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# The Pt-Enriched PtNi Alloy Surface and its Excellent Catalytic Performance in Hydrolytic Hydrogenation of Cellulose

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Ni-based catalysts are currently a subject of intense research in the hydrolytic hydrogenation of cellulose. We previously reported that Ni/ZSM-5 catalyst gave high yield of hexitols. However, Ni-based catalysts suffered fast deactivation in hot-compressed water. In this follow-up study we designed highly active Ni-based bimetallic catalysts with excellent hydrothermal stability for the hydrolytic hydrogenation of microcrystalline cellulose. PtNi/ZSM-5 shows a 76.9% yield of hexitols, which is the best obtained so far in the hydrolytic hydrogenation of microcrystalline cellulose over Ni-based catalysts. Furthermore, the yield of hexitols remained greater than 55% after the catalyst was reused for 4 times. The results showed that PtNi nanoparticles were formed with a Pt-enriched alloy surface as confirmed by XRD, H<sub>2</sub>-TPR (temperature-programmed H<sub>2</sub> reduction), XPS (X-ray photoelectron spectroscopy), and H<sub>2</sub>-TPD (temperature-programmed H<sub>2</sub> desorption). The surface features of these nano-particles were characterized by CO-TPD (temperature-programmed CO desorption), CO-FTIR (CO adsorption FTIR spectroscopy), HRTEM (high resolution TEM), and O<sub>2</sub>-TPO (temperature programmed oxidation) and this special surface structure may be responsible for the high activity, selectivity, and stability in the hydrolytic hydrogenation of cellulose in hot-compressed water.

### Introduction

Cellulose is the most abundant biomass resource in the world, and because of the depletion of fossil energy and rise in environmental pollution, the process of catalytic conversion of cellulose into fuels and chemicals has received increased attention.<sup>[1]</sup> One-pot conversion of cellulose into useful polyols in hot-compressed water by means of a hydrolytic hydrogenation process is considered to be one of the promising pathways of cellulose utilization because of the versatile uses of polyols as platform chemicals in the energy chemical industry, polymer synthesis, pesticide and medicine synthesis industries.<sup>[2]</sup>

It is well known that the selectivity to polyols in the hydrolytic hydrogenation of cellulose significantly depends on the type of active metal component used. For example, over supported noble-metal catalysts, such as Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/ZSM-5 (zeolite socony mobil–5), Ru/C, Ru/CNTs, and Ru/H-USY catalysts, hexitols (sorbitol and mannitol) were obtained as major products;<sup>[3]</sup> on using nickel-promoted tungsten carbide or physical-

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ly mixed WO<sub>3</sub> and Ru/C catalysts, high yields of ethylene glycol and/or propylene glycol were achieved.<sup>[4]</sup> Modified Ni-based catalysts, such as reshaped Ni particles on carbon nanofibers and nickel phosphide on activated carbon, were also reported to enhance the yield of hexitols.<sup>[5]</sup> Monometallic Ni catalysts with various supports gave poor yields to hexitols because hexitols readily underwent the subsequent hydrogenolysis into C<sub>2</sub>-C<sub>3</sub> polyols.<sup>[6]</sup> Our previous work demonstrated that the activity and selectivity of Ni/ZSM-5 could be tuned by changing the microstructure of nickel particles; petaloid-like nickel particles within ZSM-5 zeolite exhibited 58.1% yield of hexitols at 85.9% conversion, comparable to the best result obtained with Rh-modified Ni catalysts (58.9% yield of hexitols).<sup>[6b]</sup> In addition to the intrinsic activity of the metal, the reaction temperature also played an important role in the polyols yield. For example, the hydrogenolysis of hexitols occurs smoothly with various Ru or Ni catalysts at 150-200°C; at higher temperatures over 230°C, however, poor yield of hexitols was obtained.

High temperature (always > 230 °C) is essential for the fast depolymerization of crystalline region in cellulose in aqueous phase. However, Ni-based catalysts were readily deactivated in the presence of water. Thus, it is of great importance to develop an active Ni catalyst with high hydrothermal stability in hot-compressed water. The present work examines the performance of various monometallic and bimetallic catalysts supported on ZSM-5 and carbon materials in the hydrolytic hydrogenation of microcrystalline cellulose (MCC). A high yield of hexitols of 76.9% can be achieved with a PtNi/ZSM-5 catalyst at complete conversion of MCC. Furthermore, a good yield of

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hexitols >55% can still be obtained after the catalyst was reused 4 times. The excellent performance of this catalyst observed may be explained by the function of the PtNi alloy formed on the surface of bimetallic nanoparticles supported on ZSM-5.

The effects of metal alloying on the electronic structure as well as on the catalytic properties have been studied by B. Hammer and J. K. Nørskov by means of density functional theory (DFT) calculations.<sup>[7]</sup> According to their research, the dband center of a noble metal shifts relative to the Fermi level when the metal forms a monolayer on (or is alloyed into) the top of the first layer of Ni (1 1 1). Table 1. The hydrolytic hydrogenation of microcrystalline cellulose on Ni-based catalysts and other noble metal catalysts<sup>[a]</sup>

Entry	Catalyst	Conversion [%]	Carbon efficiency <sup>[b]</sup> [%]	Yield [%]				Ref.
				Hexitols	Glycerol	EG	PDO	
1	Ni/ZSM-5	100	58.4	52.7	1.4	3.2	1.1	
2	PtNi/ZSM-5	100	86.0	76.9	6.1	2.3	0.7	
3	Ru-Ni/ZSM-5	100	63.2	55.6	4.6	2.0	1.0	
4	Pd-Ni/ZSM-5	100	64.1	58.9	2.6	1.8	0.8	
5	Rh-Ni/ZSM-5	100	68.3	60.6	2.5	2.0	0.7	
6	Ir-Ni/ZSM-5	100	61.5	49.2	9.1	2.3	1.2	
7	Ru/ZSM-5	100	49.2	26.2	17.3	2.7	3.0	
8	Pt/ZSM-5	100	12.0	1.5	0.7	5.1	4.7	
9	Pd/ZSM-5	100	17.2	2.3	2.2	5.6	7.1	
10	Rh/ZSM-5	100	19.7	1.9	2.5	7.2	8.1	
11	lr/ZSM-5	100	13.2	0.3	1.7	9.3	1.9	
12	10%Ni2.9%P/C	92	-	66.5	-	0.9	0.7	[5a]
13 <sup>[c]</sup>	7.5 %Ni/CNF	93	-	75.6				[5b]
14	1 %Rh5%Ni/MC	100	-	58.5	5.4	5.3	3.5	[8a]

[a] 240 °C, 4.0 MPa H<sub>2</sub>, 0.3 g micrycrystalline cellulose, 10 mL H<sub>2</sub>O, 4 h, 0.1 g catalyst, Ni loading 17 wt%, M loading 1 wt% (M=Ru, Pt, Pd, Rh, and Ir). [b] The carbon efficiency was calculated by the ratio of moles of carbon in the polyols to moles of carbon in the cellulose. [c] Ball-milled cellulose, 190 °C, 24 h.

The variation in the position of d-band center will significantly change the reactivity of the alloy surface.<sup>[7d,e]</sup> Our previous study demonstrated that hydrogenolysis was the main reason for the loss in the yield of hexitols in the hydrolytic hydrogenation of cellulose over Ni catalysts at high temperature.<sup>[6b]</sup> In the present work, we introduce the noble metals (Ru, Pd, Pt, Rh, Ir) to monometallic Ni/ZSM-5 to modify the surface electronic and chemical properties of Ni particles, aiming at designing a catalyst that is highly active for hydrogenation but inactive for the undesired hydrogenolysis.

# **Results and Discussion**

### Catalytic performance of Ni-based catalysts

Microcrystalline cellulose was treated at 240 °C and 4.0 MPa H<sub>2</sub> for 4 h without any pretreatment, in order to evaluate the activity of the catalysts prepared at harsh reaction conditions. Table 1 shows the catalytic performance of various Ni-based bimetallic catalysts at almost complete cellulose conversion. Besides the hexitols yield, carbon efficiency is also used to evaluate the performance of the catalysts in converting cellulose into the target polyols in aqueous phase. All the noble-metal-modified bimetallic catalysts, except for IrNi/ZSM-5 (1 wt% Ir and 17 wt% Ni), gave enhanced hexitols yields in an order of IrNi/ ZSM-5 < RuNi/ZSM-5 < PdNi/ZSM-5 < RhNi/ZSM-5 < PtNi/ZSM-5. The PtNi/ZSM-5 showed a 76.9% yield of hexitols, which is the best obtained so far in the hydrolytic hydrogenation of MCC over Ni-based catalysts. As a comparison, corresponding monometallic noble metal catalysts were also tested and the results are also shown in Table 1. Very low yields of hexitols (< 3%) and low carbon efficiencies were obtained over ZSM-5 supported Pt, Pd, Rh, and Ir catalysts, while Ru/ZSM-5 gave 26.2% yield of hexitols and 49.2% of carbon efficiency, which are consistent with the data reported in the literature.<sup>[3d]</sup>

Fast deactivation is the most serious problem for Ni catalysts used in hot-compressed water.<sup>[8]</sup> Zhang et al. reported that the MC-supported IrNi bimetallic catalysts gave about 45% yield of hexitols after four recycles.<sup>[8a]</sup> The synergistic effect of bimetallic MNi (M=Rh, Ir, Pd, Pt, Ru) catalysts is expected to be responsible for the durability under hydrothermal conditions. Herein, the recycling of the PtNi/ZSM-5 catalyst was tested and the results are shown in Figure 1. The yield of hexitols was 76.9% in the first reaction run, it decreased to 63.7% in the



Figure 1. The reuse of PtNi/ZSM-5 catalysts in cellulose conversion. Reaction conditions: 0.3 g microcrystalline cellulose, 10 mL water, 4.0 MPa initial  $H_2$  pressure at RT, 240 °C, 4 h, 0.1 g PtNi/ZSM-5 catalyst (1% Pt and 17% Ni)

second run, and then it changed very slightly in the following recycles. Thus, the PtNi/ZSM-5 catalyst showed a good stability for the hydrolytic hydrogenation of MCC in hot-compressed water.

### PtNi alloy on PtNi/ZSM-5 catalyst

Since noble metal modified Ni catalysts presented promising activity and stability in the hydrolytic hydrogenation of microcrystalline cellulose, these catalysts were characterized by different methods to find factors responsible for the promoting effect of noble metals added.

The reducibility of the bimetallic and monometallic catalysts was examined by  $H_2$ -TPR. As shown in the TPR profiles (Figure 2), the major reduction peaks for all the bimetallic Ni



Figure 2. H<sub>2</sub>-TPR profiles of ZSM-5 supported Ni-based bimetallic catalysts.

catalysts appeared at lower temperatures compared with that of Ni/ZSM-5, indicating that the reduction of NiO was promoted by the addition of noble metals. This promoting effect is due to the hydrogen spillover; the dissociated hydrogen species moved from noble metal to the surface of NiO. Moreover, the reducibility of surface species varied with the kind of the noble metals added. More than two reduction peaks were found for the bimetallic catalysts, except for PtNi/ZSM-5, on which only one single symmetrical peak was observed. According to the study of Beltramini et al., the single symmetrical peak suggests that PtNi alloy was formed homogeneously.<sup>[9]</sup> It is also concluded that a homogeneous reduction is due to the close interaction of platinum with nickel cluster.

Figure 3 shows the XRD patterns of reduced monometallic and bimetallic PtNi catalysts before and after use in the reaction. In the case of PtNi/ZSM-5, the (1 1 1) and (2 0 0) diffrac-





Figure 3. XRD patterns of Ni-based catalysts.

tion peaks of  $Ni^0$  became broader and shifted to lower  $2\theta$ values and no specific diffraction peaks of Pt was detected. This indicated that PtNi alloy was formed; the Pt existed in the form of PtNi alloy but not in monometallic Pt particles.<sup>[10]</sup> Moreover, the size of metal particles decreased to 13 nm in the presence of Pt, indicating that the addition of Pt resulted in a higher dispersion of the PtNi particles. It should be noted that the qualitative determination of the Pt/Ni ratio in a quite diluted PtNi alloy (theoretical Pt/Ni is 0.018) by Vegard's law is not accurate because the error of lattice constant estimated from XRD patterns is quite large. Therefore, the morphology and size distribution of alloy particles was estimated by TEM. From a TEM image in Figure 4a, the average size of PtNi particles is 8.4 nm, which is much smaller than the results of XRD. The TEM images showed that more than 35% of alloy particles were in a range of particle size less than 6.5 nm, much smaller than that calculated from XRD. The HRTEM (high resolution TEM) image and the corresponding fast fourier transform pattern (inset image) of a single PtNi alloy particle is given in Figure 4. The lattice fringes with a distance of 0.218 nm was detected, which is larger than the (1 1 1) interplanar spacing of Ni (0.203 nm). The increase in interplanar spacing is probably caused by the effect of alloying of Pt and Ni. On the other hand, the EDX (energy dispersive X-ray spectroscopy) spectra taken from three randomly chosen points (A-C in Figure 4)

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Figure 4. TEM images and corresponding particle size distribution (insets) of PtNi/ZSM-5 catalyst.

showed the co-existence of Pt and Ni in these particles with different Pt/Ni ratio (as shown in Figure S1), revealing that a random fcc alloy was formed.

Figure 5 shows the XPS (X-ray photoelectron spectroscopy) spectra for the reduced PtNi/ZSM-5 catalyst; the binding energy of Pt 4d  $_{5/2}$  was 315.0 eV, suggesting that no shift was observed with respect to metallic Pt. These results suggest the absence of electron transfer between Pt and Ni.<sup>[11]</sup> The Pt/Ni surface ratio was 0.087 as calculated from the intensity of the corresponding peaks, which was about 5 times larger than the theoretical value (0.018) in the bulk. The migration of Pt onto the topmost surface generally occurred in the process of reduction.<sup>[12]</sup> The surface of PtNi alloy particles is likely to be enriched with Pt. The formation of a Pt-enriched PtNi alloy surface, rather than a homogeneous solid solution in the bulk, was further confirmed by the XPS spectra after Ar<sup>+</sup> sputtering; the Pt 4d<sub>5/2</sub> signal became negligible, while the intensity of the Ni 2p<sub>3/2</sub> peak still remained (Figure 5).



**Figure 5.** XPS profiles of a) Ni 2p and b) Pt 4d for PtNi/ZSM-5 catalyst as a function of the Ar<sup>+</sup> sputtering time.

#### Chemisorption properties of PtNi alloy

These results demonstrated that the Pt-enriched PtNi alloy was formed, and this is probably the primary reason for the enhanced hydrogenation activity of PtNi/ZSM-5. The PtNi alloy introduced surface heterogeneity that generated exceptional active sites for hydrogenation. Such an alloy effect has been in particular studied by using in situ CO-FTIR, temperature-programmed H<sub>2</sub> desorption (H<sub>2</sub>-TPD), and CO temperature-programmed desorption (CO-TPD) in the present work.

An FTIR study of CO adsorption behavior was performed on the bimetallic PtNi/ZSM-5 catalyst as well as the monometallic Pt and Ni catalysts, and is shown in Figure 6. For Pt/ZSM-5, a large absorption band at 2089 cm<sup>-1</sup> is assigned to the terminal carbonyls at electron-deficient Pt clusters inside the highly acidic zeolite matrix.<sup>[13]</sup> For Ni/ZSM-5, the bands at 1953 and 1890 cm<sup>-1</sup> were associated with bridging species on Ni<sup>0</sup> nanoparticles.<sup>[14]</sup> For PtNi/ZSM-5, the spectra of surface species arising from CO adsorption is different from Ni/ZSM-5 and Pt/ ZSM-5, indicating that the bonding geometries of CO adsorption on PtNi/ZSM-5 changed significantly as the Pt-enriched alloy surface was formed. According to previous studies, (1 1 1) and (1 0 0) surfaces tend to be Pt-enriched.<sup>[15]</sup> The band at 1902 cm<sup>-1</sup> might be assigned to bridging species on Pt (1 1 1) or (1 0 0) alloy surfaces.

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Figure 6. FTIR spectra of CO adsorption on Pt/ZSM-5, Ni/ZSM-5, and PtNi/ZSM-5 catalyst with N $_2$  purging for 30 min at 30  $^\circ\text{C}.$ 

The PtNi alloy surface was further examined by CO-TPD. As shown in Figure 7, the peaks can be categorized in two broad regions  $(\alpha, \beta)$  for all the catalysts. All the samples presented a peak in the  $\alpha$  region. According to literature,<sup>[9a]</sup> the desorption peak in the  $\alpha$  region originates from a single site for CO chemisorptions, while the peaks in the  $\beta$  region are assigned to two-site chemisorptions. For Pt/ZSM-5, the large peak in the  $\alpha$  region is likely to be due to desorption of terminal carbonyl of CO on Pt as observed in the IR spectra, and the weak peak in the  $\beta$  region is attributed to the bridging species. From the CO-FTIR and CO-TPD results, the single site chemisorption is dominant on Pt/ZSM-5. For Ni/ZSM-5, three peaks presented at 360, 433, and 497 °C in the  $\beta$  region, and were assigned to the desorption from two-site chemisorptions, in agreement with the existence of bridging species on Ni/ZSM-5 at low coverage  $(N_2 purging for 20 min).$ 



Figure 7. CO-TPD profiles of PtNi/ZSM-5, Ni/ZSM-5, and Pt/ZSM-5 catalysts.

As compared to the two monometallic catalysts, PtNi/ZSM-5 gave a smaller desorption peak in the  $\alpha$  region, indicating that the Pt-enriched alloy surface presented the lower CO adsorption capability. Moreover, a broad peak in the  $\beta$  region (320– 590 °C) is also observed over PtNi/ZSM-5. This peak is attributed to the Ni-like surface sites. It is clearly seen that the peak area in the  $\beta$  region is smaller compared to Ni/ZSM-5, suggesting the decrease in two-site chemisorption. According to the DFT calculations for many combinations of catalytically interesting metals reported by J. K. Nørskov et al, when a Pt monolayer forms on top of (or is alloyed into) the first layer of Ni (111), the d-band center of Pt relative to the Fermi level shifts down by 0.80 eV.<sup>[7c]</sup> It is well established that a downshift of the d-band center of metal atoms increases the occupancy of the antibonding states, thus weakening the adsorption and dissociation energy of a probe molecule (CO, N<sub>2</sub>, and other adsorbates). This may explain the differences in the CO adsorption and desorption among the bimetallic and monometallic catalysts observed in the present work.

 $H_2$ -TPD profiles of the catalyst samples are shown in Figure 8. A very weak desorption peak at 411 °C found on Ni/



Figure 8. H<sub>2</sub>-TPD profile of PtNi/ZSM-5, Ni/ZSM-5, and Pt/ZSM-5 catalysts.

ZSM-5 is due to the high Wheatstone bridge current value (100 mA) used in the TCD (thermal conductivity detector). This peak is attributed to the Ni sites covered by spillover hydrogen.<sup>[16]</sup> Two kinds of active sites are present on the PtNi/ZSM-5 as the two desorption peaks were observed at 201°C and at 362°C. The former peak is associated with the Pt-enriched alloy surface having Pt-like desorption behavior because the desorption peak on PtNi/ZSM-5 (204°C) is almost the same as that on Pt/ZSM-5 (190°C). The latter peak is assigned to the Ni-like sites covered by spillover H species migrating from the PtNi surface alloy. It is clearly seen that the peak area related to spillover H species is significantly large compared to Ni/ZSM-5. The formation of PtNi alloy should promote the dissoci-

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ation of molecular hydrogen on the Pt atom and the subsequent hydrogen spillover on PtNi/ZSM-5.

#### Relationship between catalytic activity and structure

Accordingly, the relationship between the catalytic performance and the nature of PtNi alloy is discussed. A 76.9% yield of hexitols was obtained on PtNi/ZSM-5 which is higher than the 52.7% obtained on Ni/ZSM-5 at similar conversion levels, indicating that the presence of Pt-enriched alloy surface could significantly enhance the selectivity to hexitols. Recently, we reported that the selectivity of hexitols depended on the hydrogenation and dehydrogenation activity of the catalyst.<sup>[17]</sup> Both high hydrogenation activity and low dehydrogenation activity are essential for high hexitols selectivity. The low dehydrogenation activity of ZSM-5-supported Ni-based catalyst is expected because of the lack of acid-base pair sites on the zeolite (As shown in Figure S2). In addition, PtNi/ZSM-5 presents much higher hydrogenation activity compared to Ni/ZSM-5. The  $H_2$ -TPD of PtNi/ZSM-5 shows that more H species migrate from the Pt-like sites to the Ni-like ones, which means that more activated hydrogen species can participate in glucose hydrogenation. Moreover, the metal particle dispersion on PtNi/ZSM-5 is higher than that on Ni/ZSM-5 and this is another reason for the higher hydrogenation activity of PtNi/ ZSM-5 catalyst.

For Ni/ZSM-5 catalyst, the hexitols yield reached 52.7% with 100% conversion but the complete loss of activity is observed in the second recycle, indicating that the deactivation of the monometallic Ni/ZSM-5 occurred during the reaction. The XRD pattern of the spent catalyst reveals that the nickel particles increase from 21 nm to 29 nm (Figure 9), but the growth of nickel particles was not so significant after reaction. The ICP analysis of the reaction solution shows that about 10% nickel was leached out under a hydrothermal condition at 240°C. However, it is unreasonable to attribute the complete deactivation of Ni/ZSM-5 catalyst to the partial leaching of Ni species or the agglomeration of nickel nanoparticles, which was considered to be the primary reason for the deactivation of Ni/W/ SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.<sup>[18]</sup>Very recently, Fukuoka et al demonstrated that the



Figure 9. XRD pattern of reused PtNi/ZSM-5 and Ni/ZSM-5 catalysts.

oxidation of surface Ni atoms was the major cause of deactivation.<sup>[19]</sup> We demonstrated that the reaction of metallic nickel with water-forming crystalline Ni(OH)<sub>2</sub> was the main reason for deactivation of Ni catalysts in aqueous phase.<sup>[20]</sup> Thus, the high oxidation resistance is crucial for the stability of the Ni catalysts in aqueous-phase reaction. Herein, the features of the oxidation of the catalysts were examined by O<sub>2</sub>-TPO (temperature programmed oxidation, Figure 10). Negative peaks observed at



Figure 10. O<sub>2</sub>-TPO profile of PtNi/ZSM-5, Ni/ZSM-5, and Pt/ZSM-5 catalysts.

low temperatures (about 200 °C) are caused by oxygen released from metal lattices. A positive peak at high temperature (300–450 °C) is the consumption of oxygen by metal nanoparticles; the PtNi/ZSM-5 catalyst presents an oxidation peak at a higher temperature compared to Ni/ZSM-5. This indicates that the Pt-enriched alloy surface may have a higher resistance to oxidation. The Pt-enriched alloy surface could inhibit the oxidation of metallic Ni and suppress the leaching of the active Ni species; this can be confirmed by the XRD results, which show that no Ni(OH)<sub>2</sub> phase was detected for the used PtNi/ZSM-5 catalyst.

ICP analysis showed that about 0.8% Ni was leached out and no Pt was detected in the reaction solution after the first run. The slight increase in particle size of metallic Ni particles (from 13 to 16 nm based on XRD in Figure 9) was observed from the TEM and XRD results for the used catalyst (Figure 9 and S3); this is responsible for the considerable activity loss in the second run. The Pt-enriched alloy surface had higher resistance to oxidation; this is the major reason for the high stability of PtNi/ZSM-5 in hot-compressed water in the following runs.

### Conclusions

The bimetallic PtNi/ZSM-5 shows high activity, selectivity, and stability in the hydrolytic hydrogenation of cellulose in hotcompressed water. Pt-enriched alloy surface is formed on PtNi/ ZSM-5 catalyst, which has weak adsorption ability to CO. A downshift of the d-band center of Pt occurs as a result of the formation of Pt-enriched alloy surface, and is responsible for the poor CO adsorption on the PtNi alloy surface. The main cause of the enhanced hydrogenation activity is the higher dispersion of PtNi alloy particles and the remarkable hydrogen spillover from the alloy surface to the working Ni sites. The Ptenriched alloy surface could inhibit the oxidation of metallic Ni and suppress the leaching of active Ni species; this results in excellent hydrothermal stability. Such an alloy surface has promising practical applications in the hydrogenation reaction of biomass-derived chemicals under hydrothermal conditions.

### **Experimental Section**

The catalysts were prepared by a modified impregnation method. ZSM-5 (NKF-5, H type, Si/Al=25, Catalyst Plant of Nankai University) was impregnated into an aqueous solution of Ni(NO3)<sub>2</sub> (AR, Sinopharm Chemical) and noble metal chlorides (H<sub>2</sub>PtCl<sub>6</sub>, RuCl<sub>3</sub>, H<sub>2</sub>PdCl<sub>4</sub>, IrCl<sub>3</sub>, and RhCl<sub>3</sub>, Sinopharm Chemical), followed by drying at 70 °C for 12 h. The samples were calcined in N<sub>2</sub> at 450 °C and then reduced at 360 °C for 2 h. The loading of Ni was 17 wt% and that of the other noble metals were 1 wt%.

Cellulose (Alfa Aesar, microcrystalline) was hydrogenated in water (10 mL) in a teflon-lined stainless autoclave (30 mL) at 240 °C and 4.0 MPa H<sub>2</sub> (RT) for 4 h. The conversion was determined by the change of solid weight before and after the reaction. The products were analyzed by HPLC system (Shimadzu LC-20 AB) with RI detector (Shimadzu RID-10 A) and an Aminex HPX-87H column (Bio-Rad,  $300 \times 7.8$  mm), using 5 mM H<sub>2</sub>SO<sub>4</sub> as eluent at a flow rate of 0.7 mLmin<sup>-1</sup>.

XRD was recorded on a Bruker D8 Advance X-ray diffract meter with a Cu<sub>Ka</sub> source ( $\lambda$ =0.154 nm) in the 2 $\theta$  range 10–80° with a scan speed of 10° min<sup>-1</sup>. H<sub>2</sub>-TPR, H<sub>2</sub>-TPD, and CO<sub>2</sub>-TPD were conducted on a Tianjin XQ TP-5080 chemisorption instrument with a thermal conductivity detector (TCD). TEM images were taken with a JEOL JEM-2010 instrument with an accelerating voltage of 200 kV. The in situ IR spectroscopic study was recorded on a Bruker V 70 spectrometer. Typically, 100 scans were recorded at a resolution of 4 cm<sup>-1</sup> using an MCT detector. XPS were performed using XPS (VG Microtech 3000 Multilab). Binding energy (BE) values were referenced to the binding energy of the C 1 s core level (284.8 eV).

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