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Nickel Catalyzed Conversion of Cyclohexanol into Cyclohexylamine in Water and Low Boiling Point Solvents

Yunfei Qi [1,2], Haiyun Yu [1,*], Quan Cao [2], Bo Dong [2], Xindong Mu [2] and Aiqing Mao [1]

[1] Key Laboratory of materials Science and Processing of Anhui Province, School of Materials Science and Engineering, Anhui University of Technology, Ma'anshan 243002, Anhui, China; yunfei_q0218@foxmail.com (Y.Q.); maoaiqin@ahut.edu.cn (A.M.)

[2] Key Laboratory of Bio-Based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China; caoquan@qibebt.ac.cn (Q.C.); xiguxilan@gmail.com (B.D.); muxd@qibebt.ac.cn (X.M.)

* Correspondence: yuhyahut@foxmail.com; Tel.: +86-532-8066-2725; Fax: +86-532-8066-2724

Abstract: Nickel is found to demonstrate high performance in the amination of cyclohexanol into cyclohexylamine in water and two solvents with low boiling points: tetrahydrofuran and cyclohexane. Three catalysts, Raney Ni, Ni/Al$_2$O$_3$ and Ni/C, were investigated and it is found that the base, hydrogen, the solvents and the support will affect the activity of the catalyst. In water, all the three catalysts achieved over 85% conversion and 90% cyclohexylamine selectivity in the presence of base and hydrogen at a high temperature. In tetrahydrofuran and cyclohexane, Ni/Al$_2$O$_3$ exhibits better activity than Ni/C under optimal conditions. Ni/C was stable during recycling in aqueous ammonia, while Ni/Al$_2$O$_3$ was not due to the formation of AlO(OH).

1. Introduction

Amines find wide application in polymers, dyes, surfactants, pharmaceuticals, and biologically active compounds [1–10]. The amine is usually produced through direct amination of alcohol with ammonia. As shown in Scheme 1, this process includes dehydrogenation of alcohol to carbonyl compounds, amination of carbonyl compounds to imine, and hydrogenation of imine [11] to amine to produce primary, secondary and tertiary amine. Among the three, primary amine is the most useful intermediate for synthesizing value-added derivatives [12]. However, it is subject to subsequent amination due to its higher activity than ammonia and thus produces secondary and tertiary amine [5]. By now, great efforts have been made to find and develop a catalyst system to convert alcohol into primary amine. Homogeneous catalysts, such as Ru complexes, demonstrate high performance in converting secondary alcohol into primary amine [1–3]. However, these catalysts are either costly or difficult in recycling. Recently, work by Shimizu *et al.* showed that heterogeneous supported nickel catalysts, especially Ni/Al$_2$O$_3$, is a choice catalyst for amination of alcohol into a primary amine with more than 80% amine yield [13]. In their work, the toxic *o*-xylene ais high in boiling point (144 °C) and consumes more energy during the separation. Moreover, the solubility of alcohol in *o*-xylene is limited due to the presence of hydroxyl group. Therefore, much work needs to be done to find and use non-toxic or low boiling solvents.
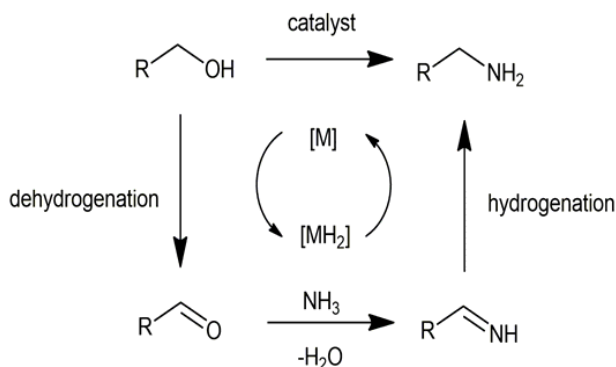
**Scheme 1.** The mechanism for amination of alcohol.

In the present work, aqueous ammonia, tetrahydrofuran, and cyclohexane are employed as solvents on the amination of cyclohexanol into cyclohexylamine using Raney Ni, Ni/γ-Al$_2$O$_3$ and Ni/C catalysts. Water is non-toxic and the other two solvents are low in boiling points.

2. Results and Discussion

2.1. Raney Ni in Aqueous Ammonia

The reactivity of cyclohexanol was first investigated in aqueous ammonia using Raney Ni catalyst, which has already been commercialized. It is theoretically difficult to convert cyclohexanol in aqueous ammonia, because it is reversible to produce imine through dehydration of carbonyl with NH$_3$ [14]. The existence of a large amount of water will do no good to the formation of imine. It can be seen from Table 1 that Raney Ni itself only achieved 44% cyclohexanol conversion (Entry 1). After NaOH is added, it dramatically enhanced its catalytic activity and obtained more than 90% conversion, indicating the base is helpful for the reaction. This result is consistent with the literature that base can promote the amination of alcohol [15]. However, it can be seen from Table 1 Entries 2 to 6 that it will not affect the conversion even further increasing the NaOH amount after 0.3 g NaOH is added. When the Raney Ni catalysts in Table 1, Entry 6, were recycled for the second time, only 57% cyclohexanol conversion was achieved (Entry 7). Raney Ni before and after the reaction (Entry 6) was observed by X-ray diffraction (XRD) with the results displayed in Figure 1. According to Scherrer equation in Equation (1), Raney Ni before and after reaction was estimated to be 7 nm and 15 nm in crystallite size. The reason why the catalyst deactivates may be ascribed to the growth of the crystallite size.

$$D = K\lambda/B\cos\theta \tag{1}$$
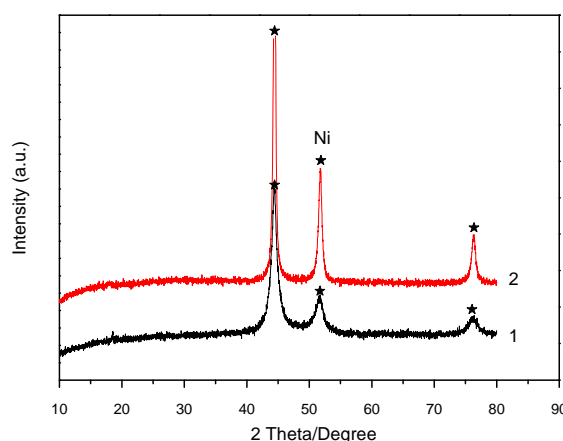
Figure 1. X-ray diffraction (XRD) patterns of (**1**) fresh Raney Ni; (**2**) Raney Ni used in Table 1, Entry 6.

Table 1. Conversion of cyclohexanol into cyclohexylamine over Raney Ni in aqueous ammonia with different amount of NaOH [a].

Entry	NaOH/g	Conversion/%	Yield/%
1	0	44	41
2	0.3	93	79
3	0.4	95	78
4	0.5	95	84
5	0.6	96	90
6	0.7	96	89
7 [b]	0.7	57	52

[a] Reaction conditions: Raney Ni 6 g; aqueous ammonia 28 g; cyclohexanol 1 g; 160 °C; 17 h; [b] Raney Ni (Entry 6) was recycled for the second time.

Table 2 shows that both the conversion and yield increase as the reaction time extends, while the selectivity decreases over time. Eight hours is enough for the reaction to achieve 94% conversion. It will not significantly improve the conversion even if the reaction time is prolonged.

Table 2. Conversion of cyclohexanol into cyclohexylamine over Raney Ni with different time.

Entry	Time/h	Conversion/%	Yield/%	Selectivity/%
1	4	71	68	95
2	6	83	76	91
3	8	94	81	86
4	12	95	82	86
5	17	96	82	85
6	24	98	83	84
7	30	98	83	84

Reaction conditions: Raney Ni 6 g; aqueous ammonia 28 g; cyclohexanol 1 g; 160 °C; 0.5 g NaOH.

The effect of cyclohexanol concentration on the reaction was displayed in Table 3, indicating that higher concentration leads to lower selectivity. Because theoretically the cyclohexylamine produced can further react with cyclohexanol to produce dicyclohexyl amine and even tricyclic hexylamine [6]. However, only dicyclohexyl amine was produced while tricyclic hexylamine was not detected in this work. Further investigation demonstrated that dicyclohexyl amine could not be converted into cyclohexylamine under the reaction conditions in Table 3.

Table 3. Conversion of cyclohexanol into cyclohexylamine over Raney Ni with different amount of cyclohexanol.

Entry	Alcohol/g	Conversion/%	Yield/%	Selectivity/%
1	1	96	88	93
2	1.5	93	86	92
3	2	89	76	85
4	2.5	93	72	77

Reaction conditions: 6 g Raney Ni, 28 g aqueous ammonia, 0.5 g NaOH, 160 °C, 17 h.

2.2. Ni/Al_2O_3 and Ni/C Systems

Supported catalyst is generally more popular due to its less use of active metal. Moreover, the support is found to exert great influence to the activity of the catalyst [13,16,17]. Two supports Al_2O_3 and active carbon were investigated in aqueous ammonia with the results shown in Table 4. From Entries 1 to 3, as the temperature was raised form 160 °C to 200 °C, it resulted in an increase of conversion from 51% to 71%. The conversion increases with the reaction time prolonging and then

reaches a plateau for both Ni/Al$_2$O$_3$ and Ni/C catalysts (Entries 4 to 6 and 10 to 12). Through the comparison between Entry 3 and 7, Entry 8 and 9, the conversion increased from 48% to 71% and 37% to 87%, respectively, indicating that NaOH can improve the catalytic activity of both Ni/Al$_2$O$_3$ and Ni/C. In the amination reaction, hydrogen also participated in the dehydrogenation and the hydrogenation process. The effect of hydrogen is also tested, and as shown in Table 4 Entries 3, 6, 9 and 10 for Ni/Al$_2$O$_3$ and Ni/C, the conversion increases from 71% to 87% and 87% to 92%, respectively, suggesting that hydrogen has positive, though slight effect on the reaction for both Ni/Al$_2$O$_3$ and Ni/C. At the same temperature of 160 °C (Entries 1 and 9), Ni/C exhibits better activity than Ni/Al$_2$O$_3$, indicating the support may affect the activity of nickel [13]. From Figure 2, Ni in the fresh Ni/Al$_2$O$_3$ and Ni/C catalysts were 14 nm and 6 nm, respectively, in crystallite size based on the Scherrer equation. C (1211 m^2/g) is larger than Al$_2$O$_3$ (163 m^2/g) in surface area. Therefore, Ni on C gives higher Ni surface areas than that of Ni on Al$_2$O$_3$. The difference in nickel surface area could explain the better activity of Ni/C catalyst.
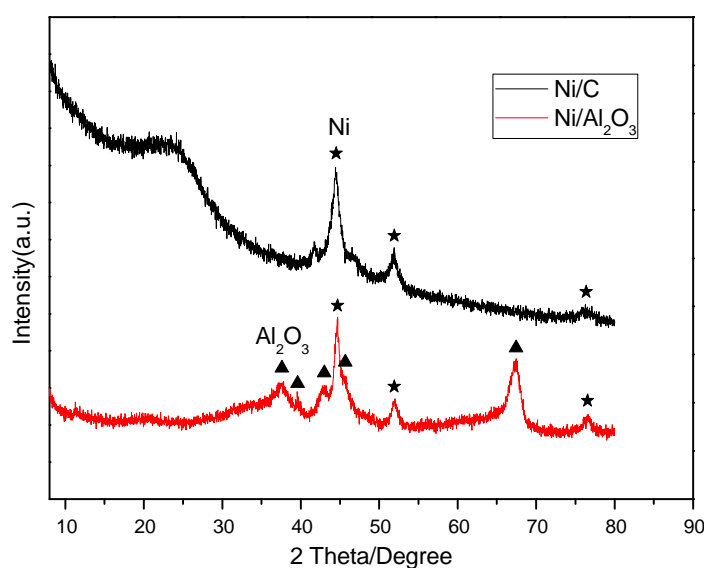

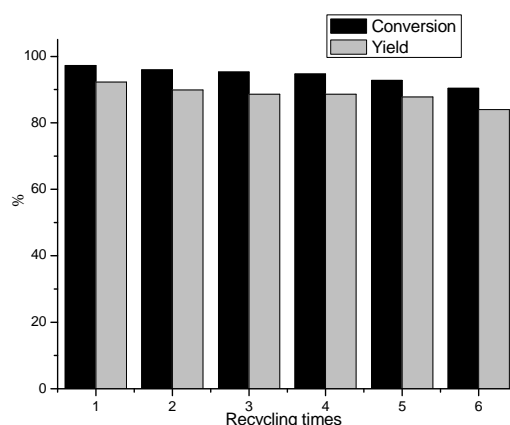**Figure 2.** XRD patterns of fresh Ni/Al$_2$O$_3$ and Ni/C.

Table 4. Catalytic activity of Ni/Al$_2$O$_3$ and Ni/C in aqueous ammonia.

| Entry	Catalyst	T/°C	t/h	H$_2$/MPa	NaOH/g	Conversion/%	Yield/%
1	Ni/Al$_2$O$_3$	160	17	0	0.3	51	42
2	Ni/Al$_2$O$_3$	180	17	0	0.3	54	49
3	Ni/Al$_2$O$_3$	200	17	0	0.3	71	65
4	Ni/Al$_2$O$_3$	200	8	1	0.3	63	54
5	Ni/Al$_2$O$_3$	200	14	1	0.3	82	72
6	Ni/Al$_2$O$_3$	200	17	1	0.3	87	79
7	Ni/Al$_2$O$_3$	200	17	0	0	48	41
8	Ni/C	160	17	0	0	37	34
9	Ni/C	160	17	0	0.3	87	81
10	Ni/C	160	17	1	0.3	92	85
11	Ni/C	160	6	1	0.3	76	69
12	Ni/C	160	24	1	0.3	91	81
13	Ni/C	180	17	1	0.3	91	86

Reaction conditions: cyclohexanol 1 g, aqueous ammonia 28 g, catalyst 1 g (Ni 10 wt %).

## 2.3. Recycling of the Catalysts

Ni/C exhibits better activity than Ni/Al$_2$O$_3$, thus its stability during the reaction is further investigated. The results, as shown in Figure 3, indicate that in the presence of NaOH and H$_2$, Ni/C could be reused six times without losing its activity and each cycle generated more than 80% cyclohexylamine yield. However, after being recycled two times, Ni/Al$_2$O$_3$ (Table 4 Entry 6) became less active. It only achieved 61% conversion and 53% yield for the second run. The XRD characterization shown in Figures 4 and 5 demonstrated that Ni/C retained its structure after being recycled, while Al$_2$O$_3$ reacted with water and produced AlO(OH). From Figures 4 and 5 Ni in Ni/Al$_2$O$_3$ and Ni/C catalysts increased from 14 nm to 23 nm and 6 nm to 7 nm after being recycled, respectively in crystallite size according to the Scherrer equation. High Resolution Transmission Electron Microscopy (HRTEM) analysis of Ni/Al$_2$O$_3$ catalysts before and after the reaction as shown in Figures 6 and 7 further proved that some of Ni were lost from the surface of Al$_2$O$_3$ because of the formation of AlO(OH). The Inductively Coupled Plasma optical emission spectrometry (ICP-OES) analysis demonstrated that 11% Ni on Ni/Al$_2$O$_3$ was lost. As to Ni/C catalyst, HRTEM analysis (Figures 8 and 9) indicated that less Ni on C was lost than that on Al$_2$O$_3$, which is consistent with the fact that only 0.5% Ni on C was lost by ICP-OES analysis. The substantial loss of metal and the growth of the crystallite size may be the reason for the deactivation of the Ni/Al$_2$O$_3$ catalyst; while the small decrease of cyclohexylamine yield of Ni/C catalyst after being recycled in Figure 3 may be ascribed to slight loss of Nickel and growth of crystallite size. It can thus be concluded from the above analysis that Ni/C is a better choice than Ni/Al$_2$O$_3$ during the amination of cyclohexanol in aqueous ammonia.
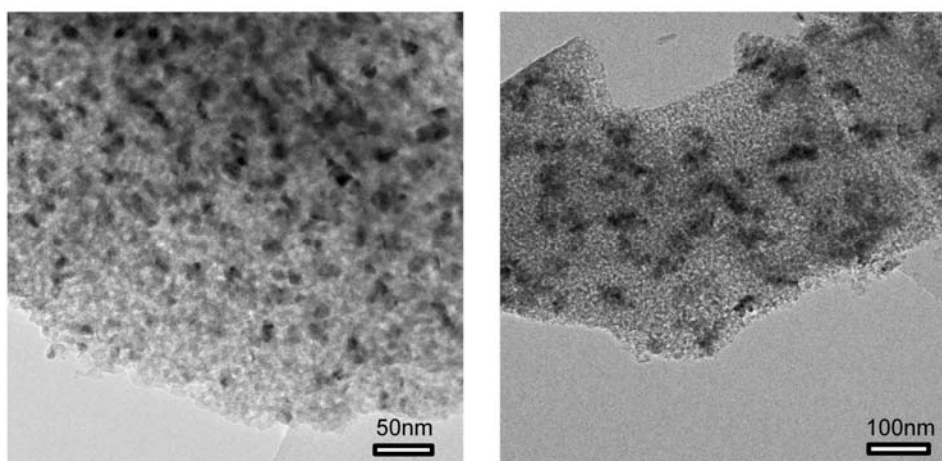

Figure 3. Recycling of Ni/C catalyst. Conditions: 160 °C, 17 h, 1 MPa H$_2$, 1 g cyclohexanol, 1 g 10 wt % Ni/C catalyst, 28 g (25 wt %) aqueous ammonia.
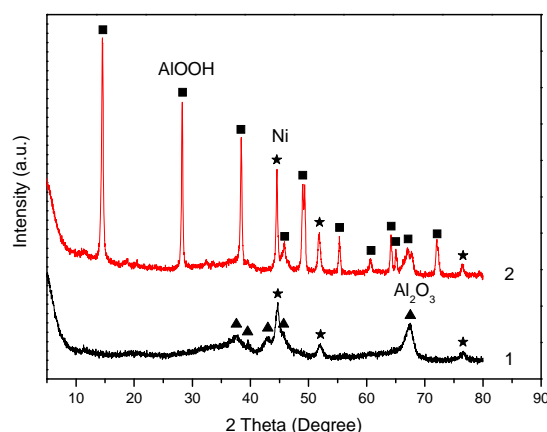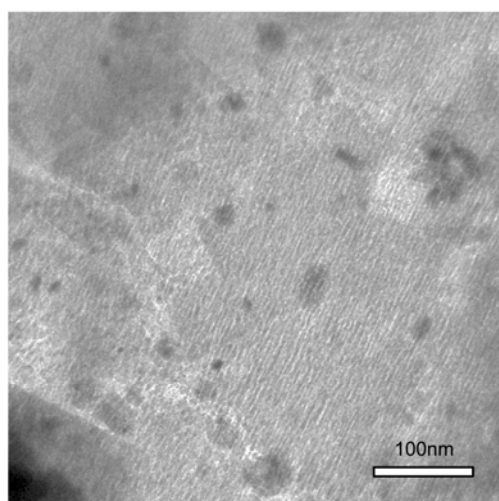

Figure 4. XRD patterns of (**1**) fresh Ni/Al$_2$O$_3$; (**2**) Ni/Al$_2$O$_3$ after the reaction.
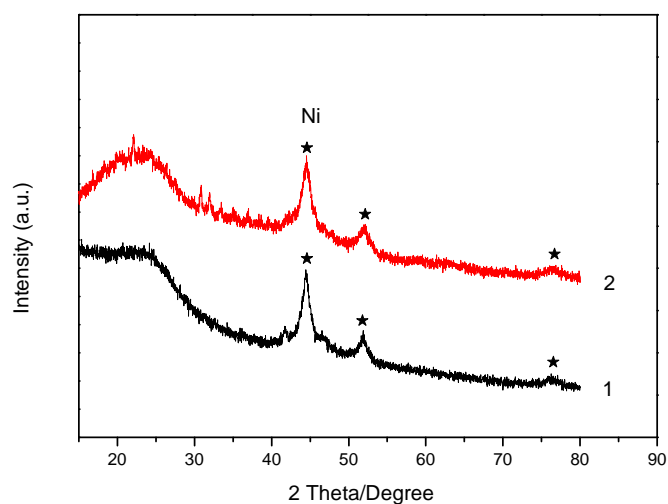
Figure 5. XRD patterns of (**1**) fresh Ni/C; (**2**) Ni/C after six times reaction.
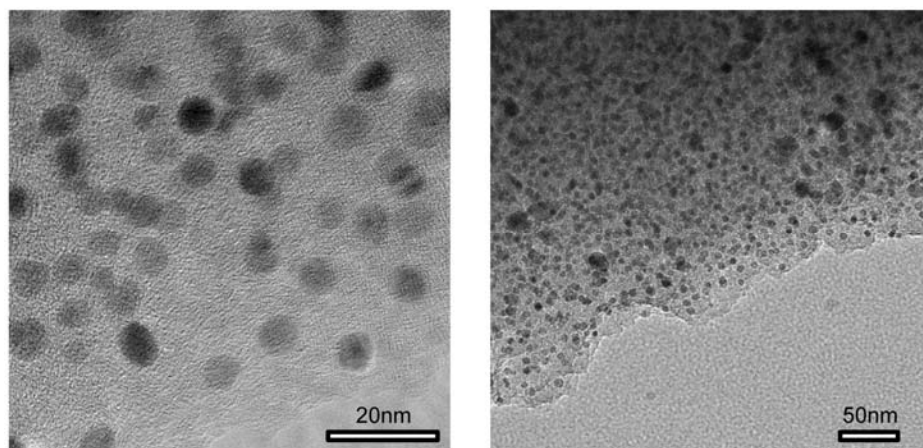

Figure 6. High Resolution Transmission Electron Microscopy (HRTEM) micrographs of the fresh Ni/Al$_2$O$_3$ catalyst.
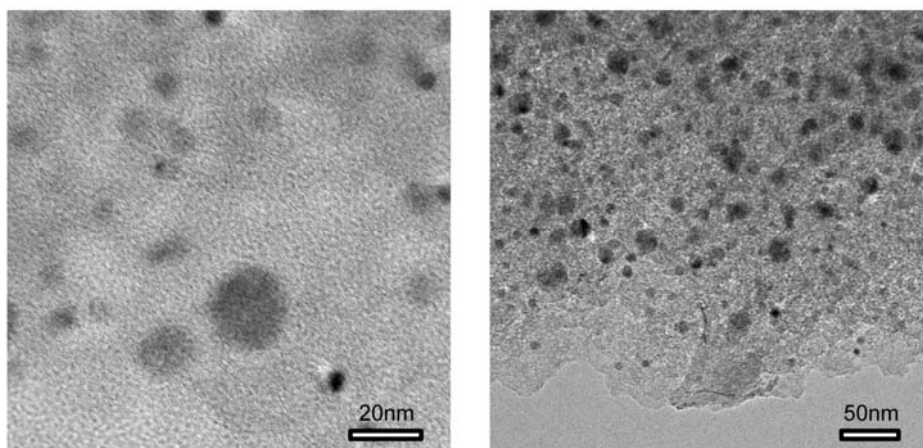

Figure 7. HRTEM micrograph of Ni/Al$_2$O$_3$ catalyst after the reaction.

Figure 8. HRTEM micrographs of the fresh Ni/C catalyst.

Figure 9. HRTEM micrographs of Ni/C catalyst after six times reaction.

2.4. Conversion in Low Boiling Point Solvents

Although cyclohexanol could be efficiently converted in aqueous ammonia, the high boiling point of water may lead to high energy consumption during the separation process. Two solvents with low boiling points tetrahydrofuran (THF) and cyclohexane were therefore investigated. Amination of cyclohexanol in non-aqueous solvents goes on well with the absence of water. The polarity of the two solvents follows the order THF > cyclohexane, which influences the solubility of both the substrate and NH_3 in them. It can be seen from Table 5 (Entries 1 to 4) that, in THF, NaOH plays a more important role than H_2. The base can improve the conversion from 13% to 50% while hydrogen has no such dramatic effect. Raising the temperature from 160 $^\circ$C to 180 $^\circ$C can lead to an increase of conversion from 50% to 85% (Entry 4 and 5). In the case of cyclohexane, the base is not soluble in it. The effect of the base in cyclohexane was thus not investigated. As can be seen from Table 5 Entries 6 and 7, hydrogen can improve the conversion from 31% to 96%. Comparing Entries 5 and 7, more cyclohexylamine yield is obtained in cyclohexane, indicating the solvent can affect the activity of Ni/Al_2O_3, as the polarity of cyclohexane is smaller than that of THF. In cyclohexane, it is easier for cyclohexanol to adsorb on the surface of Al_2O_3 and facilitate the catalytic reaction. However, the major disadvantage of cyclohexane lies in its low ability to solubilize some polar alcohol. In that case, THF may be a better choice.

Table 5. Conversion of cyclohexanol into cyclohexylamine over Ni/Al_2O_3 in tetrahydrofuran (THF) and cyclohexane.

Entry	Solvents	T/°C	H_2/MPa	NaOH/g	Conversion/%	Yield/%
1	THF	160	0	0	13	11
2	THF	160	1	0	11	9
3	THF	160	0	0.3	50	46
4	THF	160	1	0.3	50	41
5	THF	180	1	0.3	85	76
6	cyclohexane	180	0	0	31	28
7	cyclohexane	180	1	0	96	87

Reaction conditions: cyclohexanol 1 g, Ni/Al_2O_3 (Ni 10 wt %) 1 g, solvent 25 mL, NH_3 0.4 MPa, 17 h.

Table 6 shows the activity of Ni/C in cyclohexane and THF. Similar with Ni/Al_2O_3, NaOH still plays a more important role than H_2 (Entries 1, 2 and 3) in THF. At 180 °C in the presence of H_2 and NaOH, only 32% conversion was achieved for Ni/C catalyst (Entry 4). While at 180 °C in cyclohexane, 42% conversion was obtained (Entry 5). Compared with Table 5, Ni/Al_2O_3 is superior to Ni/C both in THF and cyclohexane.

Table 6. Conversion of cyclohexanol into cyclohexylamine over Ni/C in THF and cyclohexane.

Entry	Solvent	T/°C	H_2/MPa	NaOH/g	Conversion/%	Yield/%
1	THF	160	0	0	11	9
2	THF	160	0	0.3	22	20
3	THF	160	1	0	12	10
4	THF	180	1	0.3	32	28
5	cyclohexane	180	1	0.3	42	35

Reaction conditions: cyclohexanol 1 g, Ni/C (Ni 10 wt %) 1 g, solvent 25 mL, NH_3 0.4 MPa, 17 h.

3. Experimental Section

3.1. Materials

Cyclohexanol ($\geqslant$99%), cyclohexylamine ($\geqslant$99%), aqueous ammonia (25%–28%), NaOH ($\geqslant$99%), cyclohexane ($\geqslant$99%) and tetrahydrofuran ($\geqslant$99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Nickel nitrate hexahydrate ($\geqslant$98%) was purchased from Tianjin Science and Technology Co., Ltd. (Tianjin, China). Active carbon was supplied by Cabot Co., Ltd. (Boston, MA, USA). γ-Al_2O_3 was purchased from ShanDong Aluminium Industry Co., Ltd. (Shandong, China). Raney Ni was obtained from Dalian General Chemical Industry Co., Ltd. (Dalian, China). And 1, 6-hexanediol (>99%) was bought from Aladdin (Shanghai, China).

3.2. Catalyst Preparation

Ni/Al_2O_3 and Ni/C (Ni 10 wt %) catalysts were prepared by impregnation. A mixture of γ-Al_2O_3 or C and an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ was evaporated at 40 °C under reduced pressure, then dried at 110 °C for 12 h. The as-synthesized Ni/Al_2O_3 and Ni/C were reduced in a tubular furnace under a flow of H_2 at 500 °C for 6 h.

3.3. Catalyst Characterization

X-ray diffraction (XRD) measurements were carried out by a Bruker D8 Advanced X-ray diffractometer using Cu K_{α} radiation (λ = 1.5147 Å, Karlsruhe, Germany).

High Resolution Transmission Electron Microscopy (HRTEM) measurements were carried out using an emission Tecnai G2F20 electron microscope (FEI, Hillsboro, OR, USA).

The Brunauer-Emmett-Teller (BET) surface area of Al_2O_3 and active carbon was measured using a micromeritics (ASAP-2020 M + C). Samples were pretreated at 180 °C for 3 h under vacuum. N_2 adsorption/desorption isotherms were measured at 77 K. The surface areas were determined from adsorption values using the Brunauer-Emmett-Teller (BET) surface method.

The loss of Ni was determined using a Thermo IRIS IntrepidIIXSP Inductively Coupled Plasma Emission Spectrometer (Labcompare, South San Francisco, CA, USA).

3.4. Typical Procedures for the Reactions

Aqueous ammonia, cyclohexanol, NaOH and Raney Ni were charged into an autoclave, which was sealed and then heated under magnetic stirring at a preset temperature.

Tetrahydrofuran (or cyclohexane) and cyclohexanol were poured into the autoclave. The catalyst Ni/Al_2O_3 or Ni/C was then charged into the autoclave immediately after reduction under the protection of N_2. The autoclave purged three times with H_2 was pressured to 0.4 MPa NH_3 under stirring for 30 min. After being pressured to 1 MPa H_2, the autoclave was heated under stirring at a preset temperature.

3.5. Analytical Methods

Gas chromatography (GC) analysis was conducted using a Varian-450 gas chromatograph (Varian, Salt Lake City, UT, USA) with a flame ionization detector. The temperature of the column (DB-5, 30 m $\times$ 0.32 mm $\times$ 0.25 μm) was maintained at 60 °C for 1 min and then raised to 280 °C with a ramp rate of 16 °C/min for 1 min. The flowing rate of nitrogen was 1 mL/min with a split ratio of 30:1. The yield of cyclohexylamine and the conversion of cyclohexanol were calculated using 1, 6-hexanediol as an internal standard.

4. Conclusions

It was found in the amination of cyclohexanol into cyclohexylamine over Ni catalysts in aqueous ammonia, THF and cyclohexane that the base had positive effect on the activity of Raney Ni, Ni/Al_2O_3 and Ni/C in aqueous ammonia and THF. Hydrogen could also improve the conversion of cyclohexanol. In aqueous ammonia, Ni/C showed higher activity, thus was a better choice than Ni/Al_2O_3. While in THF and cyclohexane, Ni/Al_2O_3 was superior to Ni/C. The reasons why different supports influence the activity of Ni may be ascribed to their varying Ni surface areas. Stability study shows that Ni/C is better than Ni/Al_2O_3 in aqueous ammonia. This work is helpful for us to further understand the factors that could affect the amination of alcohol.

Author Contributions: Y.Q. and H.Y. conceived and designed the experiments; Q. Y. performed the experiments; Y.Q., H.Y., Q.C and X.M. analyzed the data; B.D. and A. M. contributed reagents/materials/analysis tools; Y.Q. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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