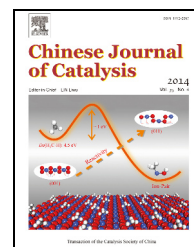


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Article

Promotion of Ni/clay catalytic activity for hydrogenation of naphthalene by organic modification of clay

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ABSTRACT

A Ni/montmorillonite (MMT) catalyst was prepared by an impregnation method using cetyltrimethylammonium bromide (CTAB)-pillared MMT as the supporting matrix and was characterized using infrared spectroscopy, X-ray diffraction, H₂ temperature-programmed desorption, N₂ adsorption-desorption, and ultraviolet diffuse reflectance spectroscopy. The catalytic activity of the Ni/MMT for the hydrogenation of naphthalene was also evaluated. The results show that the organic modification of MMT greatly improved the Ni dispersion and textural properties of the Ni/MMT catalyst. The as-prepared Ni/MMT catalyst showed high naphthalene conversion (88.2%) in the hydrogenation reaction; this is much higher than those achieved using Ni supported on pristine MMT (13.1%), Al₂O₃-pillared MMT (24.2%), and SBA-15 (68.2%). As a result of thermal decomposition of CTAB pillars during reduction of the Ni/MMT catalyst, the CTAB pillars mainly play a role in the Ni/MMT catalyst during impregnation. A mechanism for the promotion of the Ni/MMT catalytic activity by organic modification during impregnation is proposed.

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1. Introduction

Supported Ni catalysts are used in various industrially important chemical processes such as (de)hydrogenation, methanation, reforming, and hydrocracking [1–5]. Inorganic-pillared clays (PILCs) have been widely used as catalysts due to their high specific surface areas and pore volumes, and tunable pillars [6–8]. Therefore, PILC-supported Ni catalysts have been investigated [9–12]. However, the use of organic-PILCs is limited because of their low thermal stability at high temperatures.

Recently, supported noble-metal catalysts with excellent performance have been designed and prepared, based on the organophilic characteristics of organic-PILCs [13,14], which improve catalyst dispersion in organic solvents [13] and enable tuning of the catalyst polarity [14]. The organophilic characteristics of the catalysts are destroyed by thermal decomposition of the organic pillars at high temperatures, so catalysts derived from organic-PILCs need to be prepared and used at low temperatures (usually below 100 °C) [13,14]. Ni catalysts are usually used at high temperatures, so they are not suitable for use in catalysts designed on the basis of the organophilic charac-

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teristics of organic clays. However, highly dispersed metal oxide catalysts can be obtained using as-prepared mesoporous materials because the templates in such materials can occlude and interact with introduced species [15]. Organic clays are very similar to the mesoporous materials; an organic pillar such as cetyltrimethylammonium bromide (CTAB) is usually used as a template in the preparation of MCM-41, and the basal spacing of the clay is enlarged by the large organic pillar molecules. Highly dispersed Ni catalysts could therefore be obtained using organic-PILCs as the supporting matrixes.

Hydrogenation of aromatic hydrocarbon is normally used for catalytic tests because it is not only a useful model reaction for evaluating the activity of metal catalysts, but is also of commercial importance in the upgrading of coal liquids and diesel fuels [16–19]. Here, a highly active Ni/montmorillonite (MMT) catalyst for naphthalene hydrogenation was prepared via an impregnation method, using CTAB-pillared MMT as the supporting matrix. Ni supported on Al₂O₃-pillared MMT was also prepared for comparison. The mechanism of the promoting effect of CTAB pillars on the Ni/MMT catalyst is discussed.

2. Experimental

2.1. Catalyst preparation

Preparation of CTAB-pillared MMT (MMT-CTAB). Na-MMT (Zhejiang Sanding Group Co., Ltd.) was used directly without further purification. Na-MMT (2.0 g) was dispersed in H₂O (100 mL) and CTAB (2.0 g) was dissolved in H₂O (50 mL). The CTAB aqueous solution was slowly added to the Na-MMT suspension at 80 °C. After ion exchanging for 8 h, the suspension was subjected to centrifugation. Excess CTAB was removed by washing the solid several times with 50% ethanol until no Br⁻ ions were detected using AgNO₃ solution. After drying at 80 °C for 12 h, MMT-CTAB was obtained.

Preparation of Al₂O₃-pillared MMT (MMT-Al₂O₃). Na-MMT (1.0 g) was dispersed in H₂O (200 mL). The Al polycations as the pillar agent [20] were obtained by microwave-assisted hydrolysis of AlCl₃ via decomposition of urea. The Na-MMT suspension was then equilibrated with the Al polycation solution (25 mmol) for 20 h, and the product was separated by centrifugation. The solid was washed several times with H₂O until no Cl⁻ ions were detected using AgNO₃ solution. After drying at 120 °C for 12 h, and then calcined at 550 °C for 4 h, the MMT-Al₂O₃ was obtained.

Preparation of Ni/MMT, Ni/MMT-CTAB, and Ni/MMT-Al₂O₃. MMT, MMT-CTAB, or MMT-Al₂O₃ (1.0 g) was impregnated with an aqueous solution containing required amount of Ni(NO₃)₂·6H₂O (0.3 mol/L) under stirring at 60 °C until dryness, and drying at 100 °C overnight. The supported Ni precursors were then reduced at 550 °C by H₂ flow (30 mL/min) for 4 h, and passivated in 1.0% O₂/N₂ flow at room temperature for 3 h to obtain the supported Ni catalysts, i.e. Ni/MMT, Ni/MMT-CTAB, and Ni/MMT-Al₂O₃. The Ni loading on each catalyst was 10.0 wt%, determined by flame atomic absorption spectroscopy (TAS-990F, Beijing Purkinje General Instrument Co., Ltd.).

2.2. Catalyst characterization

Fourier-transform infrared (FT-IR) spectra were recorded using a Nicolet 6700 FT-IR spectrometer at a resolution of 4 cm⁻¹. X-ray diffraction (XRD) data were obtained with a Shimadzu XD-3A diffractometer, using Cu K_α radiation ($\lambda = 0.15418$ nm) at 40 kV and 40 mA. The specific surface areas and pore structure were determined by N₂ adsorption-desorption at -196 °C using a Micromeritics ASAP 2420 analyzer. H₂ temperature-programmed desorption (H₂-TPD) experiments were carried out using a Quantachrome instrument (ChemBET 3000) as described previously [21,22]. Before the measurements, the catalyst (50 mg) was heated to 550 °C in 10% H₂/Ar at a rate of 20 °C/min, and kept at 550 °C for 0.5 h. The catalyst was then cooled to 40 °C and kept at this temperature for 0.5 h. The H₂/Ar flow was then switched to pure Ar (40 mL/min) for 0.5 h at 40 °C. Finally, the catalyst was heated from 40 to 500 °C at a rate of 10 °C/min, and the H₂-TPD curve was recorded. The peak area was used to calculate the volume of chemisorbed H₂. The peak area was calibrated by running a pure H₂ pulse-titration experiment on a blank sample. The Ni surface area (*S*, m²/g), dispersion of metallic Ni (*D*, %) and average particle size of metallic Ni (*d*, nm) were calculated from the volume of H₂ chemisorbed, using the reported method [21,22]. Ultraviolet diffuse reflectance spectroscopy (UV-DRS) was performed in the range 200–800 nm using a PE Lambda 750S spectrophotometer.

2.3. Catalytic hydrogenation of naphthalene

Naphthalene hydrogenation was performed in a 60 mL stainless-steel autoclave (Ordino CS340, Premex) equipped with a heating system and a magnetic-coupled paddle stirrer. In a typical run, a solution of naphthalene in *n*-dodecane (10.0 wt%; 10 g) and catalyst (0.12 g) were loaded into the reactor. The reaction conditions were 300 °C and *p*(H₂) = 5.0 MPa. Each catalytic test was performed for 2.0 h. The reaction products were analyzed using a gas chromatograph (GC-7890II, Tech-Com) equipped with an OV-1 column (30 m × 0.25 mm × 0.33 μm) and a flame ionization detector.

3. Results and discussion

3.1. Characterization of MMT-CTAB

MMT-CTAB was obtained by ion exchange of CTAB onto MMT. FT-IR spectra of MMT, MMT-CTAB, and CTAB were recorded between 4000 and 400 cm⁻¹ to determine whether the organic cations were exchanged onto MMT (Fig. 1(a)). Unlike the spectrum of pristine MMT, the C–H bonds (2919, 2849 cm⁻¹) of methylene groups for CTAB are clearly observed in the MMT-CTAB. CTAB adsorbed on the external surface of MMT was washed out during preparation of MMT-CTAB, so it indicates CTAB intercalation into MMT interlayers. The basal spacing of MMT-CTAB was characterized using XRD in the small-angle range (Fig. 1(b)). Similar to the results obtained by Su group [23], the basal spacing of MMT was 1.24 nm, and the

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