



Nickel nanoparticles highly dispersed with an ordered distribution in MCM-41 matrix as an efficient catalyst for hydrodechlorination of chlorobenzene



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ABSTRACT

Ni/MCM-41 materials in which highly dispersed nickel nanoparticles with an ordered distribution were successfully prepared by crystal lattice locating method. The synthesized samples were characterized by XRF, XRD, XPS, HRTEM, and N₂ adsorption–desorption isotherm techniques. The results suggest that the materials possess highly ordered hexagonal mesostructure of MCM-41 and the highly dispersed nickel nanoparticles with a uniform size smaller than 20 nm are in an ordered configuration in MCM-41 matrix. The materials with high specific surface area, large pore volume, and big pore diameter exhibit an excellent catalytic performance in hydrodechlorination of chlorobenzene.

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1. Introduction

The active components of a catalyst are usually transition metal atoms, which can be highly dispersed in a carrier with large specific surface area. Such supported metal catalysts are one of the most important class of catalysts in petroleum refining and petrochemical processing, such as catalytic oxidation [1,2], selective catalytic reduction of NO_x [3], hydrogenation [4] and reforming [5,6]. The impregnation of porous silica supports with a transition metal ion containing solution is a traditional method to prepare the supported metal or metal oxide catalysts. In the drying stage of the method, the active metal component precursor is often deposited in the form of aggregates on the surface of the carriers due to the liquid surface tension and the solution effects. And it is difficult to break up this aggregation in the subsequent activation processes. In addition, calcinations and reduction at high temperature are usually required for the traditional catalyst preparation process, and these can result in further migration of the metal species and lead to the formation of large particles due to the weak interaction between the active metal species and the carrier [7]. So in many cases the metal particles cannot uniformly disperse in the carriers with an out-of-order distribution, which result in a ghastly limitation in catalytic performance, including activity, selectivity and life-span. To overcome these disadvantages, many researchers

have made great efforts in preparing highly dispersed supported metal catalysts [8,9]. Although the highly dispersed metals were obtained, the arrangement of which are scattered casually without special orders, the stability and the selectivity of the materials are not satisfactory.

MCM-41 possesses high specific surface area, narrow pore distribution, ordered pore arrangement, and the pore diameter can be adjusted [10,11]. However, the applications of the pure silica MCM-41 mesoporous molecular sieves are limited in industries because they possess some disadvantages, such as the weak surface acidity and low catalytic activity. In order to enhance the catalytic performance, there are enormous efforts having been devoted to modify the pure siliceous MCM-41, including grafting [12], incorporation [13], loading of various metals [14,15] and metal oxide species [16,17]. By heteroatom doped or loaded, for example, Ni, Co, Cu, V, Ti etc., the physical chemistry properties of MCM-41 can be modified, the catalytic performance can be enhanced, and the application domains can be extended.

The catalysts with nickel have been applied widely in industries, such as hydrogenation of aromatic compounds [18], methanation of CO, steam reforming of hydrocarbons, amination of alcohols and carbon nanotube preparations etc [19–21]. The MCM-41 loaded nickel catalysts can be used in hydrogenation of gaseous acetonitrile [22], decomposition of amines [23], hydrogenation of benzene [24,25], oxygenation of benzene to prepare phenol and oxygenation of styrene to prepare benzaldehyde [26]. The activation energy of the reaction of hydrogenation of

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benzene on the Ni/MCM-41 catalyst is 36.5 kJ mol^{-1} , which is much lower than $50.5\text{--}52.3 \text{ kJ mol}^{-1}$ on the Ni/MyO_x catalysts (MyO_x is an oxide supporter, such as SiO₂, Al₂O₃ and MgO etc.) [27]. So, MCM-41 supporter is very attractive for catalysts. The preparation methods of Ni/MCM-41 catalysts have been reported including impregnation methods with nickel nitrate or nickel citrate solutions [24,25,28–32], ion-exchange methods [33] and direct syntheses methods [26,34,35]. All the reports have been focused on the high disperse of metal nickel or NiO_x on the supports and the ordered arrangement distribution of which were hardly ever mentioned.

In the present paper, the Ni^{II}-MCM-41 precursors were firstly synthesized by direct hydrothermal method, in which the nickel atoms were highly dispersed and embedded into the framework of MCM-41, that is, the nickel atoms were placed into the crystal lattice of the MCM-41. Then the nickel atoms were reduced from the Ni^{II}-MCM-41 precursor in hydrogen flow at a moderate temperature without destroyed the structure of MCM-41. So the Ni atoms would be anchored to the framework of MCM-41 and the localization of the framework made agglomeration of the metal nanoparticles difficult, which ensures the nanoparticles stable in the molecular sieve framework. This method can be distinguished as the crystal lattice locating method. The catalytic performance of the result samples were examined by using the reaction of HDC of CB. The significance of the work is that high amount of metal nanoparticles can be highly dispersed in the structure of molecular sieve with an ordered distribution and the result materials possess the advantages of molecular sieves and metal nanoparticles for catalysis, simultaneously.

2. Materials and methods

2.1. Materials

Nickel nitrate (AR), sodium hydroxide (AR, Beijing Yili Fine Chemical Product Limited Company, China); tetraethyl orthosilicate (TEOS, AR, Beijing Chemical Factory, China); ammonia solution (25%, AR, Beijing Beihua Fine Chemical Product Limited Company, China); cetyltrimethylammonium bromide (CTAB, AR), ethanol (AR), chlorobenzene (CB, AR, Tianjin Jinke Fine Chemical Institute, China), and hydrogen (>99.99%, Beijing Beiwen Gas Factory, China) were used. All solvents and reactants are commercially available and were used without further purification.

2.2. Methods

2.2.1. Synthesis of the precursor Ni^{II}-MCM-41

The Ni^{II}-MCM-41 mesoporous materials were prepared by a direct hydrothermal synthesis method. A typical synthesis was conducted as follows: CTAB was dissolved in deionized water in a flask with vigorous stirring for 30 min in order to obtain a clear solution. A certain amount of nickel nitrate was dispersed in deionized water in a beaker and an ammonia solution was added to obtain a solution containing the Ni(NH₃)₆²⁺ complex. The solution of Ni(NH₃)₆²⁺ was poured into the CTAB solution at room temperature. After stirred vigorously for 30 min, TEOS was added dropwise into the mixture and then stirred for another 30 min. The pH was adjusted to 10.0 by using an ammonia solution, and the final mixture was stirred for 5 h. The molar composition of the mixture was 1 TEOS: 0.152 CTAB: 2.8 NH₃: 1/x Ni: 141.2 H₂O. The mixture was transferred to a static Teflon-lined stainless steel autoclave and heated under autogenous pressure at 110 °C for 48 h. After that, the sample was filtered, washed with deionized water, dried overnight at 50 °C and finally calcined at 550 °C in air for 6 h. The Ni^{II}-MCM-41 precursor was gained.

2.2.2. Reduction of Ni^{II} from the Ni^{II}-MCM-41 precursor

The synthesis of Ni/MCM-41 by reduction of the Ni^{II}-MCM-41 precursor was carried out as follow: Ni^{II}-MCM-41 was put into a quartz tube and then heated in hydrogen flow from room temperature to 750 °C at a heating rate of 5 °C/min and kept 750 °C for 1 h. Then, it was cooled naturally in hydrogen flow to the room temperature. The resulting sample was designated as A-i.

The compared sample Ni/MCM-41 with the same nickel content corresponding to the sample A-i was prepared with the traditional impregnating method. Firstly, prepared a Ni^{II}/MCM-41 precursor with MCM-41 doped in a solution of Ni(NH₃)₆²⁺ complex (same as the above) and heated treatment. Then the Ni^{II}/MCM-41 precursor was reduced with the same process as the sample A-i. The resulting sample was designated as B-i.

2.2.3. Characterizations

X-ray diffraction (XRD) patterns were recorded with a Rigaku D/Max 2500 VBZ+/PC diffractometer using Cu K_α radiation (40 kV, 200 mA) in both low angle (2θ range of 0.5–10°) and wide angle range (2θ range of 10–80°). The X-ray fluorescence analysis (XRF) was performed on a Philips Magix-601 X-ray fluorescence spectrometer for determining the nickel content of the samples. The morphologies of the samples were examined by high-resolution transmission electron microscopy (HRTEM) on a JEM-3010 microscope with an accelerating voltage of 200 kV. Before the examination the samples were prepared by ultrasonic dispersion with absolute alcohol as solvent on a copper grid as supported membrane. The nitrogen adsorption–desorption isotherms were determined on a Micromeritics ASAP 2020 M volumetric adsorption analyzer. Before the nitrogen adsorption, each sample was degassed in a vacuum at 200 °C for 6 h. The specific surface area (S_{BET}) was estimated by the BET equation. And the pore distribution, the mesopore analysis were obtained from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) method. The X-ray photoelectron spectroscopy (XPS) analyses were conducted on an ESCALAB 250 spectrometer equipped with an Al K_α X-ray source. The carbon 1s peak at 284.6 eV was used as the reference for binding energies.

2.2.4. Catalytic performance testing

The catalytic performance of the samples was tested through the reaction of HDC of CB. The experiments were carried out in a 250 mL stainless steel autoclave with ethanol as the solvent. The reaction conditions were as follows: reaction temperature was 100 °C, H₂ partial pressure was 1.5 MPa, the catalyst dosage was 1.0 wt.%, and the reaction time was 60 min. The reactants and the products were analyzed by GC with a flame ionization detector online. And the conversion was calculated by the formula:

$$\text{Conversion (\%)} = \frac{C_{\text{C}_6\text{H}_5\text{Cl}_0} - C_{\text{C}_6\text{H}_5\text{Cl}_t}}{C_{\text{C}_6\text{H}_5\text{Cl}_0}} \times 100$$

$C_{\text{C}_6\text{H}_5\text{Cl}_0}$ and $C_{\text{C}_6\text{H}_5\text{Cl}_t}$ denotes the molar concentration of CB before and after reaction, respectively.

3. Results and discussion

3.1. Characterizations

The nickel contents of the samples were determined by XRF and the results are listed in Table 1. The sample A-1, A-2 and A-3 in Table 1 is corresponding to the sample of nominal Si/Ni molar ratio of 10, 20, and 30, respectively. The actual nickel content in the sample A-1, A-2 and A-3 is 9.3%, 5.9%, and 3.4%(wt.), respectively.

Fig. 1 shows the XRD patterns of the A samples. The small-angle XRD patterns (Fig. 1a) indicate that all the samples possess the

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