Catalytical Performance of Supported Nano-amorphous Alloy NiB/MCM-41 on Hydrogenation of Rosin

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Abstract: Hydrogenation of rosin catalyzed by supported nano-amorphous alloy NiB/MCM-41 prepared by chemical reductive deposition method was investigated. The catalyst showed excellent catalytic activity for hydrogenation of rosin. Under the optimum conditions for hydrogenation of rosin i. e. load volume of Ni 13 % –15 % (mass fraction), H_2 pressure 7–9 MPa, reaction temperature 180–190 ℃, reaction time 5 h, the contents of dehydroabietic acid(DEHAA) and abietic acid (AA) in the product were less than 2.5 % and 0.5 % respectively. The distribution of hydrogenation products remained basically stable during the repeated using of the catalyst. The amorphous alloy structure of NiB active sites, typical mesoporous structure and high BET area in the prepared catalyst had been proved by XRD, TEM, EOAX, ICP and N_2 adsorption-desorption.

Key words: rosin hydrogenation; supported amorphous alloy catalyst; mesoporous molecular sieves

负载型纳米非晶合金NiB/MCM-41催化松香加氢反应性能研究

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摘 要：将采用化学还原沉积法制备的负载型非晶合金 NiB/MCM-41 中孔分子筛催化剂用于松香的氢化反应，表现出很高的加氢催化活性。研究确定在 Ni 负载量为 13 % ~15 %、反应温度180~190 ℃、反应压力7~9 MPa 条件下加氢反应 5 h，去氢枞酸(DEHAA)、枞酸(AA)在加氢产物中的含量分别小于 2.5 % 和 0.5 %，且在催化剂重复使用过程中加氢产物分布基本保持稳定。分别采用 XRD、TEM、EDAX、ICP 和比表面测定等手段对催化剂进行了表征。研究表明：NiB 活性组分具有非晶结构特征、催化剂具有典型的中孔结构和较大的比表面积。

关键词：松香加氢；负载型非晶态合金催化剂；中孔分子筛

Rosin is an abundant and vital resource of forest products, a series of valuable fine chemicals can be manufactured from it, of which hydrogenated rosin is regarded as one of the most important modified rosins. Hydrogenated rosin which has good oxidation resistance, high heat-stability, light color and low crispiness, can be used for preparing many functional products, e.g. adhesive, news printing ink, food additives, etc.[1-3]. Preparation of hydrogenated rosin is often carried out by using Pd/C or Raney Ni catalysts under the conditions of high temperature, pressure and long reaction time which may result in pyrolysis, dehydrogenation and decarbonylation, which are mainly caused by low catalytic activity and transfer effects[4-5]. Recently, much attention has been paid to the study of amorphous alloy supported on various carriers because of their

markedly improved catalytic performance and increased industrial and academic interests on the fundamental understanding of its preparation-structure-performance relationships[6-13]. However, in many researches, only the traditional carriers such as active carbon, silica gel or alumina gel were concerned and the catalysts based on these carriers are not good enough in many characteristics of reaction engineering, such as poor stability and transfer factors owing to dispersion of active constituent, unavailable pore structures, especially for high space-structure molecules such as rosin[14-18]. Since the MS41 mesoporous molecular series were synthesized in 1992, the studies on mesoporous molecular sieves have been proceeded in many cases. It may become an outstanding carrier owing to its high surface area (>800 m^2/g), uniform and adjustable mesoporous pore diameter (2-10 nm)[19-21]. In this paper, the performance of hydrogenation of rosin catalyzed by supported nano-amorphous alloy NiB/MCM-41 prepared by chemical reductive deposition has been investigated. Not only the preparation methods of the catalyst and MCM-41 carrier but also the hydrogenation of rosin have been studied.

1　Experimental

1.1　Preparation of MCM-41 mesoporous molecular sieve carrier

MCM-41 carrier was prepared by hydrothermal synthetic method as follows[20]. The precursor gel mixture was prepared by mixing the solution of hexadecyltrimethylammonium bromide and sodium silicate under stirring at room temperature for 30 min, then the solution containing modifier salts was added to obtain white gel solution. After the gel solution had been adjusted to pH value 10-11 with 5 mol/L sulfuric acid, the mixture was heated to 145-150 ℃ in a sealed container for 24 h in order to give grains. Finally the solid product was filtered, and dried in air (60 ℃, 12 h). MCM-41 carrier was obtained in a calcinator at 550 ℃ for 8 h in static air.

1.2　Preparation of supported NiB/MCM-41 catalyst

The solution of nickelous chloride was added to MCM-41 carrier (375-750 μm) and kept for 12 h. After vacuum drying, an aqueous solution of KBH$_4$ (2 mol/L) was added dropwise into the carrier. The reaction was lasted until no gas was released. The resulted black precipitate was washed several times with distilled water and subsequently with ethanol. The final product was kept in EtOH for reaction or characterization.

1.3　Catalyst characterization

The as-prepared catalyst was characterized by the following methods：

The structure characterizations of mesoporous molecular sieve and amorphous state of the catalyst were measured by D/max-1200 X-ray diffractometer with nickel-filtered Cu Kα radiation at 40 kV, 30 mA, λ = 0.154 18 nm in a 2 θ range of 1-10 ° (for mesoporous characteristic structure) and 20-70 ° (for amorphous state characteristic structure).

BET surface area, pore volume and distribution were calculated from the adsorption branches of N$_2$ isotherm using BJH model at 77 K carried out with a Micromerirics ASAP2400 glass volumetric apparatus, the samples were previously degassed at 150 ℃, 1.3 Pa overnight.

TEM images were performed on a JEM-1200EX electron microscope operating at 80 kV. Before TEM imaging, the samples were dispersed in *n*-butanol with ultrasonic wave. The SEM images of the catalyst were obtained with an FE-SEM (JEOL-6700F, Japan Electron Co. Ltd.). Before SEM imaging, the samples were sputtered with thin layers of gold. The load of the amorphous alloy on the support was measured by Jarrel-ASH1000 inductively coupled plasma (ICP).

1.4　Catalytic activity measurements of NiB/MCM-41 for hydrogenation of rosin

The hydrogenation of rosin using the as-prepared catalyst was performed in a 250 mL stainless steel

autoclave. Rosin(super-degree, softening point 75 ℃, acid value > 166 mg/g, crushed $d < 3$ mm), cyclohexane and as-prepared NiB/MCM-41 catalyst were heated to 150–200 ℃ with stirring under 5.0–8.0 MPa H_2 pressure until H_2 was not consumed. After cooling and filtering, the catalyst was reused; the solution was analyzed by GC after methylated with $(CH_3)_4NOH$. Fig. 1 shows the reaction scheme for the production of hydrogenated rosin.
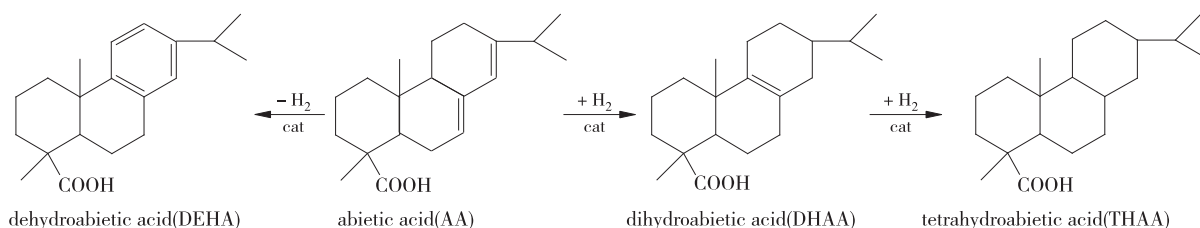

Fig. 1   Reaction scheme for rosin hydrogenation

1.5   Analysis of the reaction products

The catalytic hydrogenation products of rosin were analyzed by gas chromatography on a HP5890 chromatography with FID detector, equipped with DB-5 column (30 m long, 0.25 mm i. d., film thickness of 0.2 μm), working between 200–250 ℃ with heating rate of 2 ℃/min. The qualitative analysis of the main hydrogenation-product constituents were determined by HP5890-HP5989A GC-MS. Both transfer line and ion source temperature were set to 270 ℃. Ions were generated by a 70 kV electron impact (EI), and 20 scans per second with a scanning range of m/z 50–650 were recorded. The acceleration voltage was turned on for all GC running time.

2   Results and discussion

2.1   The suitable loading volume of Ni in NiB/MCM-41

In order to determine the suitable load volume of Ni in the NiB/MCM-41 catalyst for the production of hydrogenated rosin, the experiment was performed under reaction conditions: rosin 100 g, cyclohexane 100 mL, catalyst 2.0 g, H_2 pressure 7 MPa, 180 ℃, 5 h, and the results are shown in Fig. 2. The catalytic activity for hydrogenation of rosin is increasing with the growing of Ni load volume. The contents of dehydroabietic acid(DEHAA) and unreacted abietic acid(AA) in the products remained low at loading volume of Ni 13 % –15 % in NiB/MCM-41.

2.2   Determination of optimum conditions for hydrogenation of rosin catalyzed by NiB/MCM-41

To determine the optimum conditions for rosin hydrogenation using NiB/MCM-41 catalyst, the effects of reaction temperature, H_2 pressure and the reusability of the catalyst have been observed. From Fig. 3 (reaction conditions are same at 2.1), we can see that increasing reaction temperature is helpful for the hydrogenation of rosin, the contents of DHAA and THAA in the products are also increasing. However, when reaction temperature exceeded 180 ℃, the content of DEHAA (the dehydrogenation product) also increased, while the content of THAA obviously decreased. These results can be explained by the heat of reaction, i. e. ΔH_r is negative or exothermic for hydrogenation, while ΔH_r is positive or endothermic for dehydrogenation. Increased H_2 pressure benefits the hydrogenation of rosin, but it is limited by the investment of equipment and operation. The optimum reaction time was determined to be 5 h by analyzing the product distribution at different reaction time.

Table 1 shows the catalytic performance of NB/MCM-41 which remains basically stable during the

repeated used of catalyst. Under the optimum conditions for rosin hydrogenation using NiB/MCM-41 catalyst, i. e. hydrogen pressure 7–9 MPa, reaction temperature 180–190 ℃. During the recycle use of catalyst, there is no obvious change for mass fraction of DEHAA, AA, DHAA, THAA in the products.
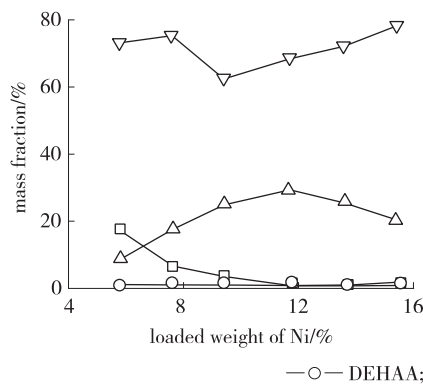
—○— DEHAA; —△— THAA; —□— AA; —▽— DHAA

Fig. 2　Effect of Ni loading capacity on the content of hydrogenation products
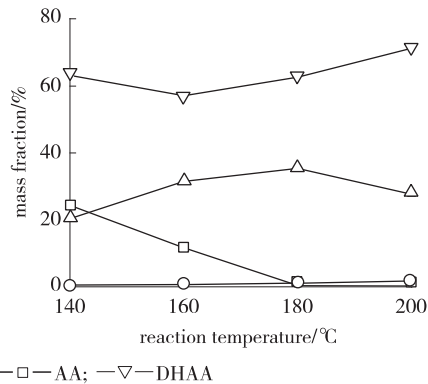
Fig. 3　Effect of temp. on the content of hydrogenation products

Table 1　The situation of catalysts reused on the reaction

times of catalysts used	mass fraction of products/%			
	DEHAA	AA	DHAA	THAA
1	1.38	0.12	61.34	21.42
2	2.36	0.10	62.79	18.54
3	2.27	0.32	60.27	19.07

2.3　The structure determination of supported amorphous NiB/MCM-41 catalyst

2.3.1　XRD patterns for amorphous NiB/MCM-41 catalyst　The XRD patterns for supported amorphous NiB/MCM-41 catalyst are presented in Fig. 4. From Fig. 4, there is a very strong diffraction peak at $2\theta \approx 2.2$ belonging to (100) crystal face diffraction peak, which is the characteristic peak of the mesoporous molecular sieve[22]. Besides (100), there are also (110) and (200) crystal face diffraction peaks, which prove that the as-prepared NiB/MCM-41 catalyst has very good long-range ordering and degree of crystallinity. In Fig. 4, the broad peak around $2\theta = 45°$ belongs to characteristic diffraction peak of amorphous NiB[23]. The amorphous structure of active sites leads to the high activity of the catalyst for rosin hydrogenation.
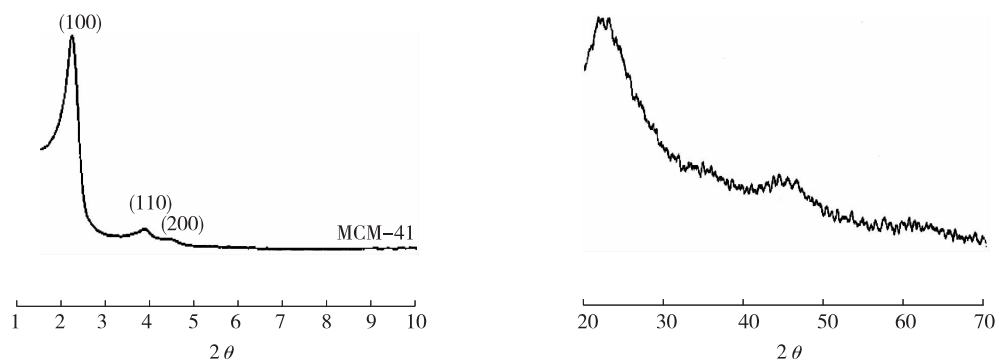
Fig. 4　XRD patterns for supported amorphous NiB/MCM-41 catalyst

2.3.2　The active sites dispersion in NiB/MCM-41 catalyst　As shown in Fig. 4 by TEM and SEM-EDAX replica shows the TEM replica of as-prepared amorphous NiB/MCM-41 catalyst. It can be seen that the hexagonal crystal system of NiB/MCM-41 catalyst is kept very well, and the nano-particles of NiB are also well dispersed on the MCM-41 carrier.

2.3.3 The pore structure characterization of the catalysts The N_2 adsorption-desorption isotherms of the catalysts at 77 K can be classified as type Ⅳ isotherms based on the IUPAC classification[19] since they feature the hysteretic loop generated by the capillary condensation in mesopores. It shows that the catalyst has cylindrical porous structure. BET surface area and porous diameter are respectively 979 m^2/g and 2.99 nm. The average pore size of the catalyst can be allocated in the mesoporous range (2 – 50 nm) and fit well with the size of the acetanilide-some molecules belonging to a typical synthetic dye material. These results indicate that the catalyst has mesoporous structure which coincided

Fig. 5　TEM replica of amorphous NiB/MCM-41 catalyst

with the results of XRD spectra and TEM replica. This mesoporous and opening structure of catalyst provides good transfer factors and improves the catalytic activity and selectivity.
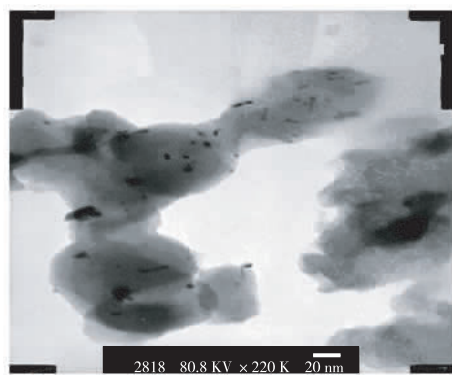
3　Conclusion

3.1 The supported nano-amorphous alloy NiB/MCM-41 catalyst prepared by chemical reductive deposition method exhibited excellent catalytic activity for hydrogenation of rosin. The prepared catalyst consists of MCM-41 mesoporous molecules and nano-amorphous alloy NiB which is well-dispersed in the surface of secondary ions.

3.2 Under the optimum conditions using NiB/MCM-41 for rosin hydrogenation, i. e. load voulme of Ni 13 % –15 % (mass fraction), H_2 pressure 7 – 9 MPa, reaction temperature 180 – 190 ℃, the contents of dehydroabietic acid(DEHAA) and abietic acid(AA) in the product were less than 2.5 % and 0.5 % respectively.

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