

Synthesis of a supported nickel boride catalyst under microwave irradiation

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Abstract

Supported nickel boride (Ni–B) catalysts were prepared by a silver-catalyzed electroless plating method under microwave irradiation. Two solvents of plating solution, water and ethylene glycol, were used to study the effect of microwave irradiation on plating. The Ni–B catalysts were characterized by X-ray diffraction, transmission electron microscopy, and X-ray photoelectron spectroscopy. Their catalytic performances were evaluated by hydrogenation of acetophenone. The results showed that the particle size and load of Ni–B increased much more under microwave irradiation, when the water was used as solvent. The supported Ni–B catalyst prepared from ethylene glycol bath exhibited higher catalytic activity and selectivity in the hydrogenation, due to its higher boron content in Ni–B particles.

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1. Introduction

Metal boride catalyst has attracted much attention over the past 50 years, due to its refractory nature, resistance to sulfur poisoning, desulphurization ability in organic synthesis, and catalytic properties [1,2]. Among various metal borides, nickel boride (Ni–B) is regarded as a potential industrial catalyst for hydrogenation reactions [3,4]. Ni–B nanoparticles are deposited on various supports to prepare supported catalysts, which exhibit better thermal stability and catalytic activities [5]. The supported Ni–B catalyst is usually synthesized by an impregnation-reduction method [4,5]. However, such method is difficult to carry out in industrial preparation [4]. Chen et al. synthesized a Ni–B catalyst by an electroless plating method, and found it showed superior catalytic property to the corresponding Ni–B catalyst prepared by a chemical reduction method [6]. It suggests that the electroless plating method is a

promising route to synthesize active Ni–B catalysts. We also have found that supported Ni–B catalysts can be prepared by a silver-catalyzed electroless plating method [7–11]. In this work, we prepared the supported Ni–B catalyst under microwave irradiation to change the properties of Ni–B particle, such as its morphology and particle size.

Microwave irradiation as a heating method has been found a number of applications in chemistry since 1986 [12,13]. The effect of heating is generated by the interaction of a dipole moment of the molecules with high frequency electromagnetic radiation. Unlike conventional heating, microwave irradiation is characteristic in its selective, local heating [14]. Conner et al. studied the effect of microwave irradiation on the sorption of oxides [14–18]. They found that the temperature at the surface where sorption occurs was “effectively” greater than the measured solid or gas temperature, since oxides had a low permittivity and were relatively transparent to microwave during the sorption on oxide solids [17]. As different adsorbates had different capabilities to adsorb microwave energy, different local temperatures and sorption selectivities on oxides solids

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occurred under microwave irradiation [15]. It means that the adsorbates are adsorbed selectively on the oxides under microwave irradiation. Consequently, this principle can be extended to prepare oxides supported catalysts, in order to control the selective deposition of active metal on supports. For studying the effect of microwave irradiation on the deposition of Ni–B particles, water and ethylene glycol (EG) with different permittivity were selected as solvents for experiments. The resulting catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The catalytic performances of catalysts were evaluated by a selective hydrogenation of acetophenone (AP).

2. Experiment section

2.1. Catalyst preparation

Ag/MgO was synthesized as Ref. [7]. 0.02 g AgNO₃, 0.15 g ammonia, 0.005 g NaOH, and 0.002 g HCHO were dissolved in 425 distilled water. Then, some MgO was added to the solution and stirred at 313 K for 4 h. The resulting Ag/MgO was washed with water and dried at 363 K for 4 h. The Ag loading was controlled at 0.2 wt%. Deposition of Ni–B on the Ag/MgO support was performed by adding the support to a basic borohydride bath of the following compositions: NiSO₄ · 6H₂O, 12.0 g/L; KBH₄, 5.5 g/L; ethylenediamine (en), 10.0 g/L; and NaOH, amount needed to maintain the desirable pH value (ca. 13.4–13.5). The plating was carried out by conventional heating or microwave irradiation (2455 MHz) at 323 K. It lasted until no significant bubbles were observed. The product was washed with water thoroughly to get a pH value of 7, then washed with ethanol for several times and stored in ethanol. The theoretic nickel loading was controlled between 15 and 20 wt%. The microwave irradiation power was selected between 0 and 180 W. The solvent of plating solution was water or ethylene glycol (EG), and the resulting Ni–B/MgO catalysts were denoted as Ni–B/MgO(W) and Ni–B/MgO(EG), respectively.

2.2. Catalyst characterization

XRD patterns of the samples were acquired on a Rigaku D/max-2500 powder diffractometer employing Cu K α source ($\lambda = 1.5418 \text{ \AA}$). The chemical compositions of the samples were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) on an IRIS Intrepid spectrometer. TEM images of catalysts were acquired using a JEOL-2010 FEF high resolution transmission electron microscope. XPS was carried out with a Kratos Axis Ultra DLD spectrometer employing a monochromated Al K α X-ray source, hybrid (magnetic/electrostatic) optics and a multi-channel plate and delay line detector (DLD). To avoid the influence of the surface oxygen, argon etching for 10 min was performed to remove the surface oxide layer.

2.3. Catalyst testing

The catalytic experiments were carried out in a 100 ml stainless steel autoclave. The stirring effect was preliminarily investigated and a stirring rate of 800 rpm was employed, which turned out to be sufficient to eliminate the diffusion limit. In the hydrogenation of AP, 0.6 g dry catalyst (dried in 100 ml/min N₂ flow), 5.0 g (42.8 mmol) AP and 60.0 ml ethanol were mixed. The reaction was carried out at 373 K for 1 h. The H₂ pressure was 1.0 MPa. The hydrogenation product was analyzed by a gas chromatograph equipped with a flame ionization detector.

3. Results and discussion

For the silver-catalyzed electroless plating [7], the plating is activated by the silver clusters preloaded on the supports, and the Ni–B clusters are formed and distributed selectively on the defective sites of supports, such as edges, pores, or corners [19,20], which result in new active sites for Ni–B deposition. The plating is driven by an autocatalysis effect of the resulting Ni–B clusters after silver catalyzing, then all the Ni–B clusters deposit selectively on the active surface of supports. In short, the dispersion and properties of Ni–B particles are mainly depended on the interaction between surface of support and plating solution (Stern–Grahame electrical double layer) [21]. In other words, the properties of Ni–B can be modified by changing supports or solvents to affect the sorption of supports. In this paper, two solvents, water and EG, were used to study the sorption of MgO under microwave irradiation according to work of Conner et al. [14–18].

3.1. Synthesis of supported Ni–B catalyst

Fig. 1 shows the TEM micrographs of supported Ni–B/MgO(W) and Ni–B/MgO(EG) prepared by conventional heating. The Ni–B particles are distributed homogeneously over MgO. The particles size of Ni–B is $\sim 45 \text{ nm}$ for Ni–B/MgO(EG) and $\sim 40 \text{ nm}$ for Ni–B/MgO(W). The compositions of both samples are listed in Table 1. The content of boron in Ni–B/MgO(EG) is higher than that in Ni–B/MgO(W), suggesting that the deposition process of nickel and boron is affected by the solvent. Table 1 also shows the compositions of supported Ni–B prepared in different solvents with different microwave irradiation powers. For Ni–B/MgO(W) samples, the composition of Ni–B is almost identical without the influence of irradiation power. The nickel content of Ni–B particles in Ni–B/MgO(EG) decreases when microwave irradiation is applied. The Ni loading on Ni–B/MgO(W) and Ni–B/MgO(EG) catalysts increases under microwave irradiation, especially when a lower irradiation power is used. The increase of Ni loading may be ascribed to two factors: (1) the interaction between the active sites for deposition of Ni–B and adsorbates was affected by the microwave irradiation. For instant, it may change the oxidation potential of the borohydride to be less

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