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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 the 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 Al_2O_3 and SiO_2. By eliminating acid-catalyzed side reactions, therefore, green chemistry could be achieved through reducing resources and energy consumption in chemical reactions. Furthermore, the preparation and recycling of the polymer-supported catalysts are also much more eco-friendly than for traditional Al_2O_3-/SiO_2-supported catalysts. The methodology developed in this study to use alkalescent polymers as the catalyst support could be applied 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.

The 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. Catalysts, as the soul of the chemical industry, play a key role in reducing these negative effects for the chemical industry. It is well recognized that environmental pollution and consumption of resources and energy can be reduced significantly by improving catalyst selectivity to minimize side reactions. It is well known that 90% of chemical reactions in chemical industry are based on heterogeneous catalytic processes,[1] and the majority of industrial catalysts are supported catalysts.[2] While Al_2O_3 (ref. 3–11) and SiO_2 (ref. 12–17) are the two major catalyst supports, they both have faint acidity, which often leads to side reactions, such as hydrogenation of *n*-butyraldehyde to *n*-butanol, hydrogenation of adiponitrile to 1,6-hexanediamine[18] and hydrogenation reactions of alkenes and alkynes.[19] Without a revolutionary change in the catalyst support, these 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.*, Al_2O_3 and SiO_2), many investigations have been carried out to neutralize the acidity of catalyst supports by, for example, adding alkaline agents into conventional supports or reactants.[19–26] However, side reactions caused by the support acidity cannot be completely avoided as mixing at the molecular level is hardly achieved in these cases. Besides, the addition of alkalescent agents into reactants often leads to 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, polymers could be optimum catalyst supports for clean chemical reactions as long as the specific surface area of the final catalyst could be large enough. Fortunately, RANEY® metals with large specific surface area could be suitable components for polymer-supported catalysts.

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 chemicals.[27] Commercially, *n*-butanol is mainly obtained from hydrogenation of *n*-butyraldehyde (obtained from the oxo reaction of propylene) in the presence of a hydrogenation catalyst.[28] The most widely used commercial hydrogenation

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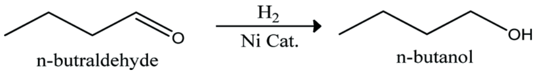
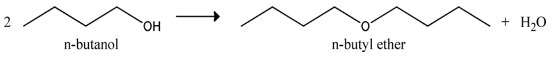
catalyst is Al_2O_3-supported Ni catalyst. Reaction (1) shows the hydrogenation reaction of *n*-butyraldehyde to *n*-butanol, whereas reaction (2) represents the main side reaction, which generates *n*-butyl ether. In order to separate *n*-butyl ether from *n*-butanol, a large amount of energy is required 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 the catalyst support.



(1)



(2)

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 (2 MPa) and heated to 200 °C. The heating caused the PP to melt and expand and fill the surrounding gaps amongst the alloy powder. In other words, Ni–Al alloy powders were embedded into the surface of the expanded PP particles (see Fig. 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 the PP granule surface, as shown in Fig. 1b. After sieving out Ni–Al/PP granules from the excess Ni–Al alloy powder, a PP-supported RANEY® Ni catalyst (RANEY® Ni/PP) was obtained by alkaline leaching of the Ni–Al/PP.

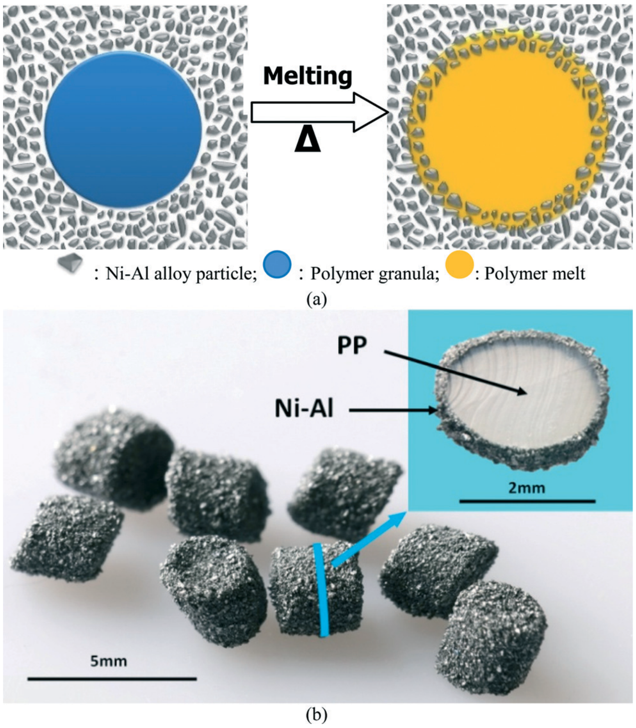


Fig. 1 (a) Schematic representation of the process of Ni–Al alloy particles embedding in the polymer surface. (b) Photograph of Ni–Al/PP granules. Inset shows the cross-sectional view of a cut sample.

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 procedure as that for the RANEY® Ni/PP catalyst. The Ni/Al_2O_3 catalyst was prepared according to a commercial impregnation method, using Al_2O_3 and $Ni(NO_3)_2 \cdot 6H_2O$ 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 4.0 MPa and at a temperature ranging from 100 to 140 °C. The amount of catalyst used was 20 ml. The flow of *n*-butyraldehyde was controlled by a micro-syringe pump with a flow rate of 30 ml h^{-1}. 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 the 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

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
	140	100	1.843
Ni/Al2O3	100	100	0.159
	110	100	0.292
	120	100	0.677
	140	100	1.706
RANEY® Ni/PA	100	99.99	0.000
	110	100	0.000
	120	100	0.015
	140	100	0.016

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 conditions. Clearly, therefore, the neutral support PP did effectively reduce the acid-catalyzed side reaction with respect to the acidic supports (*i.e.*, MAHPP and Al_2O_3). However, the RANEY® Ni/PP catalyst didn't eliminate the *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 element analysis by X-ray photoelectron spectrometry (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 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 alloy.[31] Therefore, it is the Al_2O_3 in RANEY® Ni that is responsible for the small fraction of *n*-butyl ether produced by Ni/PP catalyst with a neutral polymer support.

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 in every repeating unit (Fig. 2) was selected as a new support to replace PP. The RANEY® Ni/PA catalyst was prepared through the same procedure as the RANEY® Ni/PP catalyst except that the compressing temperature was increased to 250 °C.

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 noting 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/Al_2O_3 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 Al_2O_3 in the RANEY® Ni, we consider two possibilities: 1) the acidity of Al_2O_3 in the RANEY® Ni was neutralized by the basic PA6; and 2) there was no adsorption of *n*-butanol by the acidic Al_2O_3 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 Al_2O_3. However, our XPS measurements confirmed that the basic N atom in the PA6 cannot affect the acidity of the Al atom because of the relatively large intermolecular distance. Indeed, the XPS Al 2s peaks of the RANEY® Ni/PA and Ni/Al_2O_3 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 Al_2O_3 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 Al_2O_3, 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 Al_2O_3. 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/Al_2O_3 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) are summarized in Table 3.

We have performed SEM imaging to further elaborate the difference between the RANEY® Ni/PA catalyst and Ni/Al_2O_3 catalyst. As can be seen in Fig. 3, they showed quite different surface morphologies and different porosities. The BET specific surface area of the RANEY® Ni/PA catalyst is only 4.5 $m^2\ g^{-1}$, much lower than that of the Ni/Al_2O_3 catalyst, which is usually in several tens to hundreds $m^2\ g^{-1}$. At 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/Al_2O_3 catalyst. Unlike the Ni/Al_2O_3 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

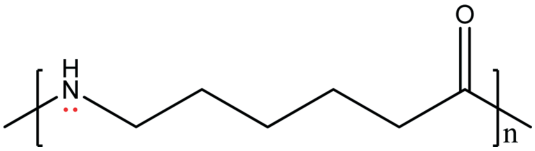


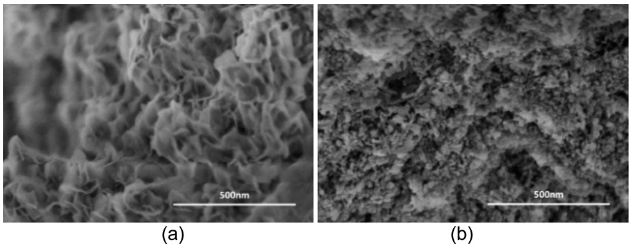
Fig. 2 Chain structure of PA6.

Table 2 Element analysis results of the RANEY® Ni/PP, RANEY® Ni/PA and Ni/Al_2O_3 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_2O_3	19.1	46.0	—	31.1	3.8

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_2O_3 (acidity)	PP (neutral)	PP-g-MAH (acidity)	PA6 (alkalinity)
n-Butyl ether content	High	Low	Very high	Very low to undetectable



(a) (b)

Fig. 3 SEM images of (a) the Ni/PA catalyst and (b) the Ni/Al_2O_3 catalyst.

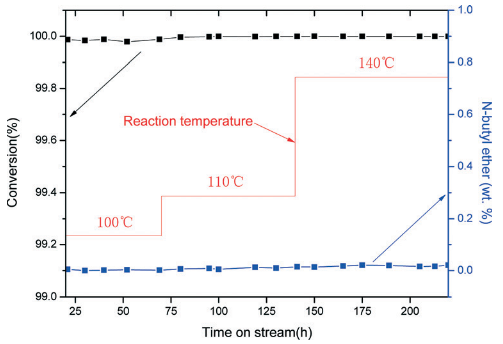


Fig. 4 Long-term catalytic test for the RANEY® Ni/PA catalyst under a pressure of 4.0 MPa at different temperatures over 100–140 °C; red stepwise lines represent the temperature sequence used for the test.

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/Al_2O_3 catalyst surface.

We have also investigated the long-term activity and selectivity of the RANEY® Ni/PA catalyst over a temperature range of 100–140 °C. Fig. 4 shows an almost constant catalytic activity and *n*-butyl ether content over 220 h and 100–140 °C, indicating an excellent performance in terms of both activity and selectivity for RANEY® Ni/PA catalyst over long-term operation.

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 alkalescent polymer support to enhance the selectivity of the catalyst 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 Al_2O_3 and SiO_2 supports. Polymer supported catalysts do not need calcination at high temperatures and hydrogen reduction, as required by traditional Al_2O_3-supported catalysts; therefore, energy and hydrogen consumption can also be reduced. Furthermore, the recycling of polymer supported catalysts needs only calcining in air to remove polymer and the remaining metal alloys could be reused directly. In contrast, recycling of the traditional supported catalysts needs nitro-hydrochloric acid, which produces a lot of NO_x and the acid-solubilized metals are difficult to separate. Because a series of important RANEY® metal catalysts, including but not limited to RANEY® nickel, RANEY® cobalt, and RANEY® copper, are routinely used in the chemical industry, we believe that the use of polymers as catalyst supports can be applied to the whole catalyst family to achieve green chemistry by eliminating side reactions and cutting down resources and energy consumption caused by side reactions in chemical industries.

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