Synthesis of a nano-nickel catalyst modified by ruthenium for hydrogenation and hydrodechlorination

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ABSTRACT

A nano-nickel catalyst was prepared by chemical reduction with $N_2H_4 \cdot H_2O$, and was modified with ruthenium by chemical replacement. The nano-Ni and NiRu catalysts were characterized by X-ray diffraction, transmission electron microscope, and X-ray photoelectron spectroscopy. The catalysts were evaluated in the liquid phase hydrogenation of cinnamaldehyde and hydrodechlorination of chlorobenzene. The NiRu catalyst exhibited a much higher selectivity to the hydrocinnamaldehyde and a better hydrodechlorination activity and stability than those of the Ni catalyst.

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1. Introduction

Nickel catalyst has been of great interest due to its applications, such as hydrogenation, hydrodechlorination, and hydrotreating reactions [1]. Its catalytic activity, selectivity and stability were promoted by adding other metals [2]. Wang et al. modified a bulk nickel catalyst with Pd or Pt by replacement reaction [3–5]. They found that a metal, Pd or Pt, could disperse on the surface of Ni metal to form a monolayer-dispersed bimetallic system because of the formation of bonds between the two metals [3–5]. Such monolayer-dispersed bimetallic system promoted the hydrogenation activity of nickel catalysts greatly. However, the nickel catalyst used was prepared by the hydrogen reduction of nickel oxide at a high temperature, which could result in a larger particles size and smaller surface area. Here, we synthesized a nano-nickel with uniform size by a modified hydrazine reduction route [6].

The NiRu bimetallic catalysts were excellent catalysts for various reactions, such as hydrogenation [7–9], oxidation [10,11], reforming reactions [12,13], and hydrodechlorination [14]. Unlike the formation of a solid solution or compound between Ni and Pd or Pt, Ni and Ru could not react to form a solid solution or compound [7–14]. In this paper, the as-prepared nano-Ni particles were modified by Ru via a replacement reaction to study the effect of Ru on the catalytic properties of nano-Ni catalyst. The replacement reaction is defined as a reaction of a metal ion with a more

reactive metal solid. As it has been confirmed that the catalytic activity of mono Ni catalyst could be promoted greatly by the surface modification [3–5], the as-prepared catalysts were evaluated by the selective hydrogenation of cinnamaldehyde (CAL) and hydrodechlorination (HDC) of chlorobenzene for studying the effect of surface modification on the catalytic selectivity and stability.

2. Experimental

2.1. Catalyst preparation

The nano- nickel catalyst was prepared with 4.0 g $NiCl_2 \cdot 6H_2O$ dissolved in 30.0 ml ethanol solution and 10.0 g 80 wt.% $N_2H_4 \cdot H_2O$ alkaline solution containing 10.0 g NaOH and 10.0 ml distilled water. The reaction, with stirring, lasted for several hours until there were no bubbles released any more at room temperature. The obtained black nano-nickel catalyst was washed with distilled water till pH = 7, then washed with absolute alcohol to remove water and kept in absolute alcohol. The NiRu catalyst was prepared by replacement reaction with the as-prepared nano-nickel catalyst and a 1 g/100 ml $RuCl_3$ aqueous solution for 4 h. The chemical replacement reaction can be described as reaction in the following equation:

$$Ni + xRu^{3+} \rightarrow 1.5xNi^{2+} + Ni_{1-1.5x}Ru_x \qquad (1)$$

Firstly, some amount of nano-nickel was added into a $RuCl_3$ aqueous solution. Then, a redox reaction occurred between Ru^{3+} ions and Ni metal as reaction (1). The Ni^{2+} ions were gradually formed,

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and Ru^{3+} ions were reduced to Ru atoms and deposited on the surface of nano-nickel. The loading of Ru on the nano-nickel catalyst was 1.0 wt.%. For comparison, polyvinylpolypyrrolidone (PVP) supported Ru catalyst was also prepared. PVP (K-30) was added to a 1 g/100 ml $RuCl_3$ solution (N/Ru = 20, molar ratio), then the mixture was reduced by KBH_4.

2.2. Catalyst characterization

The chemical compositions of the samples were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) on an IRIS Intrepid spectrometer. The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max 2500 X-ray diffractometer (Cu Kα, λ = 1.54178 Å). Transmission electron microscope (TEM) images were acquired using a FEI Tecnai G2 high resolution transmission electron microscopy operating at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis of the catalysts was carried out using a Kratos Axis Ultra DLD spectrometer employing a monochromatic Al Kα source, hybrid magnetic/electrostatic optics, and a multi-channel plate and delay line detector (DLD). The surface of the samples was etched with Ar^+ ions for 10 min prior to remove the oxidized layer.

2.3. Catalyst testing

The hydrogenation of cinnamaldehyde was performed at 100 °C and 1.5 MPa of hydrogen pressure with stirring at 800 rpm for 3 h in a 250 ml stainless steel autoclave which contained 1.0 g catalyst, 20.0 ml CAL and 100.0 ml ethanol.

The HDC of chlorobenzene was carried out in a 100 ml stainless steel autoclave containing 1.0 g catalyst, 10.0 mmol of chlorobenzene, 50.0 ml of ethanol, and 0.5 g NaOH for adjusting pH value to ∼14. The HDC reaction was performed at 90 °C with stirring at 800 rpm to eliminate external diffusion. The hydrogen pressure in all experiments was 1.0 MPa. For comparison, the Ru/PVP containing 0.01 g Ru was also used in both hydrogenation and HDC reactions. All the products were analyzed by a gas chromatograph equipped with a flame ionization detector.

3. Results and discussion

The XRD patterns of as-prepared nano-Ni and NiRu catalysts are shown in Fig. 1. Three peaks centered at 2θ = 44.39, 51.72 and 76.46 are corresponding to the characteristic (111), (200) and (220) crystallographic planes of metallic nickel with a FCC structure (PDF No 65-0380). There is hardly any difference between
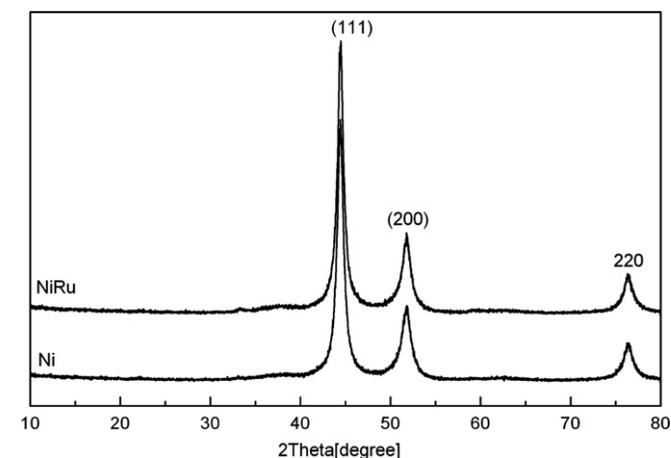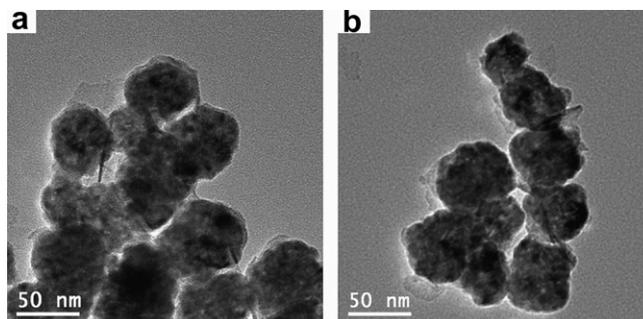

Fig. 2. TEM morphologies of the samples. (a) nano-nickel and (b) NiRu.

Ni and NiRu samples from the XRD patterns, which indicates that the Ru species is highly dispersed in the NiRu sample. The TEM images (Fig. 2) show that the mean sizes of the Ni and NiRu particles are around 50 nm. The size of the NiRu particles is not obviously changed in comparison with that of the Ni particles. Ruthenium is hardly observed in Fig. 2b due to its low loading and high dispersion, which is in accordance with the result of the XRD pattern.
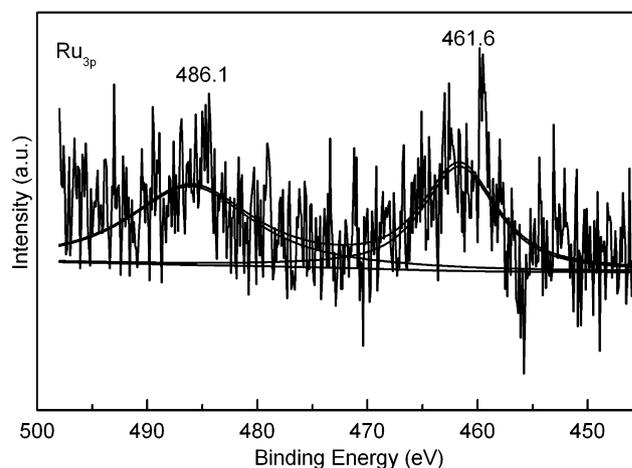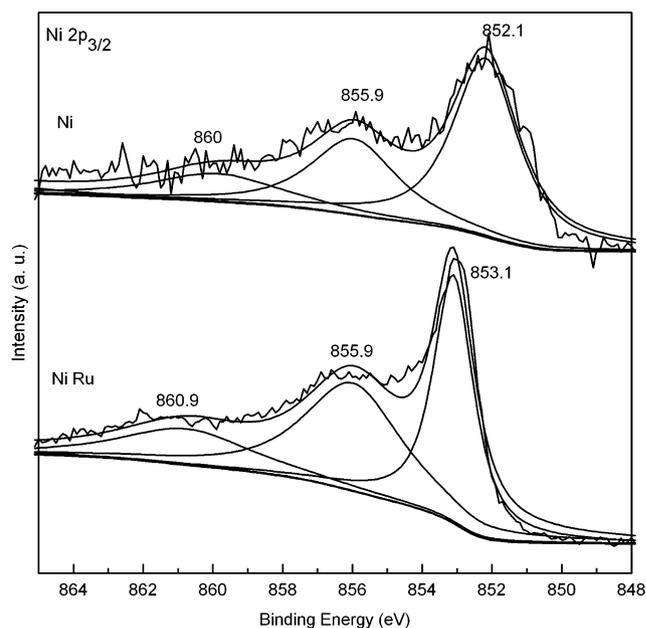

Fig. 3. Ni 2p and Ru 3p XPS spectra of the nano-nickel and NiRu catalysts.

Fig. 1. XRD patterns of the nano-nickel and NiRu catalysts.

Fig. 3 shows the XPS spectra of Ni and NiRu catalysts. As shown in the spectra of Ni 2p$_{3/2}$, the Ni species are present in two states for the Ni sample, the metallic state with the binding energy (BE) of 852.1 eV (satellite peak at 860 eV) similar with the reported BE value of 852.2 eV [15], and the oxidized state (NiO) with the BE of 855.9 eV. After the replacement reaction of Ni by Ru, the BEs of Ni increase to 853.1 and 860.9 eV. The Ru species is present in metallic state with the BE of 461.6 eV in Ru 3p$_{3/2}$ level and 486.1 eV in Ru 3p$_{1/2}$ level. In comparison with the standard BE of 462.2 eV [16], the BE of Ru 3p$_{3/2}$ decreases 0.6 eV. This suggests that Ni atoms transfer electrons to Ru atoms, resulting in Ni metal with deficient electrons while Ru metal with enriched electrons. The electron-deficient Ni centers are favorable for the hydrogen dissociative chemisorption [17] and the hydrogen is activated by adsorbing on the electron-deficient nickel atoms [18]. It has been reported that in the hydrogenation, a decreased electron density on nickel strengthens the adsorption strength of the reactants, resulting in the promotion of self-poisoning effects by the adsorbed reactants. The catalytic activity is dependent on the amount of the nickel species in the different electronic states on the surface [18]. The electronic transformation enhances the interaction between the Ni and Ru, thus improves the catalytic properties of the NiRu bimetallic catalysts. Furthermore, since the d-band center position is a general measure of surface reactivity, both the chemisorption energies and activation barriers are lowered as the d-band center of Ni shift up [14].

The selective hydrogenation of a C=C bond or a C=O bond in a molecule with both the C=C and C=O bonds is important for the preparation of fine chemicals [19]. An example is the selective hydrogenation of CAL. CAL is a vinylogue of benzaldehyde, and the aldehyde group behaves with catalysts as if it is an aromatic aldehyde. This carbonyl group is reduced easily and competes with saturation of the carbon–carbon double bond [19,20]. The hydrogenation of CAL leads to a mixture of hydrocinnamaldehyde (HCMA, C=C bond hydrogenation), cinnamyl alcohol (CMO, C=O bond hydrogenation) and phenylpropanol (PP) [19].

The results of CAL catalytic hydrogenation are shown in Fig. 4. It can be found that the conversion of CAL on the Ni catalyst is the highest up to 94.2%. The Ru catalyst has the highest selectivity to the HCMA while the lowest conversion. After depositing Ru on Ni by the replacement reaction, the activity of NiRu catalyst is similar with nano-nickel catalyst, but its selectivity of HCMA is promoted greatly. The catalytic conversion on the NiRu catalyst
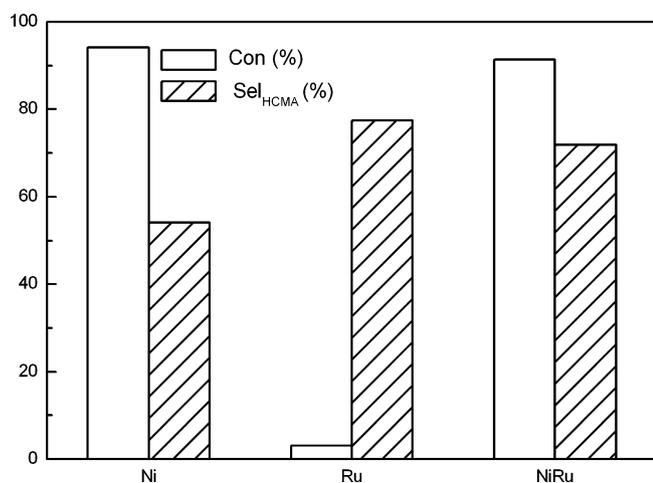
Table 1
HDC activities of fresh and recycled catalysts

Samples	First	Recycle 1	Recycle 2	Recycle 3	Recycle 4
Ni	43%	42%	38%	32%	–
Ru/PVP	21%	21%	17%	–	–
Mixture of Ni and Ru/PVP	56%	56%	47%	–	–
NiRu	76%	76%	74%	75%	71%

decreases somewhat to 91.3%, while the selectivity of HCMA increases from 54.1% to 71.9% comparing with that of Ni catalyst. The results suggest that the selectivity of HCMA is promoted by the surface interaction of Ni and Ru (Fig. 3). It has been reported that the modification of Ni surface with other metal, such as Au or Rh, could promote its catalytic activity and stability [21,22]. However, the CAL hydrogenation shows that the selectivity can also be promoted by the electron transformation from the Ni to the Ru atoms. Then, the NiRu bimetallic catalyst was applied in the HDC of chlorobenzene, in which the catalyst was always deactivated by the adsorption of Cl species [23–25]. Table 1 shows that the conversion of chlorobenzene increases from 43% to 76% when Ni is modified by Ru, higher than total conversion for the mixed catalyst of Ni and Ru/PVP with the same content of metals. The conversion for Ni catalyst decreases to 32% when it was recycled for three times, while the conversion for NiRu catalyst is 71% after four times recycle. This suggests that NiRu catalyst exhibits better HDC activity and stability. And it could be explained by that the electron-deficient Ni particles are more resistant to chlorine attack as the chlorine is weakly adsorbed due to its electrophilic character [25].

4. Conclusions

The nano-Ni catalyst was modified by Ru metal via a replacement reaction. The XRD patterns and TEM characterization showed that the Ru was dispersed homogeneously over nano-Ni. The interaction between Ni and Ru occurred by transferring electrons from Ni to Ru atoms according to XPS characterization. This interaction improved the selectivity of HCMA for the CAL hydrogenation, and activity and stability for the HDC of chlorobenzene.

Acknowledgements

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Fig. 4. Hydrogenation activity and selectivity of cinnamaldehyde on different catalysts.

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