



Ni₂P clusters on zeolite nanosheet assemblies with high activity and good stability in the hydrodesulfurization of 4,6-dimethyldibenzothiophene



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ABSTRACT

Developing highly active hydrodesulfurization (HDS) catalysts is very important for ultraclean fuel production. Here, we report the successful preparation of crystalline mordenite nanosheet assemblies (NS-HMOR) with large external surface area and micro–mesoporous structure. After introduction of nickel and phosphorus species into NS-HMOR and its activation, the obtained Ni₂P/NS-HMOR catalyst exhibits higher HDS activity (TOF = $1.9 \times 10^{-3} \text{ s}^{-1}$) and better stability in 4,6-dimethyldibenzothiophene HDS than a silica-supported Ni₂P catalyst (TOF = $1.3 \times 10^{-3} \text{ s}^{-1}$). The large number of acidic hydroxyl groups on the NS-HMOR surface facilitates the formation of very small Ni₂P clusters on the outer surface, and the open micropores at the NS-HMOR surface help to prevent their aggregation.

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1. Introduction

The high sulfur content in diesel fuel lowers its quality and contributes to the formation of undesirable exhaust gas emissions [1–3]. In many countries, strict environmental laws limit the sulfur content in diesel fuel to no more than 10 ppm [4–6]. To obtain this ultralow sulfur level, highly sterically hindered sulfur compounds such as 4,6-dimethyldibenzothiophene (4,6-DM-DBT) must be removed [7–9]. Currently, the sulfur in these fuels is removed by the hydrodesulfurization (HDS) of sulfur-containing compounds over conventional alumina-supported metal sulfide catalysts (CoMoS/γ-Al₂O₃ and NiMoS/γ-Al₂O₃) [10–12]. However, it is difficult to remove 4,6-DM-DBT over these catalysts, even under severe operating conditions, because of their insufficient catalytic activity [13–15]. Generally, hydrogenating a 4,6-DM-DBT phenyl ring imparts flexibility to the methyl group, resulting in the formation of less sterically hindered, flexible intermediates, and then desulfurization occurs [16–18]. Therefore, the deep desulfurization

of 4,6-DM-DBT requires catalysts with high hydrogenation activity [19,20]. It is well known that noble metal catalysts (Pd, Pt, and Pd–Pt) exhibit high hydrogenation activity [21], but they are sensitive to sulfur and expensive, which strongly limits their applications [22–24]. Metal phosphides (MoP, WP, and Ni₂P) are a novel group of catalysts for deep hydrotreating [25–27]. In particular, Ni₂P supported on silica (Ni₂P/SiO₂) [28,29] and mesoporous siliceous materials (Ni₂P/MCM-41) [30,31] has received much attention due to its high intrinsic hydrogenation activity. However, the industrial applications of these catalysts are still limited due to their unsatisfactory total HDS activity and instability.

It has been reported that the hydrogenation activity of Ni₂P catalysts can be improved by decreasing the crystallite size, increasing the particle dispersion, and modifying the Ni₂P active phase morphology [32–34]. On the other hand, the metal catalyst stability can be improved by strengthening the metal–support interactions [35]. Therefore, increasing the Ni₂P dispersion and Ni₂P–support interactions could greatly improve the HDS activity and stability of Ni₂P.

It is well known that aluminosilicate zeolites have large surface areas and acidic properties that could facilitate metal dispersion. Moreover, the unique zeolite framework enables strong metal–support interactions [36,37]. In addition, the metal clusters can be confined to the microporous zeolite channels. Thus, it should be possible to exploit the surface properties and unique porous

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structures of zeolites to design and synthesize highly active, stable catalysts with well-dispersed Ni₂P clusters.

This paper presents continuing research on the preparation of highly active HDS catalysts supported on zeolites [38–40]. Specifically, a facile method for synthesizing mordenite nanosheet assemblies (NS-NaMOR) with large external surface area and micro-mesoporous structure is reported. The H-form of the sample (NS-HMOR) was obtained by ion exchange with an NH₄NO₃ solution. After NS-HMOR was impregnated with a nickel and phosphorus solution and the resulting sample was activated, the obtained Ni₂P catalyst (Ni₂P/NS-HMOR) showed high activity and good stability in the HDS of 4,6-DM-DBT compared to a Ni₂P/SiO₂ catalyst. This feature is attributed to strong interactions between the nickel species and zeolite framework, which lead to small, well-dispersed Ni₂P clusters on the outer surface with micropore structure.

2. Experimental

2.1. Materials

Water glass (SiO₂ 24.6 wt.%, Na₂O 6.8 wt.%) was purchased from Zhejiang Tongxiang Water Glass Factory. 4,6-Dimethyldibenzothiophene (4,6-DM-DBT, 99.0%) was purchased from New Energy Chemicals Inc. Porous SiO₂ and other chemicals, including NaAlO₂ (41% Al₂O₃), Al₂(SO₄)₃·18H₂O (99%), NH₄NO₃ (99%), Ni(NO₃)₂·6H₂O (98%), (NH₄)₂HPO₄ (99%), and decalin (99.5%), were purchased from Sinopharm Chemical Reagent Co., Ltd. All of the reagents were used without further purification.

2.2. Zeolite synthesis

Crystalline MOR zeolite nanosheet assemblies (NS-NaMOR) were synthesized in a 100 L stainless steel autoclave. The aluminosilicate gel used in the synthesis had the following molar ratio of the various components: 1 Al₂O₃:12.6 Na₂O:46 SiO₂:0.019 RCC:760 H₂O, where RCC is a random cationic copolymer synthesized according to our previous work [39]. In a typical run, 44.4 L water glass and 15.0 L of a 1.3 wt.% NaAlO₂ aqueous solution were mixed in the autoclave. After they were stirred at room temperature for 40 min, 11.0 L RCC was slowly added to the mixture under vigorous stirring. Then 8.0 L of an Al₂(SO₄)₃ aqueous solution (7.7 wt.%) was added to the mixture, which was subsequently stirred for 100 min at room temperature. The resulting aluminosilicate gel was dynamically crystallized at 170 °C for 2 days. The crystallization product was filtered, washed, dried at 100 °C overnight, and calcined in air at 550 °C for 5 h. The obtained sample was denoted NS-NaMOR (Na-form). The microporous MOR zeolite was synthesized by the same procedure in the absence of RCC. For comparison, the mesoporous zeolite ZSM-5 (M-ZSM-5) was also synthesized according to our previously reported procedure [40]. The H-forms of these samples were ion-exchanged with a 1 M NH₄NO₃ solution at 80 °C for 4 h, followed by drying at 100 °C overnight and calcination at 500 °C for 3 h. The samples obtained after ion exchange were denoted as NS-HMOR, HMOR, and M-HZSM-5. The ordered mesoporous molecular sieve (MCM-41) was synthesized according to a previously reported method [41].

2.3. Catalyst preparation

To prepare the Ni₂P catalysts, the supports were impregnated by incipient wetness with a solution containing the required amount of diammonium hydrogen phosphate ((NH₄)₂HPO₄) and nickel nitrate (Ni(NO₃)₂·6H₂O). The Ni:P molar ratio in the impregnation solution was 1:2. The Ni loading in the catalyst

was 6.0 wt.%. After impregnation, the sample was dried under ambient atmosphere for 20 h and then dried at 100 °C for 12 h. The sample was pelleted, sieved to 20–40 mesh, and calcined at 500 °C for 3 h. The catalysts on the different supports were denoted as Ni₂P/NS-HMOR, Ni₂P/NS-NaMOR, Ni₂P/HMOR, Ni₂P/M-HZSM-5, Ni₂P/MCM-41, and Ni₂P/SiO₂.

2.4. Characterization

X-ray diffraction (XRD) patterns were collected with a RIGAKU Ultima IV diffractometer using CuK α radiation. Nitrogen physisorption experiments were conducted at –196 °C on a Micromeritics ASAP 2020M apparatus after the sample was degassed for 8 h at 200 °C. The specific surface area was calculated from the adsorption data using the Brunauer–Emmett–Teller (BET) equation. The pore size distribution was calculated according to the Barrett–Joyner–Halenda (BJH) model. The argon adsorption isotherm was obtained at liquid argon temperature (–186 °C). The micropore size distribution was calculated using the Horvath–Kawazoe (H–K) model.

A scanning electron microscopy (SEM) image was obtained using a SUPRA55 field emission scanning electron microscope operating at an acceleration voltage of 5 kV. Before the analysis, the sample was coated with gold to create contrast. Transmission electron microscopy (TEM) images were obtained on JEM-2100 and Tecnai G² F30 instruments. Before the TEM characterization, the sample was ultrasonically dispersed in an ethanol solution and dropped onto a carbon membrane-coated Cu grid.

X-ray photoelectron spectroscopic (XPS) experiments were performed using an ESCALAB MK II system. For the reduced Ni₂P catalyst, the sample was transferred to a bottle filled with absolute cyclohexane under a H₂ stream. After the cyclohexane was removed, the residual sample was quickly moved to the sample holder before being loaded into the XPS chamber.

The nature and change in the surface hydroxyls on the zeolite and silica supports before and after Ni₂P was loaded onto them were measured by infrared spectroscopy (IR) on a Bruker TENSOR 27 instrument equipped with an in situ reactor cell. Before the IR measurement, the sample was outgassed overnight at 400 °C under 7.5 Pa.

The acidities of the supports and catalysts were measured by ammonia temperature-programmed desorption (NH₃-TPD) on a Micromeritics ASAP 2920 instrument. For the supports, 200 mg of the sample were placed in a quartz tube and pretreated in a helium stream at 450 °C for 2 h. After the sample was cooled to 120 °C, an NH₃-He gas mixture (10 vol.% NH₃) was flowed over the sample for 30 min. After the physically adsorbed NH₃ was removed by flowing helium for 2 h at 120 °C, the sample was heated from 120 to 700 °C at a rate of 10 °C min^{–1}. For the catalysts, 200 mg of the passivated catalyst (treated in 0.5 wt.% O₂/N₂ at room temperature for 3 h) was placed in a quartz tubular reactor and pretreated in a H₂-Ar gas mixture (10 vol.% H₂), heated to 500 °C at a heating rate of 10 °C min^{–1}, and kept at 500 °C for 2 h. After the sample was cooled to 120 °C under a He stream, an NH₃-He gas mixture (10 vol.% NH₃) was flowed over the sample for 30 min. After physically adsorbed NH₃ was removed by flowing a He stream over the sample for 2 h at 120 °C, the sample was heated from 120 to 700 °C at a rate of 10 °C min^{–1}. The amount of NH₃ desorbed was measured by a thermal conductivity detector (TCD).

Temperature-programmed reduction (TPR) of the catalysts was performed on a Micromeritics ASAP 2920 instrument using a H₂-Ar gas mixture (10 vol.% H₂). The calcined sample (60 mg) was heated from room temperature to 950 °C at a heating rate of 15 °C min^{–1}. The dynamic CO pulse chemisorption was measured using a Micromeritics ASAP 2920 instrument. The passivated

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