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Catalytic Hydrogenation Properties of Noncrystalline Ni-B Nanotubes

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Noncrystalline Ni-B nanotubes were prepared by reduction of nickel chloride with an aqueous solution of sodium using lyotropic non-ionic-anionic mixed surfactant liquid crystals as template. In comparison with other Ni-based catalysts, the noncrystalline Ni-B nanotubes exhibited higher activity and better selectivity. The relationships between catalysts performance and the structure of catalysts, surface electronic state of catalysts were discussed based on various characterizations including X-ray diffraction, transmission electron micrographs (TEM) and selected area electron diffraction (SAED).

Key Words: Noncrystalline Ni-B nanotubes, Catalytic hydrogenation, Activity, Selectivity.

INTRODUCTION

Noncrystalline transition-metal-boron alloys with short-range-ordered and long-range-disordered structures have been intensively investigated owing to their important practical or potential applications in various fields, such as ferrofluids, powder metallurgy, magnetic applications composite materials and catalysis[1-3]. Noncrystalline metal-boron (M-B) alloys prepared by melt-quenching or chemical reduction date back to the 1950s. Since 1991, when carbon nanotubes were discovered by Iijima[4], a variety of inorganic nanotubes have been synthesized[5-12]. Recently, Ding group first reported the synthesis of noncrystalline metal-boron nanotubes[13].

Non-crystalline metal-boron alloys have been used as hydrogenation catalysts for a long time and their application in magnetically stabilized bed reactors for hydrogenation reaction has made great progress recently[14]. In this paper, noncrystalline Ni-B nanotubes were prepared and characterized with XRD, TEM and SAED. The authors report non-crystalline Ni-B nanotubes which are more effective than the corresponding noncrystalline Ni-B nanoparticles and Raney Ni for catalytic hydrogenation of cyano, halogenated nitrobenzene and crotonaldehyde.

EXPERIMENTAL

Preparation of non-crystalline Ni-B nanoparticles: Non-crystalline Ni-B nanoparticles were prepared according to method described[15].

Preparation of noncrystalline Ni-B nanotubes: $NiCl_2 \cdot 6H_2O$ (0.05 mol, 11.8 g) was dissolved in H_2O (100 mL) containing (1S)-(+)-camphorsulfonic acid (0.05 mol, 11.5 g) and Tween60 (0.05 mol, 65.6 g) at 333 K. The mixture was then cooled to 293 K and allowed to stand at that temperature for 1.5 h. A mixture of 4M $NaBH_4$ and 0.1M NaOH was added to the above homogeneous mixture and kept for 48 h under an inert gas atmosphere (N_2). The resulting solid was collected, washed with distilled water and ethanol and dried in flowing nitrogen.

Hydrogenation of 4-cyanotetrahydropyran (4-CTH) with different Ni-based catalysts: 250 mL autoclave loaded with 8.0 g of 4-CTH, 100 g of 10 % by weight ammonia-methanol solution and 2.0 g catalyst was filled with 0.8 MPa of hydrogen after air was purged out and the temperature was kept at 333 K. The stirring speed was 1200 rpm. Samples were extracted every hour and then analyzed by gas chromatography.

Non-crystalline Ni-B nanotubes characterization equipments: Powder XRD measurement was performed on Philips X'Pert MPD Pro X-ray diffractometer equipped with graphite-monochromatized high-intensity CuK_α radiation at 50 kV. Transmission electron micrographs (TEM) were taken on a JEM-100S Electron Microscope (Jeol), using an accelerating voltage of 80 kV. The sample suspended in ethanol was dropped on a polymer coated copper grid for TEM observation.

RESULTS AND DISCUSSION

Fig. 1 presents the XRD pattern of the synthesized non-crystalline Ni-B nanotubes. The sample keeps the non-crystalline features, as indicated by a broad peak located at 2θ around 45° and no presence of other obvious diffraction peaks from crystalline phases.

Fig. 2 representative TEM image revealed the formation of Ni-B nanotubes with inner diameters of 55-60 nm, outer diameters of 65-70 nm and lengths up to several micrometers (Fig. 2a). The continuous broad rings resulting from selected-area electron diffraction (SAED) (Fig. 2a), consistent with the XRD pattern of the bulk material, show the non-crystalline nature of the Ni-B nanotubes. Fig. 2b shows the TEM image and the corresponding SAED for the Ni-B nanotubes after three catalytic cycles. The structure of the nanotubes appears to have changed very little after three catalytic cycles. The nanotubular morphologies are still observed and their structures are still non-crystalline, as determined by SAED (Fig. 2b).

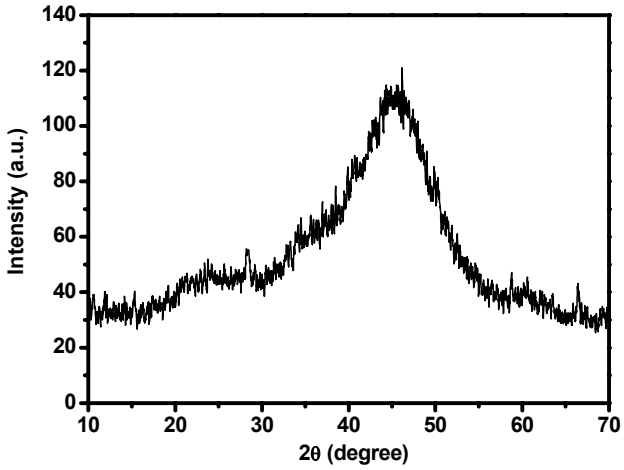

Fig. 1. XRD pattern of Ni-B nanotubes

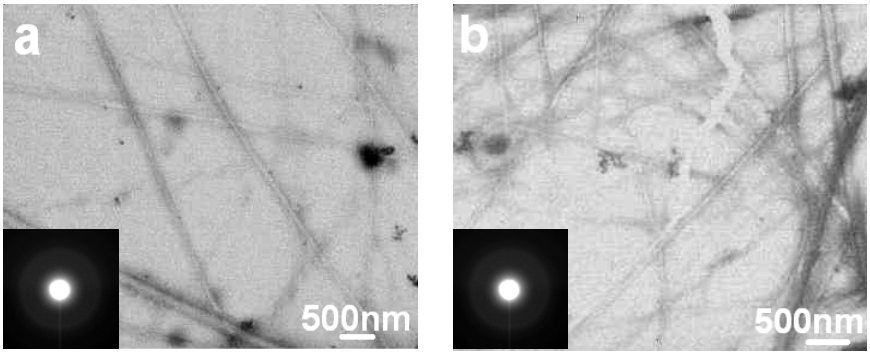

Fig. 2. TEM images of (a) Ni-B nanotubes before catalytic reaction and (b) Ni-B nanotubes after three catalytic cycles, inset: the corresponding SAED patterns.

Catalytic activity and selectivity measurements: Fig. 3 gives the conversion of 4-CTH over Ni-B nanotubes, Ni-B nanoparticles and Raney Ni, respectively. From Fig. 3, when Ni-B nanotubes used as catalyst, the reaction rate on the hydrogenation of 4-CTH was the most rapid and the conversion of raw material exceeded 99.5 % only reacting for 5 h. Raney Ni has better reaction rate than Ni-B nanoparticles, the conversion reached 98.0 % reacting for 10 h and the conversion only reached 91.6 % using Ni-B nanoparticles as the catalyst. The higher activity of the non-crystalline Ni-B nanotubes can be partially ascribed to their larger surface area (the surface area of Ni-B nanoparticles is 30.6 m^2/g and the surface area of Ni-B nanotubes is 100.2 m^2/g). Furthermore, the negative curvature of nanotube's inner surface may enhance the coordination of reaction molecules by the multiple active

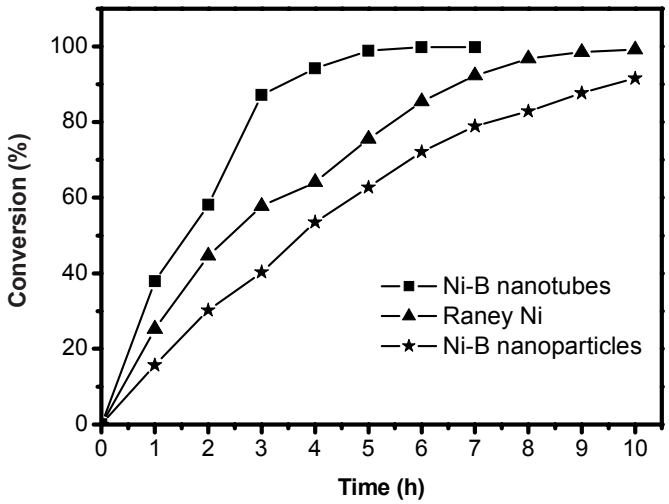

Fig. 3. Conversion of 4-CTH as a function of the reaction time over Ni-B nanotubes, Ni-B nanoparticles and Raney Ni catalyst

centers. Ding *et al.*[4] has found that the fluid molecules in the metal-boron nanotubes experience a strong interaction with the walls of nanotubes. In the hydrogenation of 4-CTH over Ni-B nanotubes, the Ni-B nanotubes strongly adsorb hydrogen and 4-CTH, which is capable of wetting and selectively adsorbing onto the solid surfaces, should experience a large attractive potential energy because of the combined interactions in the tubes. These effects must affect the reaction equilibrium. For above two reasons, the reaction rate of 4-CTH hydrogenation and the conversation of 4-CTH over Ni-B nanotubes are higher than those over Raney Ni and Ni-B nanoparticles.

Table-1 summarizes the catalytic activity and selectivity of Ni-B nanotubes, Ni-B nanoparticles and Raney Ni for hydrogenation of halogenated nitrobenzene. From Table-1, it can be seen that using Raney Ni as the catalyst, although the conversation of raw material achieved 99 %, the dehalogenation proportion was very high. In comparison with the Raney Ni, non-crystalline Ni-B alloys exhibited better selectivity for halogenated aniline, especially the Ni-B nanotubes, the dehalogenation proportion was less than 2.5 % without adding any dehalogenation inhibitor.

According to the principle of catalysis, the activity and selectivity were decided mostly by the number of active center and its hypostasis. Non-crystalline transition-metal-boron alloys have short-range-ordered and long-range-disordered characters, this structure is propitious to improve the catalytic activity of surface nickel[16]. At the same time, there exists the interaction between nickel and boron in noncrystalline Ni-B alloys[17], boron in the Ni-B catalyst donate electrons to the nickel metal, resulting in electron-rich nickel

TABLE-1
CATALYTIC ACTIVITY AND SELECTIVITY OF DIFFERENT CATALYSTS FOR HYDROGENATION OF HALOGENATED NITROBENZENE

Catalyst	Hydrogenation mass	Conversion (%)	Dehalogenation (%)
Ni-B nanotubes	*o*-Cl-nitrobenzene	99.0	2.0
	m-Cl-nitrobenzene	99.3	2.3
	3,4-diCl-nitrobenzene	99.5	1.9
Ni-B nanoparticles	*o*-Cl-nitrobenzene	96.2	6.3
	m-Cl-nitrobenzene	96.6	7.7
	3,4-diCl-nitrobenzene	97.1	5.1
Raney Ni	*o*-Cl-nitrobenzene	98.9	13.8
	m-Cl-nitrobenzene	99.2	21.4
	3,4-diCl-nitrobenzene	99.0	9.3

Reaction conditions: *m*(EtOH): 100 mL, *m*(halogenated nitrobenzene): 10 g, m(catalyst): 2 g. $P(H_2)$: 1.5 Mpa, T: 373 K, stirring speed: 1100 rpm, time: 1 h.

metal and electron-deficient boron. In the nitrobenzene, some electrons transfer from nitrogen to oxygen, nitrogen at the state of poor electron, so the active nickel adsorbs nitrogen, which can increase the sorption of nitryl and the boron adsorbs oxygen, which strengthen the sorption between the catalysts and the reactant. Once the hydrogenation was finished, nitrogen in the amido has rich electrons, it removes from nickel quickly, that prevents further reaction. Furthermore, the fluid molecules in the Ni-B nanotubes experience a strong interaction with the walls of nanotubes, which can both accelerate the reaction and decrease the contact time between catalysts and reactants effectively. So non-crystalline Ni-B nanotubes using as the catalysts for hydrogenation of halogenated nitrobenzene to halogenated aniline can decrease the dehalogenation proportion greatly, the problem of dehalogenation in the hydrogenation of halogenated nitro compound was solved commendably.

Table-2 summarizes the catalytic activity and selectivity of Ni-B nanotubes, Ni-B nanoparticles and Raney Ni for hydrogenation of crotonaldehyde. From Table-2, it can be seen that Ni-B nanotubes also show good catalytic activity and selectivity in the hydrogenation of crotonaldehyde.

When non-crystalline Ni-B nanotubes was exposed to air, it became less active due to the formation of an oxide layer on the surface, resulting in low activity. So, the care must be taken to minimize the oxidation of catalysts, keeping the catalyst soaked in ethanol can minimize the oxidation of the catalyst by air.

TABLE-2
CATALYTIC PERFORMANCE FOR HYDROGENATION CROTONALDEHYDE

Catalyst	Time (h)	Conversion (%)	Selectivity (%)		
			Butanol	Crotyl alcohol	butyraldehyde
Ni-B nanotubes	1	36.3	2.0	0	98.0
	2	71.4	2.5	0	97.5
	3	98.5	3.2	0	96.8
Ni-B nanoparticles	1	26.9	3.6	0	96.4
	2	51.7	4.4	0	95.6
	3	73.2	5.0	0	95.0
Raney Ni	1	30.6	6.2	0.9	92.9
	2	63.9	11.4	0.8	87.8
	3	82.1	14.1	0.6	85.3

Reaction conditions: *m*(EtOH):100 mL, *m*(crotonaldehyde): 10 g, *m*(catalyst): 2 g. P(H_2): 1.0 Mpa, T: 343 K, stirring speed: 1100 rpm.

Conclusion

In summary, non-crystalline Ni-B nanotubes have been prepared using liquid crystal as template. The special structure feature of Ni-B nanotubes exhibits higher catalytic activity and selectivity than Ni-B nanoparticles and Raney Ni and it have good structure stability to use repeatedly. Non-crystalline Ni-B nanotubes are promising for future potential application and might become a new kind of industrial catalyst.

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