

Effect of polyamide on selectivity of its supported Raney Ni catalyst

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A newly-developed polyamide supported Raney Ni catalyst, which is suitable for use in fix-bed reactions with high selectivity, was studied in this paper. Selective hydrogenation of acetone to isopropanol was chosen as a probe reaction. It has been found that clean preparation of isopropanol could be achieved, that is to say, the two main byproducts (isopropyl ether and methyl-iso-butyl carbinol) could be eliminated with the newly-developed polyamide supported Raney Ni catalyst. The elimination of these side reactions was attributed to the adsorption effect of polyamide support and a model was proposed. The proposed model was further proved by hydroamination reaction of acetone. According to this model, catalyst support can play an important role in chemical reactions. Different products could be produced when different catalyst support is used, the main reaction and side reactions can even be reversed sometimes when the chemicals, active component of catalyst and reaction condition are the same. This model could help to improve catalytic selectivity of many Raney metal catalysts used routinely in chemical and oil refining industry, and is also useful for hydrogenation reactions in pharmaceutical and food industry.

polyamide, Raney Ni, acetone

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1 Introduction

Ni powders have been regarded as very good hydrogenation catalysts for more than a century. The preparation of a well dispersed metal Ni, which leads to high specific activities, used to require the use of mineral supports [1]. Raney [2] discovered another way to obtain high specific activities Ni in 1925. Since then, Raney Ni has been extensively used in chemical reactions [3–5]. Raney Ni offers the advantage over supported Ni catalysts of having a high catalytic activity at a relatively low temperature. Nevertheless, Raney Ni has some disadvantages as well, which limit its application. For example, powdered Raney Ni cannot be applied in

fix-bed reactors. Therefore, currently it is mainly employed in slurry phase reactors for small batch production. In this case, catalytic selectivity is hard to control [6]; moreover, Raney Ni is demanded to be separated from the reaction medium. Another shortcoming of Raney Ni is that it inevitably contains a certain fraction of Al_2O_3 [1], and the acidity of Al_2O_3 often leads to some side reactions.

In order to overcome the disadvantages of Raney catalysts, a number of researchers have devoted their efforts to shaping Raney catalysts for fix-bed reactions. Some activated merely the superficial layer of granular Raney alloys [7–10]. In this case, the activation must be controlled in a low degree in order to maintain mechanical strength of the catalysts. Some added different substances into Raney alloy powder to shape Raney alloys [11–14] or deposited metallic vapor on certain shaped substances [15], then calcined and

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activated the shaped Raney alloys. These procedures were complex and difficult to be industrialized. Some others extruded the mixture of Raney alloy powder, polymer and mineral oil together, then calcined and activated the extrudates [16–21]. Before calcination, only a small part of alloys can be activated because of the covering polymer; after calcination, however, the mechanical strength of the catalyst was sharply diminished.

In our previous communication [22], Raney metal catalyst supported by polymer was developed for fix-bed reactions with high selectivity. It has been found that the newly-developed polymer supported Raney Ni catalyst could achieve clean preparation of *n*-butanol because the main side reaction could be reduced and even eliminated in preparation of *n*-butanol from *n*-butyraldehyde. The major disadvantages of Raney Ni catalyst were satisfactorily overcome. However, the reaction studied in our previous work had only one main side reaction. In this work, polyamide supported Raney Ni catalyst (Raney Ni/PA) was used in selective hydrogenation of acetone to isopropanol, which had two main side reactions, and the effect of polyamide support on reducing or even eliminating side reactions was studied. A model was proposed to explain the clean preparation of isopropanol and was proved by hydroamination reaction of acetone.

2 Experimental

Raney Ni/PA catalyst was prepared as follows [22]: polyamide 6 granules (PA6, BL2340-H, Sinopec Baling Company, China) were separately buried into a full mold of Ni-Al alloy (50:50) powder at 250 °C. In other words, Ni-Al alloy powders were embedded into the surface of the PA granules. Thereafter, the mold was cooled down to get special granules (Ni-Al/PA), in which the Ni-Al alloy particles were embedded into PA granule surface, as shown in Figure 1. After sieving out Ni-Al/PA granules from the excess Ni-Al alloy powder, Raney Ni/PA catalyst was obtained

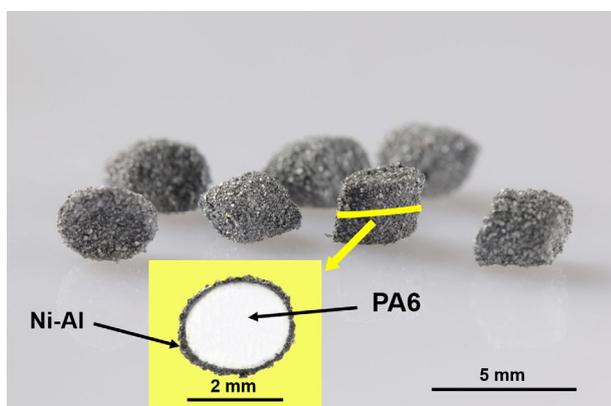


Figure 1 Photograph of Ni-Al/PA granules. Inset shows the sectional view of a cut sample (color online).

after alkaline leaching of the Ni-Al/PA granules.

For comparison, Al₂O₃-supported Ni catalyst (Ni/Al₂O₃, 20 wt% Ni), Al₂O₃-supported Raney Ni catalyst (Raney Ni/Al₂O₃, 20 wt% Ni) and unsupported granular Raney Ni catalyst were also prepared. Ni/Al₂O₃ catalyst was prepared according to the commercial impregnation method, using Al₂O₃ support and Ni(NO₃)₂·6H₂O solution, dried at 120 °C for 12 h, calcined at 360 °C for 4 h and reduced at 400 °C for 8 h. Raney Ni/Al₂O₃ catalyst was prepared according to the previous literature [23]. Granular Raney Ni catalyst was obtained by alkaline leaching of 10–20 mesh Ni-Al alloy powders (50 wt% Ni).

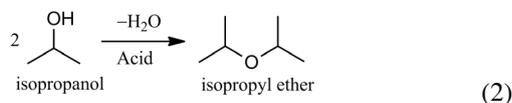
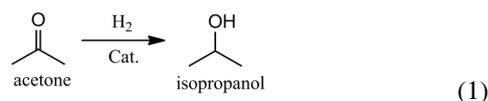
The hydrogenation of acetone reaction was performed in a 14 mm (internal diameter) tube microreactor made of stainless steel under pressure of 1.3 MPa and at temperature of 132 °C (preheated at 85 °C). The amount of catalyst used was 40 mL. The flow of acetone was controlled by a micro-syringe pump with a flow rate of 20 mL/h. H₂ gas flow was 60 mL/min. The product was analyzed by gas chromatography equipped with a flame ionization detector (FID, Agilent 7890, DB-WAX, China). The residual acetone content and isopropanol, isopropyl ether, methyl-iso-butyl carbine (MIBC) contents were determined with an external standard to indicate the activity and selectivity of the catalysts.

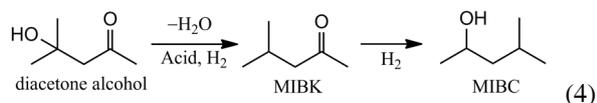
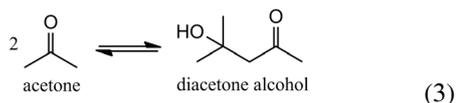
Hydroamination of acetone to isopropylamine was performed at atmosphere pressure and at the temperature of 153 °C. The amount of catalyst used was 50 mL. The flow of acetone was controlled by a micro-syringe pump with a flow rate of 25 mL/h. H₂ and NH₃ gas flow was both 75 mL/min. The product was analyzed by gas chromatography equipped with a flame ionization detector.

3 Results and discussion

3.1 Hydrogenation of acetone to isopropanol

Isopropanol, with a global growing rate of 1% to 3% per year, is widely regarded as essential commodity for fine chemical synthesis, heat pumps and hydrogen storage in fuel cell [24] in industry and academia. The commercial isopropanol is mainly from acetone hydrogenation in the presence of a hydrogenation catalyst. Reaction (1) shows the hydrogenation reaction of acetone to isopropanol; Reaction (2) represents the side reaction which generates isopropyl ether; Reactions (3) and (4) represent the side reactions which generate methyl-iso-butyl carbinol (MIBC) [25–27].





The numerical results from the hydrogenation of acetone at 132 °C with four different catalysts (Ni/Al₂O₃ catalyst, Raney Ni/Al₂O₃ catalyst, Granular Raney Ni catalyst and Raney Ni/PA catalyst) are listed in Table 1. It can be seen from Table 1 that the conversions over Raney Ni/Al₂O₃, Granular Raney Ni, and Raney Ni/PA catalysts are all beyond 99.7% whereas that over Ni/Al₂O₃ catalyst is only 98.97%. Meanwhile, the selectivity to isopropanol over Raney Ni/Al₂O₃, granular Raney Ni and Raney Ni/PA catalysts all reach higher than 99.9% and are even close to 100% over Raney Ni/PA catalyst, whereas that over Ni/Al₂O₃ catalyst is only 99.87%. It is clear that three Raney Ni-related catalysts all have both higher activity and selectivity than Ni/Al₂O₃ catalyst, indicating Raney Ni's good catalytic performance for the hydrogenation of acetone to isopropanol. The results are very simple to understand because the acidity of Al₂O₃ could catalyze the generation of byproducts in this reaction and Al₂O₃ in Ni/Al₂O₃ catalyst apparently has much more opportunities to catalyze the side reactions than the Al₂O₃ remaining inside the pores of Raney Ni resulted from the incomplete leaching of Al in Ni-Al alloy [1].

For three Raney Ni-related catalysts, the conversions are close to each other, but the selectivities are different: Raney Ni/Al₂O₃<Granular Raney Ni<Raney Ni/PA, and the selectivity over Raney Ni/PA catalyst is even close to 100%. Clearly, Al₂O₃ support diminished Raney Ni's selectivity to isopropanol because of the acid-catalyzed side reactions, while PA support eliminated these side reactions to achieve clean preparation of isopropanol. It is interesting to know why both isopropyl ether and MIBC, the two main byproducts in this reaction, could be eliminated by using PA support.

Byproduct isopropyl ether is generated from the main-product isopropanol catalyzed by acidic Al₂O₃ as Reaction (2). Once adsorbed by the remaining Al₂O₃ inside the pores of Raney Ni, isopropanol would be catalyzed to byproduct isopropyl ether. Meanwhile, it is well known that the ad-

Table 1 Hydrogenation of acetone with different catalysts at 132 °C

Catalyst	Conversion (%)	Selectivity (%)		
		isopropanol	isopropyl ether	MIBC
Ni/Al ₂ O ₃	98.97	99.87	0.05	0.08
Raney Ni/Al ₂ O ₃	99.71	99.91	0.04	0.05
Granular Raney Ni	99.76	99.94	0.04	0.02
Raney Ni/PA	99.75	100.00	undetectable	undetectable

sorption ability of a catalyst support to reactants and products can largely affect the catalytic reactivity [28,29]. The PA support, with lone pair electrons at the N atom for every repeating unit (Figure 2), possesses strong adsorption ability to isopropanol since the N atoms in PA can form hydrogen bonds with the –OH groups in isopropanol and the interval between every two neighboring N atoms in PA molecule chain is only 0.86 nm. Therefore, the following processes might have occurred (Figure 3). Process 1: acetone was adsorbed by Raney Ni of Raney Ni/PA catalyst; process 2: acetone was catalyzed to isopropanol by Ni metal; process 3: once produced, isopropanol was selectively adsorbed by N atoms in the PA, rather than the acidic Al atoms inside the pores of Raney Ni. Unlike the acidic Al atoms in Al₂O₃, the basic N atoms in the PA support cannot catalyze isopropanol to isopropyl ether. Clearly, therefore, it is the interplay of the alkalinity and strong adsorption ability to isopropanol intrinsically associated with the N atoms in the PA support that makes the elimination of isopropyl ether.

Byproduct MIBC is generated through the reaction processes as shown in Figure 4 [25]. Process 1: acetone is reversibly converted to diacetone alcohol (DAA); process 2: DAA is catalyzed to MIBK by acid; process 3: MIBK is hydrogenated to MIBC by Ni metal. As for Raney Ni, the remaining Al₂O₃ inside the pores would adsorb and catalyze DAA to MIBK, which would be hydrogenated to MIBC. This is the cause of 0.02% content of byproduct MIBC over granular Raney Ni catalyst. Obviously, removing the effect of acidic Al₂O₃ is also the key to eliminating the byproduct MIBC. As already known, the PA support possesses strong adsorption ability to –OH groups of DDA; therefore, just like the elimination of isopropyl ether, the following pro-

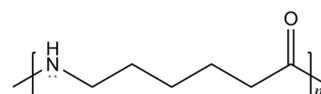


Figure 2 Chain structure of PA.

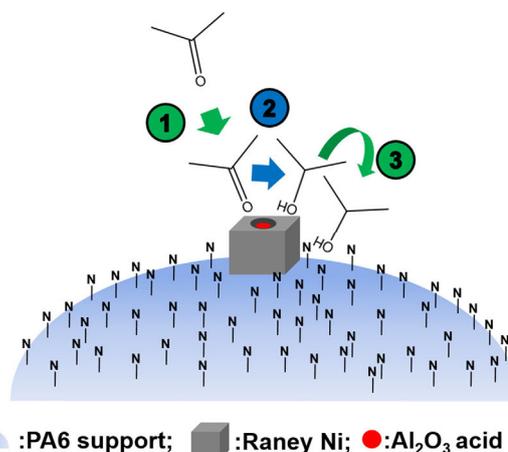


Figure 3 Schematic representation of elimination of isopropyl ether over Raney Ni/PA catalyst (color online).

cess might have occurred as shown in Figure 5. Once reversibly generated from acetone, DDA was selectively adsorbed by N atoms in the PA, rather than the acidic Al atoms inside the Raney Ni pores. Unlike the acidic Al atoms in Al_2O_3 , the basic N atoms in the PA support cannot catalyze DDA to MIBK. Therefore, byproduct MIBC cannot be generated.

It is obvious that basic N atoms having strong interaction with reactants in the PA support play a key role in clean preparation of isopropanol. In order to confirm the above conclusion, the hydroamination of acetone to isopropylamine was studied as well.

3.2 Hydroamination of acetone to isopropylamine

Reaction (5) shows the hydroamination of acetone to isopropylamine [30]; Reactions (6) and (7) represent the side reactions generate diisopropylamine (DIPA) and isopropanol, respectively. The numerical results from hydroamination of acetone at 153 °C with four different catalysts ($\text{Ni}/\text{Al}_2\text{O}_3$ catalyst, Raney Ni/ Al_2O_3 catalyst, Granular

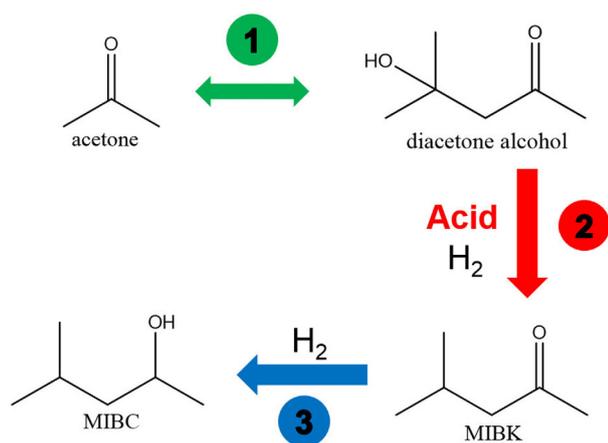


Figure 4 Schematic representation of generation process of byproduct MIBC (color online).

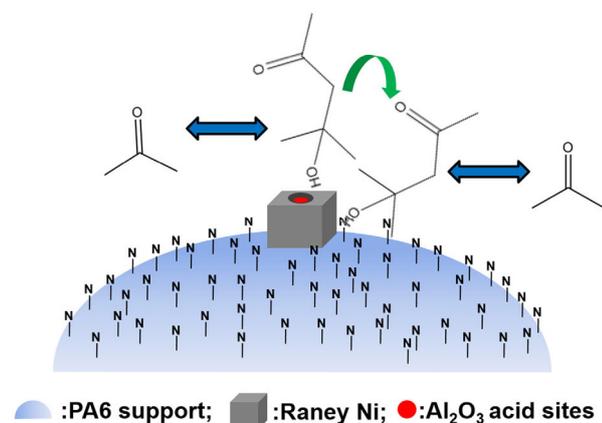
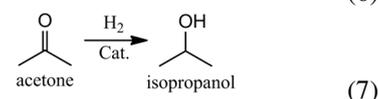
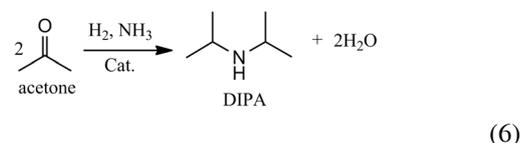
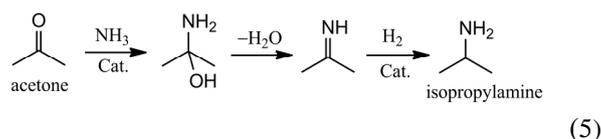


Figure 5 Schematic representation of elimination of MIBC over Raney Ni/PA catalyst (color online).

Raney Ni catalyst, and Raney Ni/PA catalyst) are listed in Table 2. It can be seen from the table that conversion, selectivity, and byproducts contents over these four catalysts have the monotonical relationship shown as follows. Conversion: $\text{Ni}/\text{Al}_2\text{O}_3 > \text{Raney Ni}/\text{Al}_2\text{O}_3 > \text{Granular Raney Ni} > \text{Raney Ni}/\text{PA}$; selectivity: $\text{Ni}/\text{Al}_2\text{O}_3 > \text{Raney Ni}/\text{Al}_2\text{O}_3 > \text{Granular Raney Ni} > \text{Raney Ni}/\text{PA}$; byproduct DIPA content: $\text{Ni}/\text{Al}_2\text{O}_3 > \text{Raney Ni}/\text{Al}_2\text{O}_3 > \text{Granular Raney Ni} > \text{Raney Ni}/\text{PA}$; and byproduct isopropanol content: $\text{Ni}/\text{Al}_2\text{O}_3 < \text{Raney Ni}/\text{Al}_2\text{O}_3 < \text{Granular Raney Ni} < \text{Raney Ni}/\text{PA}$. The above experimental results could also be explained according to the interaction of catalyst support with reactants as indicated by the proposed model for acetone to isopropanol.

NH_3 , easily adsorbed by Al_2O_3 acidic sites, is indispensable for the production of both main product isopropylamine and byproduct DIPA (Reactions (5) and (6)). Therefore, $\text{Al}_2\text{O}_3/\text{Ni}$ catalyst, with the largest Al_2O_3 content, possesses the highest activity and byproduct DIPA content among these four catalysts. Since there is just a small amount of Al_2O_3 remaining inside the pores of Raney Ni, Al_2O_3 contents of these four catalysts have this relationship: $\text{Ni}/\text{Al}_2\text{O}_3 > \text{Raney Ni}/\text{Al}_2\text{O}_3 > \text{Granular Raney Ni} > \text{Raney Ni}/\text{PA}$, which is accordant with that of conversion and byproduct DIPA content.

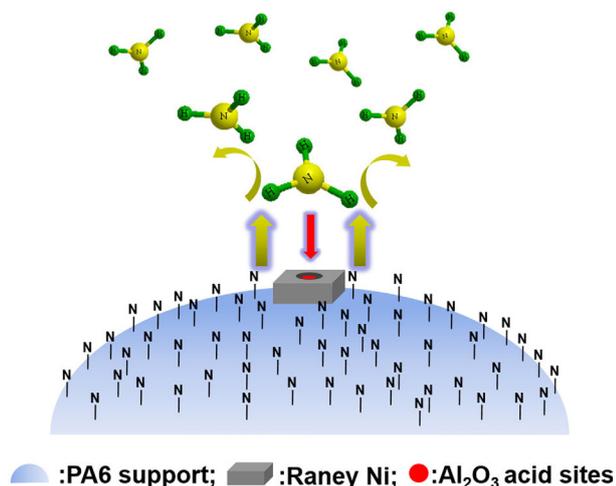


Furthermore, we still need to know why Raney Ni/PA catalyst is so special, with very low activity and selectivity, but the byproduct DIPA content is undetectable. The reason is simple, because the repulsive interaction between N atom in PA support and NH_3 is very strong. As shown in Figure 6, although the remaining Al_2O_3 inside the pores of Raney Ni can adsorb reactant NH_3 , the repulsive interaction of PA support surrounding Raney Ni prevents NH_3 from being adsorbed by Al_2O_3 inside the pores of Raney Ni. In this case, hydroamination reaction is difficult to conduct, indicating very low activity and selectivity. Besides, as the very limited amount of adsorbed NH_3 is exhausted by main Reaction (5), side Reaction (6) is eliminated. Moreover, because the generation of byproduct isopropanol does not need reactant NH_3 , the content of byproduct isopropanol over Raney Ni/PA catalyst even greatly exceeds that of main product isopropylamine.

It is clear and interesting that catalyst support can play an

Table 2 Hydroamination of acetone with different catalysts over 153 °C

Catalyst	Conversion (%)	Selectivity (%)		
		isopropylamine	DIPA	isopropanol
Ni/Al ₂ O ₃	99.38	79.06	7.00	13.94
Raney Ni/Al ₂ O ₃	98.18	71.63	3.83	24.54
Granular Raney Ni	96.49	56.83	3.52	39.65
Raney Ni/PA	90.69	37.95	undetectable	62.05

**Figure 6** Schematic representation of prevention process of NH₃ from adsorption (color online).

important role in chemical reaction. Different products could be produced when different catalyst support is used even when the chemicals, active component of catalyst and reaction condition are the same. The main reaction and side reaction can even be reversed sometimes.

4 Conclusions

A newly-developed polyamide supported Raney Ni catalyst, which is suitable for use in fix-bed reactions with high selectivity, can make the selective hydrogenation of acetone to isopropanol very clean. The two main byproducts (isopropyl ether and methyl-iso-butyl carbinol) could be eliminated completely, which could be attributed to the adsorption effect of polyamide support and a model has been proposed. The proposed model was further proved by hydroamination reaction of acetone. Based on this study, we believe that the catalytic selectivity of Raney catalysts and other hydrogenation catalysts in chemical industry, oil refining industry, pharmaceutical industry, and food industry, could be greatly improved by selecting appropriate polymer support according to the features of specific reactions.

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

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