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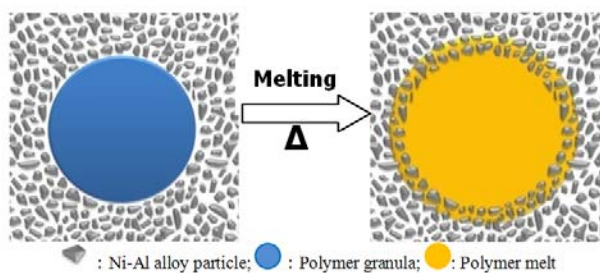
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Graphical Abstract



The heating caused polymer to melt and expand and fill into the surrounding gaps among the alloy powder

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COMMUNICATION

Polymer-Supported Catalysts for Clean Preparation of n-Butanol

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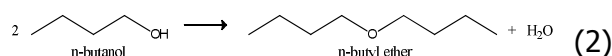
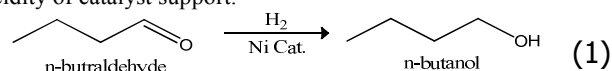
A new type of Raney metal catalyst supported by polymer was developed for clean Preparation of n-butanol. Unlike traditional supported catalysts, the newly-developed-alkalescent polyamide 6 (PA6) supported Raney nickel catalyst provided a 100.0% conversion of n-butyraldehyde without producing any detectable n-butyl ether, the main byproduct in industry. The significantly enhanced catalyst selectivity of the polymer-supported Raney metal catalyst was attributed to the elimination of the acid-catalyzed side reaction associated with Raney metals and traditional catalyst supports, such as Al₂O₃ and SiO₂. By eliminating acid-catalyzed side reactions, therefore, green chemistry could be achieved through cutting down resources and energy consumption in chemical reactions. Furthermore, the preparation and recycle of the polymer-supported catalysts are also much more eco-friendly than those traditional Al₂O₃-/SiO₂-supported catalysts. The methodology developed in this study to use alkalescent polymers as the catalyst support could be leveraged to the whole catalyst family, including a series of important Raney metal catalysts (e.g., Raney nickel, Raney cobalt, Raney copper) used routinely in the chemical industry.

Chemical industry has made irreplaceable contributions to the world, but has also caused negative impacts on our environment and consumed a huge amount of resources and energy. Catalyst, as the soul of chemical industry, plays a key role in reducing these negative effects for chemical industry. It is well recognized that environmental pollution, and consumption of resources and energy can be reduced significantly by improving the catalyst selectivity to minimize side reactions. It is well known that 90% of chemical reactions in chemical industry are based on heterogeneous catalytic processes¹, and the majority of the industrial catalysts are supported catalysts². While Al₂O₃³⁻¹¹ and SiO₂¹²⁻¹⁷ are the two major catalyst supports, they both have faint acidity, which often lead to side reactions, such as hydrogenation reaction of n-butyraldehyde to n-butanol, hydrogenation reaction of adiponitrile to 1,6-hexanediamine¹⁸ and hydrogenation reactions of alkenes and alkynes¹⁹. Without a revolutionary change in the catalyst support, the side reactions would be difficult to significantly reduce or even eliminate. In order to reduce the negative effects caused by the weak acidity of the conventional catalyst supports (e.g., Al₂O₃ and SiO₂), many investigations have been carried out to neutralize the acid of

catalyst supports by, for example, adding alkaline agents into conventional supports or reactants¹⁹⁻²⁶. However, side reactions caused by the support acidity cannot be completely avoided as mixing at molecular level is hardly achieved in these cases. Besides, the addition of alkalescent agents into reactants often lead to an increased cost, difficult operation, more byproducts, and possibly a more complicated separation process.

On the other hand, polymer materials with different structures possess excellent processibility, recyclability and surface properties. Therefore, polymer materials could be ideal alternatives for replacing current catalyst supports to meet different specific demands of catalysts for different chemical reactions. More importantly, polymer materials could be chemically functionalized to adjust the alkalinity or acidity at molecular level to minimize side reactions. As such, polymer could be an optimum catalyst support for clean chemical reaction as long as the specific surface area of final catalyst could be large enough. Fortunately, Raney metals with large specific surface area could be suitable component for polymer-supported catalyst.

In this work, polymer-supported Raney Ni was studied for the clean preparation of n-butanol, which, with a worldwide consumption of more than 3 million tons per year, is widely used as a solvent and a raw material for other chemicals²⁷. Commercially, n-butanol is mainly from hydrogenation of n-butyraldehyde (obtained from the oxo reaction of propylene) in the presence of a hydrogenation catalyst²⁸. The most widely used commercial hydrogenation catalyst is Al₂O₃-supported Ni catalyst. Reaction (1) shows the hydrogenation reaction of n-butyraldehyde to n-butanol whereas reaction (2) represents the main side reaction that generates n-butyl ether. In order to separate n-butyl ether from n-butanol, a large amount of energy is required because an azeotrope is formed. For the reduction of pollution, and energy and resource consumption in n-butanol production, it is important to eliminate this side reaction. It is well known that reaction (2) is an acid-catalyzed reaction and the yield of n-butyl ether increases with increasing the acid strength of the catalyst^{29, 30}. Use of a non-acid support is expected to reduce or even eliminate the side reaction associated with the acidity of catalyst support.



In this study, a neutral polymer, Polypropylene (PP), was selected as the first polymer support for Raney Ni catalyst. Compared with the traditional Al_2O_3 -supported Ni catalyst, the preparation of the PP-supported catalyst is relatively simple and energy efficient. In this experiment, PP granules (F280M, Sinopec Maomin Company) were buried in a scattered manner into a full mould of Ni-Al alloy powder (48 wt. % Ni). The mould was then compressed tightly (2MPa) and heated up to 200 °C. The heating caused PP to melt and expand and fill into the surrounding gaps among the alloy powder. In other words, Ni-Al alloy powders were embedded into the surface of the expanded PP particle (see Figure 1a). Thereafter, the mould was cooled down leading to the formation of the special granule (Ni-Al/PP), in which the Ni-Al alloy particles were embedded into PP granule surface, as shown in Figure 1b. After sieving out Ni-Al/PP granules from the excess Ni-Al alloy powder, PP-supported Raney Ni catalyst (Raney Ni/PP) was obtained by alkaline leaching of the Ni-Al/PP.

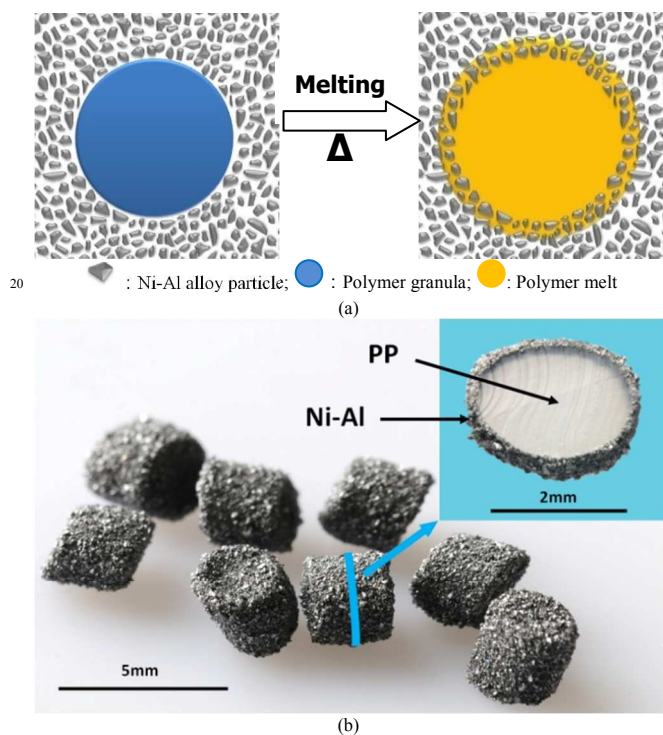


Figure 1. (a) Schematic representation of the process that Ni-Al alloy particles embedding in polymer surface. (b) Photograph of Ni-Al/PP granules. Inset shows the sectional view of a cut sample.

For comparison, maleic anhydride grafted PP (MAHPP)-supported Raney Ni catalyst (Raney Ni/MAHPP) and Al_2O_3 -supported Ni catalyst (20 wt.% Ni/ Al_2O_3) were also prepared. MAHPP (GPM200AL, with 1 wt. % MAH) was purchased from Ningbo Nengzhiguang Company, and Raney Ni/MAHPP catalyst was prepared through the same procedures as those for the Raney Ni/PP catalyst. Ni/ Al_2O_3 catalyst was prepared according to the commercial impregnation method, using Al_2O_3 and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution, dried at 120 °C for 12 h, calcined at 360 °C for 4 h and reduced at 400 °C for 8 h. The catalytic reaction was performed in a 14 mm (internal diameter) tube microreactor made of stainless steel under a pressure of 4.0MPa and at a temperature

ranging from 100 to 140 °C. The amount of catalyst used was 20ml. The flow of n-butyraldehyde was controlled by a micro-syringe pump with a flow rate of 30 ml/h. The product was analyzed by gas chromatography equipped with a flame ionization detector (Agilent 7890, DB-WAX, FID). The residual n-butyraldehyde content and n-butyl ether content were determined with an external standard to indicate the activity and selectivity of the catalysts.

The numerical results from the hydrogenation of n-butyraldehyde at 100-140 °C with three different catalysts, Raney Ni/PP catalyst, Raney Ni/MAHPP catalyst, and Ni/ Al_2O_3 catalyst, are listed in Table 1. It can be seen from the table that n-butyl ether content over the Raney Ni/PP catalyst is nearly one order of magnitude lower than that of both the Raney Ni/MAHPP catalyst and Ni/ Al_2O_3 catalyst at the same temperature, indicating an excellent selectivity for the Raney Ni/PP catalyst. More specifically, the n-butyl ether content is 0.053 wt% for the Raney Ni/PP catalyst at 100% conversion while the corresponding n-butyl ether content increased significantly to 0.632 and 0.159 wt%, respectively, for the Raney Ni/MAHPP and Ni/ Al_2O_3 catalysts under the same condition. Clearly, therefore, the neutral support PP did effectively reduce the acid-catalyzed side reaction with respect to those acidic supports (*i.e.*, MAHPP and Al_2O_3). However, the Raney Ni/PP catalyst didn't eliminate n-butyl ether byproduct completely, though the fraction of the byproduct is very small. To understand why a small fraction of the byproduct (n-butyl ether) is still produced by the Raney Ni/PP catalyst with a neutral support, we further carried out an element analysis with X-ray photoelectron spectrometer (XPS). The element analysis results are given in Table 2, which shows the presence of Al_2O_3 in the Raney Ni/PP catalyst. This is notion consistent with the literature report that Raney Ni usually contains a small fraction of Al_2O_3 because of the incomplete leaching of Al in Ni-Al alloy³¹. Therefore, it is the Al_2O_3 in Raney Ni that was responsible for the small fraction of n-butyl ether produced by Ni/PP catalyst with a neutral polymer support.

Table 1. Hydrogenation of n-butyraldehyde with different catalysts over 100-140 °C

Catalyst	T (°C)	Conversion (%)	n-butyl ether (wt. %)
Raney Ni/PP	100	99.99	0.013
	110	100	0.053
	120	100	0.095
	140	100	0.499
Raney Ni/MAHPP	100	99.99	0.300
	110	100	0.632
	120	100	1.049
Ni/ Al_2O_3	140	100	1.843
	100	100	0.159
	110	100	0.292
Raney Ni/PA	120	100	0.677
	140	100	1.706
	100	99.99	0.000

110	100	0.000
120	100	0.015
140	100	0.016

Table 2. Element analysis results from the Raney Ni/PP, Raney Ni/PA and Ni/Al₂O₃ catalyst surfaces by XPS

Catalyst	C (at. %)	O (at. %)	N (at. %)	Al (at. %)	Ni (at. %)
Raney Ni/PP	55.3	30.8	–	3.2	10.7
Raney Ni/PA	38.9	43.3	1.4	3.8	12.6
Ni/Al ₂ O ₃	19.1	46.0	–	31.1	3.8

In order to further reduce the acid-catalyzed side reaction, an alkalescent polymer, polyamide 6 (PA6, BL2340-H, Sinopec Baling Company), with lone pair electrons at the N atom for every repeating unit (Figure 2) was selected as a new support to replace PP. The Raney Ni/PA catalyst was prepared through the same procedures as the Raney Ni/PP catalyst except that the compressing temperature was increased to 250 °C.

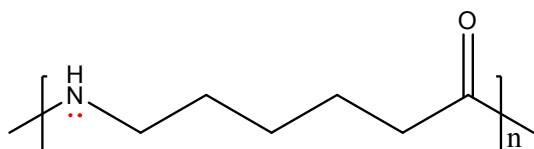


Figure 2. Chain structure of PA6

The experimental results from the Raney Ni/PA catalyst are listed also in Table 1. As can be seen, the n-butyl ether content in final product generated by Raney Ni/PA catalyst is undetectable at 100 and 110 °C whilst remaining very low (0.015 and 0.016 wt%) even at 120 and 140 °C, respectively. It is worth to note that the n-butyl ether content in the final product from the Raney Ni/PA catalyst at 120 °C and above is close to one order of magnitude lower than that for the Raney Ni/PP catalyst and nearly two orders of magnitude lower than that for both the Raney Ni/MAHPP and Ni/Al₂O₃ catalysts. Of particular significance, Table 1 shows that clean preparation of n-butanol with a 100% conversion and undetectable n-butyl ether can be achieved with the PA-supported Raney Ni catalyst at a relatively low temperature (110 °C).

To understand why the PA6 support can reduce the side reaction caused by the Al₂O₃ in the Raney Ni, we consider two possibilities: 1) the acidity of Al₂O₃ in the Raney Ni was neutralized by the basic PA6; and 2) there was no adsorption of n-butanol by the acidic Al₂O₃ associated with the Raney Ni in the Raney Ni/PA catalyst because the N atom in the PA6 support has a higher affinity to n-butanol than the Al atom in Al₂O₃. However, our XPS measurements confirmed that the basic N atom in the PA6 cannot affect the acidity of Al atom because of the relatively large “intermolecular distance”. Indeed, the XPS Al 2s peaks of the Raney Ni/PA and Ni/Al₂O₃ catalysts were located at 74.03 and 73.93 eV, respectively, which are almost the same within the experimental error and indicate no charge-transfer (base-acid neutralization) interaction between the basic PA6 and acidic Al₂O₃ in the Raney Ni. On the other hand, it is well known that the adsorption ability of a catalyst support to reactants and

products can largely affect the catalytic reactivity^{18, 23}. The PA6 support possesses strong adsorption ability to n-butanol since the N atoms in PA6 can form hydrogen bonds with the -OH groups in n-butanol. Therefore, the following process might have occurred. Once produced from n-butyraldehyde catalyzed by Ni metal, n-butanol was selectively adsorbed by N atoms in the PA6, rather than the acidic Al atoms in the Raney Ni. Unlike the acidic Al atoms in Al₂O₃, the basic N atoms in the PA6 support cannot catalyze n-butanol to n-butyl ether. For the Raney Ni/MAHPP catalyst, maleic anhydride in the MAHPP support can also selectively adsorb n-butanol over Al₂O₃. However, the acidic maleic anhydride can effectively catalyze n-butanol to n-butyl ether, leading to the formation of even more n-butyl ether by the Raney Ni/MAHPP catalyst with respect to the Ni/Al₂O₃ catalyst (Table 1). Clearly, therefore, it is the interplay of the alkalinity and strong adsorption ability to n-butanol intrinsically associated with the N atoms in the PA support that makes the clean preparation of n-butanol possible by the Raney Ni/PA catalyst. The relationship between the alkalinity or acidity of the catalyst support and the byproduct content (n-butyl ether) could be summarized in Table 3.

Table 3. The relationship between the property of catalyst support and the byproduct content

	Inorganic support	Organic support	Organic support with acid or alkaline group which can adsorb n-butanol	
Support with alkalinity or acidity	Al ₂ O ₃ (acidity)	PP (neutral)	PP-g-MAH (acidity)	PA6 (alkalinity)
n-Butyl ether content	High	Low	Very high	Very low to undetectable

We have performed SEM imaging to further elaborate the difference between the Raney Ni/PA catalyst and Ni/Al₂O₃ catalyst. As can be seen in Figure 3, they showed quite different surface morphologies and different porosity. The BET specific surface area of the Raney Ni/PA catalyst is only 4.5 m²/g, much lower than that of the Ni/Al₂O₃ catalyst, which is usually in several tens to hundreds m²/g. At the first glance, it seems strange to see that the more active polymer-supported catalyst has a lower specific surface area than that of the Ni/Al₂O₃ catalyst. Unlike the Ni/Al₂O₃ catalyst, however, most of the surface area of the Raney Ni/PA catalyst is covered by active Ni component, as indicated by XPS data in Table 2. Table 2 shows that the Ni content of the Raney Ni/PA catalyst surface is more than three times higher than that of the Ni/Al₂O₃ catalyst surface.

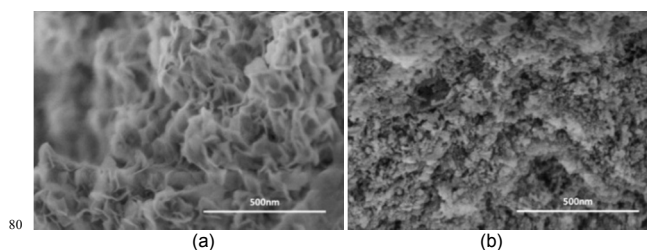


Figure 3. SEM images of (a) the Ni/PA catalyst and (b) the Ni/Al₂O₃ catalyst.

We have also investigated the long-term activity and selectivity of the Raney Ni/PA catalyst over a temperature range of 100-140 °C. Figure 4 shows an almost constant catalytic activity

and n-butyl ether content over 220h and 100-140 °C, indicating an excellent performance in terms of both activity and selectivity for Raney Ni/PA catalyst over long-term operation.

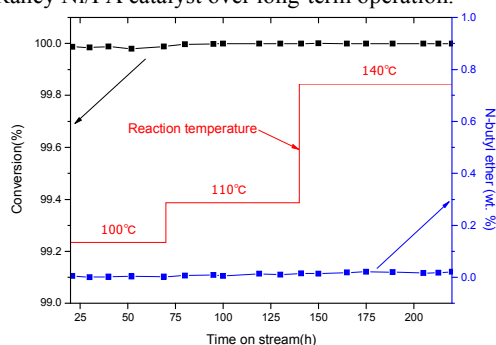


Figure 4. Long-term catalytic test for the Raney Ni/PA catalyst under a pressure of 4.0 MPa at different temperatures over 100-140 °C; red stepwise lines represent the temperature sequence used for the test.

Conclusions

A new type of catalyst, Raney Ni supported by polyamide 6 (*i.e.*, Raney Ni/PA), with a low specific surface area but a high activity has been developed, which led to clean preparation of n-butanol by using the alkaline polymer support to enhance the selectivity of catalysts and to reduce or even eliminate side reactions caused by the acidity of traditional catalyst supports. The polymer support can provide more eco-friendly catalyst preparation and recycling processes than those of traditional Al₂O₃ and SiO₂ supports. Polymer supported catalysts do not need calcinations at high temperatures and hydrogen reduction as traditional Al₂O₃-supported catalysts need; therefore, energy and hydrogen consumption can also be reduced. Furthermore, the recycling of polymer supported catalysts need only calcining in air to get rid of polymer and the remaining metal alloys could be reused directly. In contrast, the recycling of the traditional supported catalysts needs to use nitro-hydrochloric acid, which produces a lot of NO_x and the acid-solubilized metals are difficult to be separated. As a series of important Raney metal catalysts, including but not limited to Raney nickel, Raney cobalt, and Raney copper, are routinely used in our chemical industry, we believe that the use of polymers as catalyst supports can be leveraged to the whole catalyst family to achieve green chemistry by eliminating side reactions and cutting down resources and energy consumption caused by the side reaction in chemical industries.

Notes and references

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