reactions were performed at 80 °C with NH_3 (0.4 MPa, 12 mmol) and H_2 (3 MPa) in the presence of Ru catalysts (5 wt. %). The results were shown in Table 1. When alumina with three crystal phases was used as the catalytic supports of Ru (Table 1, entries 1–3), the products of reductive amination of heptaldehyde were mainly primary amines **2a**. The alumina with spinel structure (γ-Al_2O_3, θ-Al_2O_3) both presented high catalytic activity with 100% heptaldehyde conversion and primary amine **2a** yields of 92%–94%, and the reaction gave less than 1% Schiff base *N*-[heptylene]heptyl-1-amine [$CH_3(CH_2)_5CH{=}N{-}(CH_2)_6CH_3$] **2b** as a byproduct. Alumina with a corundum structure (α-Al_2O_3) gave less target amine **2a** with the yield of 66% and more **2b** was observed (23%). In order to investigate the support effects on the catalytic performance of Ru-based catalysts, purely basic (CaO, MgO), amphoteric (ZrO_2, CeO_2, γ-Al_2O_3), relative acidic (Nb_2O_5, SnO_2, MCM-41, HZSM-5) supports were chosen in terms of the classifications of acid-base character of metal oxides [35–37]. Amphoteric supports (Table 1, entries 1, 6 and 7) exhibited high selectivity toward **2a** with high yield (70%–94%). Very little byproducts, such as **2b** (<1%), diheptylamine [$CH_3(CH_2)_6{-}NH{-}(CH_2)_6CH_3$] **2c** (0.5%–2.2%), 1-(heptylamino)heptan-1-ol [$CH_3(CH_2)_5CH(OH){-}N{-}(CH_2)_6CH_3$] **2d** (0.8%–1.1%), and 1-heptanol **2e** (<0.5%) were detected. When Ru/CeO_2 was used as the catalyst, additional 1,1-dimethoxyheptane **2f** was observed as a byproduct with

15% yield, formed by acetalization of heptaldehyde with methanol. Purely basic supports (Table 1, entries 4 and 5) afforded temperate **2a** yields of 5%–53%, while high yield of **2b** (12%–67%) was obtained. Only very small amounts of other byproducts were formed with purely basic supports. Relatively acidic supports (Table 1, entries 8–11) showed poor selectivity toward **2a** (0%–18% yield). Relative high yield of **2b** (17%–77%), and a little **2d** (0.9%–2.9% yield) or **2c** (<0.5% yield), were detected. The results indicated that acidic supports was not effective on the further transformation of Schiff base **2b** by hydrogenation or hydrogenolysis. In addition, hydrogenation of heptaldehyde to **2e** was more easily to take place on acidic supports. Particularly, the yield of 1-heptanol (7%–20%) could be found with Ru/SnO_2 and Ru/ZSM-5 catalysts. Thus, the selectivity of primary amine is closely related with the supports, and the alumina with spinel structure (γ-Al_2O_3, θ-Al_2O_3) was the most active supports.

Table 1. Amination of heptaldehyde over various catalysts [a].



Entry	Catalysts	Con. (%)	Yield (%) [b]					
			2a	2b	2c	2d	2e	2f
1	Ru/γ-Al_2O_3	>99	94	0.1	0.5	0.8	0.2	-
2	Ru/θ-Al_2O_3	>99	92	1.0	0.8	0.8	0.5	-
3	Ru/α-Al_2O_3	>99	66	23	0.6	0.9	0.2	-
4	Ru/CaO	>99	5	67	<0.1	1.1	0.2	-
5	Ru/MgO	>99	53	12	0.3	1.1	0.3	-
6	Ru/ZrO_2	>99	90	1.0	2.2	0.9	<0.1	-
7	Ru/CeO_2	>99	70	0.3	0.2	1.1	0.1	15
8	Ru/Nb_2O_5	>99	18	28	0.3	1	0.3	-
9	Ru/SnO_2	>99	0	17	0.5	2.9	20	-
10	Ru/ZSM-5	>99	9	57	0.1	1.6	7	-
11	Ru/MCM-41	>99	9	77	<0.1	0.9	0.4	-

[a] Reaction conditions: heptaldehyde (6.6 mmol), catalyst (50 mg), *n*-dodecane (0.58 mmol), 0.4 MPa NH_3, 3 MPa H_2, MeOH (20 mL), 80 °C, 2 h; [b] Yields were determined by GC based on aldehyde.

The catalysts were characterized by XRD, BET, SEM, and elemental mapping images, and HRTEM. The results of nitrogen sorption and activity were summarized in Table S1. It was known that heterogeneous catalysis is a surface-based process and, thus, a large specific surface area can offer more adsorption sites and catalytic reaction centers. Thus, surface areas of supports might have an influence on their catalytic activity. However, there was no evidence that there was a close relationship between catalytic selectivity toward primary amine and surface area. As shown in Table S1, compared with Ru/α-Al_2O_3, the catalysts with relatively acidic supports (Ru/Nb_2O_5, Ru/SnO_2, Ru/ZSM-5, Ru/MCM-41) and purely basic supports (Ru/MgO) had higher surface area than that of Ru/α-Al_2O_3 (15 $m^2 \cdot g^{-1}$), but exhibited much lower selectivity towards **2a**. Particularly for ZSM-5 and MCM-41 supports, which both had large surface area (295 $m^2 \cdot g^{-1}$ for Ru/ZSM-5, 647 $m^2 \cdot g^{-1}$ for Ru/MCM-41), the Ru-based catalysts showed very poor selectivity towards **2a** (9% yield).

XRD patterns of Ru-based catalysts were also shown in Figure S1. It can be seen that except for Ru/ZSM-5 and Ru/MCM-41, there is no observable peak corresponding to crystalline Ru species, such as Ru or RuO_2. The absence of Ru species peaks in the catalysts implies that Ru might be highly dispersed on the supports (Al_2O_3, ZrO_2, CeO_2, CaO, MgO, Nb_2O_5, SnO_2). The results were further supported by the result of elemental mapping images of Ru/γ-Al_2O_3 (see Figure S2). HRTEM analysis showed that Ru/γ-Al_2O_3, Ru/MgO, and Ru/Nb_2O_5 exhibited small Ru particles with average particle sizes of 3.5 nm, 4.0 nm, and 4.2 nm, respectively (see Figure S3). These indicated that the surface area of supports, dispersion of metal, and crystal size were not the key factors for the catalytic selectivity of primary amines, other factors (e.g., acid-base character) might favorably influence the catalytic performance of Ru-based catalysts.

2.2. Effect of Various Solvents on the Reaction

The effect of solvents was studied with 5% Ru/γ-Al_2O_3 as the catalyst. The results were listed in Table 2. Notably, the choice of solvents has an obvious influence on the activity of the catalyst. Among these solvents examined, methanol was found to be the best solvent for reductive amination of heptaldehyde, giving high **2a** yield of 94% (Table 2, entry 1). The reaction in cyclohexane, THF, and toluene obtained relatively moderate yield of **2a** (Table 2, entries 2–4, 72%–84%). When water was used as the solvent, the **2a** yield sharply decreased to 32% (Table 2, entry 7). Similarly, when the reaction was conducted in 1,4-dioxane and methyl *tert*-butyl ether (MTBE), the desired **2a** yields of 39% and 34% were obtained, respectively (Table 2, entries 5 and 6). Thus, Ru/γ-Al_2O_3 and methanol were the suitable catalyst and solvent for the reductive amination of heptaldehyde. Then, all reactions were performed in methanol with Ru/γ-Al_2O_3 as the catalyst.

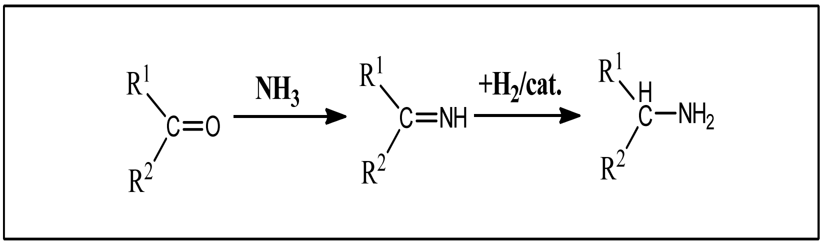
Table 2. Amination of heptaldehyde in various solvents [a].

Entry	Solvent	Yield (%) [b]
1	methanol	94
2	toluene	84
3	THF	84
4	cyclohexane	72
5	1,4-dioxane	39
6	MTBE	34
7	H_2O	32

[a] Reaction conditions: heptaldehyde (6.6 mmol), catalyst (50 mg), *n*-dodecane (0.58 mmol), 0.4 MPa NH_3, 3 MPa H_2, solvent (20 mL), 80 °C, 2 h; [b] Yields were determined by GC based on aldehyde.

2.3. Reaction Pathways

The reductive amination of carbonyl compounds generally proceeds through the formation of imines via the reaction of aldehydes with NH_3 and subsequent hydrogenation (Scheme 1). To get more information concerning the reaction process of reductive amination of aldehydes with NH_3, the effect of reaction temperatures on the product selectivity with Ru/γ-Al_2O_3 catalyst was investigated. The results were shown in Figure 1. As expected, with increase in the reaction temperature from 40 °C to 80 °C, the yield of **2a** improved from 7% to 94%. At low temperature (40 °C), the yield of **2a** was only 7%. The yield of **2a** increased to 53% when the temperature enhanced to 60 °C. A highest yield of **2a** could be obtained at 80 °C. Raising the reaction temperature to 100 °C did not further increase the selectivity of the primary amine with **2a** yield of 93%. On the other hand, low temperature brought negative effects on the further transformation of Schiff base **2b** by hydrogenation or hydrogenolysis. The yield of **2b** was about 77% at 40 °C, which declined to 0.1% when the reaction temperature increased from 40 °C to 80 °C. The similar Schiff base intermediate was also found in the previous studies [20,33,38]. A closer look was taken to analyze the products after the reaction at 80 °C. Apart from major product **2a**, very little **2b** (<1%), **2d** (<1%), **2c** (<0.1%), **2e** (<0.5%) were detected in the reaction mixture with GC/MS analysis. According to the Scheme 1, the expected intermediate heptyl-1-imine [$CH_3(CH_2)_5CH=NH$] was not observed in our experiments probably for its poor stability. The main equilibria for heptaldehyde are shown in Scheme 2.



Scheme 1. Main reactions of the reductive amination of carbonyl compounds with NH_3 and H_2.

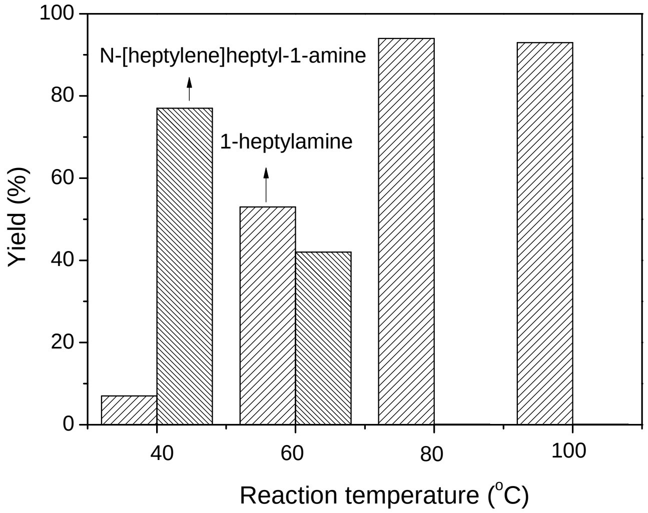
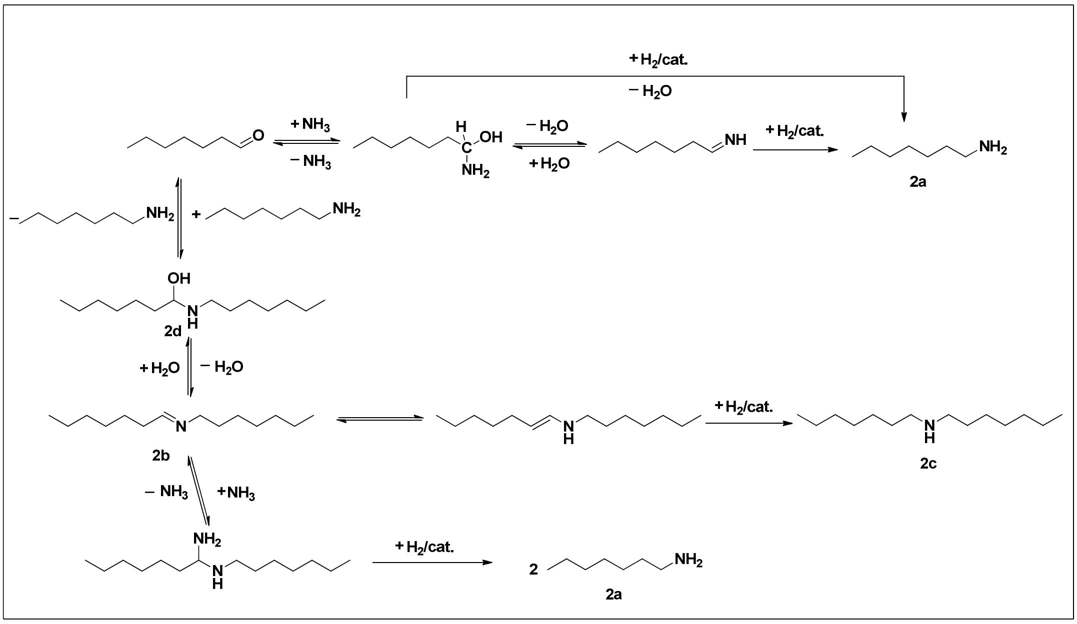


Figure 1. Reductive amination of heptaldehyde at different reaction temperature.

Some control experiments were carried out with Ru-γ-Al_2O_3 as the catalyst to study the mechanism of reductive amination of aldehydes with ammonia. First, when 3 MPa N_2 instead of H_2 was used, no primary amine was formed in the reaction, which suggested that H_2 was indispensable for the amination of heptaldehyde. We also carried out the reaction at 40 °C for 2 h in 3 MPa H_2 and 0.4 MPa NH_3, which was then pressurized with H_2 to 3 MPa again and conducted at 80 °C for another 2 h. Surprisingly, the Schiff base **2b** formed at 40 °C was mostly converted to primary amine **2a** at 80 °C. Few **2c** was detected in the products. These results suggested that **2b** was the key intermediate. The proposed reaction pathway is depicted in Scheme 2.



Scheme 2. Reaction pathways for the reductive amination of heptaldehyde over Ru/γ-Al_2O_3 catalyst.

The reductive amination of heptaldehyde to **2a** proceeds in several consecutive steps. In the first stage, the amination of heptaldehyde gives initial intermediate heptyl-1-imine via the reaction of heptaldehyde with NH_3, which is then reduced to the **2a** by hydrogenation. In the second, the initially-formed **2a** would further react with heptaldehyde immediately to form the Schiff base **2b** intermediate. The imine **2b** may directly be reduced to the **2c** by hydrogenation or added with NH_3 to form corresponding geminal diamine and subsequent hydrogenolysis to produce **2a**. The selectivity of **2a** and **2c** was governed by the relative rate of hydrogenolysis and hydrogenation. If the rate of hydrogenolysis is faster than that of hydrogenation, the hydrogenolysis towards primary amine would be the dominant pathway. The results of our experiments with Ru/γ-Al_2O_3 conducted at different temperatures (40–80 °C) showed that Schiff base **2b** can be easily produced at the low temperature of 40 °C. However, only small amount of the Schiff base was further transformed to **2a** by hydrogenolysis at low temperature, which needed a high activation energy [33]. High temperatures would accelerate hydrogenolysis rates and benefit for the production of more primary amine. The yield of **2a** is much higher at 80 °C (94%) than at 40 °C (7%). The result suggested that the adsorption-desorption equilibrium of the Schiff base **2b** was shifted much more to benefit hydrogenolysis to form primary amine at high temperature. Thus, amination and hydrogenolysis of the Schiff base towards a primary amine was the dominant pathway at high temperature. These results were also in agreement with the literature [33]. The results of our experiments also showed that only very little **2c** was formed in the catalysis system when the Ru/γ-Al_2O_3 was used as the catalyst, which may be due to the weak chemisorption of **2b** intermediate on the Ru/γ-Al_2O_3 surface, resulting in a low rate of hydrogenation to **2c**. Therefore, Ru/γ-Al_2O_3 was proved to be good hydrogenolysis catalyst, which is preferential to produce a primary amine.

To elucidate the reaction mechanism proposed, a kinetic study following the formation of key products with time was also carried out. As shown in Figure 2, at the beginning of the reaction, heptaldehyde was quickly converted to **2b** imines. When the reaction was reacted for 5 min, more than 95% conversion of heptaldehyde was completed; the **2b** yield of 55.5% and less than 0.5% **2c** were obtained. It was worth to note that no desired **2a** was detected in the reaction mixture in the first stage. This may be due to the more nucleophilic of **2a** than ammonia, resulting in the immediate reaction of the initially-formed **2a** with the remaining heptaldehyde to formed **2b** imines. When the reaction time proceeded for 15 min, no heptaldehyde remained and **2a** started to accumulate. At the same time, **2b** imines in the reaction mixture reached the highest concentration. As the reaction continues, the concentration of **2b** imines decreased gradually, while the concentration of **2a** increased rapidly. After reaction for 120 min, most of **2b** intermediate was converted to **2a** with 94% yield, and only trace amounts of **2b** imines was remained. During the process, **2c** were detected in a very low concentration. The results indicated that **2b** intermediate was mainly reacted with NH_3 to form geminal diamine and subsequent hydrogenolysis to produce **2a**. Hydrogenation of **2b** intermediate to **2c** was the minor pathway. The results were in good agreement with the mechanism mentioned above, which confirmed that Ru/γ-Al_2O_3 was a good hydrogenolysis catalyst.

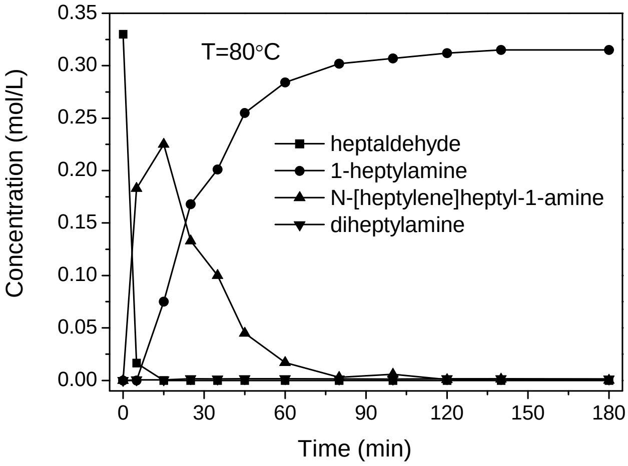
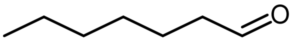
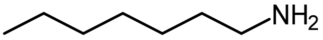
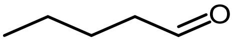
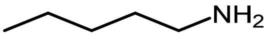
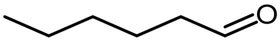
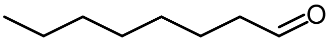
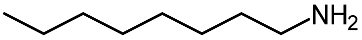
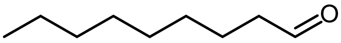
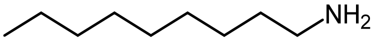
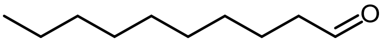
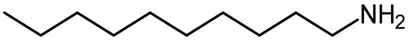
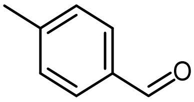
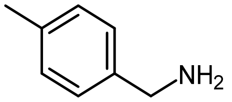
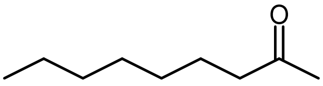
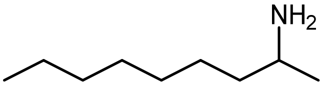
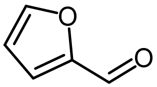
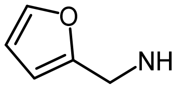


Figure 2. Concentration of key products during the reductive amination of heptaldehyde over Ru/γ-Al_2O_3.

2.4. Scope of Reactions

Under the optimal conditions for the synthesis of **2a**, a series of aldehydes (aliphatic and aromatic aldehydes) was aminated with Ru/γ-Al_2O_3 catalyst in the presence of NH_3 in order to study the scope of the present catalytic system. The results were exhibited in Table 3. Linear aliphatic aldehydes (C5–C10, Table 3, entries 1–6) and aromatic aldehyde (4-methylbenzaldehyde, Table 3, entry 7) were selectively transformed to the corresponding primary amines with excellent yields (89%–97%), while only small amounts of primary alcohols and imines by-products were detected by the GC/MS analysis. When 2-octantone was used, the corresponding 2-octylamine yield of 97% was obtained (Table 3, entry 8). Furfurylamine yield of 75% was obtained (Table 3, entry 9), when furan-2-carbaldehyde was used.

Table 3. Reductive amination of various aldehydes and ketones by Ru/γ-Al_2O_3 catalyst [a].

Entry	Substrate	Product	Yield (%) [b]
1			94
2			92
3			89
4			92
5			95
6			95
7 [c]			97
8 [d]			97
9			75

[a] Reaction conditions: heptaldehyde (6.6 mmol), catalyst (50 mg), *n*-dodecane (0.58 mmol), 0.4 MPa NH_3, 3 MPa H_2, MeOH (20 mL), 80 °C, 2 h; [b] Yields were determined by GC based on aldehyde or ketone; [c] $T = 150$ °C; [d] $T = 150$ °C, $t = 10$ h.

2.5. Recycle Study of Catalyst

From the view point of green chemistry, it is important to examine the possibility of recovery and reusability of Ru/γ-Al_2O_3 catalyst. The capability of recycling Ru/γ-Al_2O_3 catalysts was investigated by the reductive amination of heptaldehyde with NH_3 and H_2 at 80 °C for 2 h. After completion of the benchmark reaction, the catalyst was removed from the reaction mixture by filtration, washed with ethanol for several times, dried at 50 °C for 12 h, and then reused directly without other treatment. The Ru-based catalyst could be reused four times without a significant drop in **2a** yield and catalytic activity (see Figure S4). 93% of **2a** yield in the initial experiment with fresh Ru/γ-Al_2O_3 remained in the fourth run, probably caused by the weight loss of catalysts during the recovery process. The results demonstrated the sufficient stability of Ru/γ-Al_2O_3 catalyst in the reductive amination of heptaldehyde to primary amine **2a**.

3. Experimental Section

3.1. Catalyst Materials and Preparation

Commercially available inorganic compounds were used without further purification. MCM-41 and HZSM-5 zeolite with a SiO_2/Al_2O_3 ratio of 38 were supplied by Nankai University (Tianjin, China). ZrO_2 was prepared by dropping a 5 M ammonia solution into a 0.4 M aqueous solution of $ZrOCl_2 \cdot 8H_2O$ with vigorous stirring. Then, the precipitate was filtered, washed with distilled water several times, dried, and then sintered at 500 °C for 3 h. CaO, MgO, and Nb_2O_5 were synthesized by sintering of their hydroxides at 500 °C for 3 h. Ru/γ-Al_2O_3 (Ru loading = 5 wt. %) was synthesized by the impregnation method. In a typical synthesis, $RuCl_3 \cdot nH_2O$ dissolved in deionized water was mixed with γ-Al_2O_3. The mixture was dried at 110 °C for 12 h and, subsequently, reduced in hydrogen gas at 500 °C for 3 h. Ru loaded on various supports (CaO, MgO, Nb_2O_5, ZrO_2, CeO_2, SnO_2, ZSM-5, MCM-41, α-Al_2O_3, θ-Al_2O_3) were also prepared by the impregnation method under the same conditions (Ru loading = 5 wt. %).

3.2. Characterization

XRD patterns were taken by a Bruker D8 Advanced X-ray diffractometer using CuKa radiation (λ = 1.5147 Å, Karlsruhe, Germany). High resolution TEM images were collected by a field emission Tecnai G2F20 electron microscope (FEI, Hillsboro, OR, USA). The morphologies were measured by a field emission Hitachi S-4800 scanning electron microscope (Tokyo, Japan). N_2 adsorption-desorption measurements were carried out at 77 K using a micromeritics ASAP 2020 sorptometer (Micromeritics, Norcross, GA, USA). The catalysts were heated at 423 K for 6 h prior to analysis. The surface area of the catalysts was calculated using the Brunauer-Emmett-Teller (BET) equation based on the adsorption data at relative pressure P/P_0 values between 0.01–0.05.

3.3. General Procedure of Catalytic Reactions

The activity of the catalysts was evaluated by reductive amination of aldehydes with NH_3 and H_2. Unless otherwise stated, all reactions were performed at 80 °C for 2 h. In a typical reaction, heptaldehyde (6.6 mmol), Ru/γ-Al_2O_3 (50 mg, containing 0.025 mmol Ru), *n*-dodecane (0.58 mmol), and CH_3OH (20 mL) were injected to a 100 mL stainless steel autoclave. The autoclave was closed, flushed with H_2 several times to remove air, and charged with 0.4 MPa NH_3 and 3 MPa H_2 at room temperature. The autoclave was then carried out at the desired temperature under stirring for 2 h. After the reaction, the reaction mixture was cooled to room temperature and then depressurized. Conversion and yields of products were detected by GC (Shimadzu GC-2010, Kyoto, Japan) with Agilent capillary column DB-5 (Kyoto, Japan) and *n*-dodecane was used as an internal standard. The products were also identified by GC/MS (Shimadzu GCMS-QP2010) equipped with Agilent capillary column DB-5MS.

4. Conclusions

In summary, we have shown that the alumina with spinel structure (γ-Al_2O_3, θ-Al_2O_3)-supported Ru samples were active and selective catalysts for direct reductive amination of aldehydes with NH_3 and H_2 to corresponding primary amines. Up to 94% yield for 1-heptylamine could be obtained for the reductive amination of heptaldehyde using Ru/γ-Al_2O_3 catalyst. High selectivity of primary amines were also achieved in the case of the linear aliphatic aldehydes (C5–C10) and aromatic aldehydes. It was found that the supports have an important influence on the product selectivity of Ru catalyst. Compared with purely basic (MgO, CaO) and relative acidic (Nb_2O_5, SnO_2, MCM-41, HZSM-5) supports, amphoteric supports (θ-Al_2O_3, γ-Al_2O_3, ZrO_2, CeO_2) were more favorable for the primary amine formation. A reductive amination mechanism was also proposed. The Schiff base **2b** acted as a key intermediate for the reductive amination of heptaldehyde. Ru-based catalysts were a good hydrogenolysis catalyst. In this reaction, the addition of Schiff base **2b** with NH_3 to form corresponding geminal diamine and subsequent hydrogenolysis to produce **2a** was the dominate pathway.

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Author Contributions

X.C. designed the experiment; B.D. performed the experiments; B.D. and X.G. analyzed the data, discussed with B.Z., J.G., Y.Q., S.H., X.M.; B.D. and X.C. co-wrote the manuscript. All authors reviewed the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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