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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 Al_2O_3 -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 H_2O (100 mL) and CTAB (2.0 g) was dissolved in H_2O (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 AgNO_3 solution. After drying at 80 °C for 12 h, MMT-CTAB was obtained.

Preparation of Al_2O_3 -pillared MMT (MMT- Al_2O_3). Na-MMT (1.0 g) was dispersed in H_2O (200 mL). The Al polycations as the pillar agent [20] were obtained by microwave-assisted hydrolysis of AlCl_3 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 H_2O until no Cl^- ions were detected using AgNO_3 solution. After drying at 120 °C for 12 h, and then calcined at 550 °C for 4 h, the MMT- Al_2O_3 was obtained.

Preparation of Ni/MMT, Ni/MMT-CTAB, and Ni/MMT- Al_2O_3 . MMT, MMT-CTAB, or MMT- Al_2O_3 (1.0 g) was impregnated with an aqueous solution containing required amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (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 H_2 flow (30 mL/min) for 4 h, and passivated in 1.0% O_2/N_2 flow at room temperature for 3 h to obtain the supported Ni catalysts, i.e. Ni/MMT, Ni/MMT-CTAB, and Ni/MMT- Al_2O_3 . 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 $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) at 40 kV and 40 mA. The specific surface areas and pore structure were determined by N_2 adsorption-desorption at $-196 \text{ }^\circ\text{C}$ using a Micromeritics ASAP 2420 analyzer. H_2 temperature-programmed desorption (H_2 -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% H_2/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 H_2/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 H_2 -TPD curve was recorded. The peak area was used to calculate the volume of chemisorbed H_2 . The peak area was calibrated by running a pure H_2 pulse-titration experiment on a blank sample. The Ni surface area (S , m^2/g), dispersion of metallic Ni (D , %) and average particle size of metallic Ni (d , nm) were calculated from the volume of H_2 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 $p(\text{H}_2) = 5.0 \text{ MPa}$. 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 $\times$ 0.25 mm $\times$ 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

Fig. 1. (a) FT-IR spectra of MMT, CTAB, MMT-CTAB, and Ni/MMT-CTAB; (b) Small-angle XRD patterns of MMT and MMT-CTAB.

basal spacing of MMT-CTAB was enlarged to 2.26 nm as a result of incorporation of organic cations of CTAB into the MMT galleries by ion exchange.

The FT-IR spectrum of Ni/MMT-CTAB was recorded to determine whether CTAB remained in the as-prepared catalyst. In contrast to the case for MMT-CTAB, the C–H bonds of methylene groups disappeared over Ni/MMT-CTAB. This indicates that CTAB was thermally decomposed during the reduction of Ni/MMT-CTAB. So, although the Ni/MMT catalyst obtained using MMT-CTAB as the supporting matrix (Ni/MMT-CTAB), the CTAB pillars were decomposed during reduction and were not present in the Ni/MMT-CTAB catalyst.

3.2. Effect of organic modification of MMT on Ni/MMT dispersion

XRD studies of Ni/MMT, Ni/MMT-CTAB, and Ni/MMT-Al₂O₃ catalysts were performed to determine the effect of the organic modification of MMT on Ni/MMT. The characteristic peaks of MMT ($2\theta = 18.4^\circ, 19.8^\circ, 27.8^\circ, 35.1^\circ, 62.0^\circ, 68.0^\circ, \text{ and } 73.3^\circ$) and Ni metal ($2\theta = 44.4^\circ, 52.0^\circ, \text{ and } 76.5^\circ$) were observed for all the catalysts (Fig. 2). This means that the crystal structure of MMT was not destroyed and the Ni species were reduced to Ni metal in all the catalysts during preparation. In comparison with the Ni/MMT catalyst, the peak intensity for Ni metal decreased and the widths of the peaks at half height increased significantly for

Fig. 2. XRD patterns of MMT, Ni/MMT, Ni/MMT-CTAB, and Ni/MMT-Al₂O₃.

Ni/MMT-Al₂O₃, and particularly for Ni/MMT-CTAB. This indicates that the Ni metal particles in Ni/MMT-CTAB are smaller than those in Ni/MMT and Ni/MMT-Al₂O₃, suggesting that Ni/MMT dispersion is improved by organic modification of MMT.

H₂ chemisorption on all the catalysts was measured using H₂-TPD to examine the effect of the organic modification of MMT on Ni/MMT dispersion further (Fig. 3). The peak area for Ni/MMT-CTAB is much bigger than those for Ni/MMT and Ni/MMT-Al₂O₃. The H₂ chemisorption uptakes, surface areas, and dispersions were estimated based on H₂-TPD profiles, assuming adsorption of one H atom per metal atom [21,22,24]; the results are shown in Table 1. The Ni dispersion for Ni/MMT-CTAB is 14.1%, which is much higher than those for

Fig. 3. H₂-TPD profiles for Ni/MMT, Ni/MMT-CTAB, and Ni/MMT-Al₂O₃.

Table 1

H₂ chemisorption data for Ni/MMT catalysts based on H₂-TPD results.

Catalyst	Ni loading (wt %)	H ₂ uptake (mL/g-Ni)	Surface area (m ² /g)	Dispersion (%)
Ni/MMT	9.9	22.8	39.9	6.0
Ni/MMT-Al ₂ O ₃	9.8	32.5	56.8	8.5
Ni/MMT-CTAB	10.1	53.5	93.6	14.1

Fig. 4. N₂ adsorption-desorption isotherms (a) and pore size distributions (b) of different samples.

Ni/MMT (6.0%) and Ni/MMT-Al₂O₃ (8.5%), suggesting that Ni dispersion of Ni/MMT is improved greatly by organic modification of MMT.

3.3. Effect of organic modification of MMT on physical properties of Ni/MMT

Figure 4(a) shows the N₂ adsorption-desorption isotherms of MMT, Ni/MMT, and Ni/MMT-CTAB. The specific surface area, pore volume, and pore size are shown in Table 2. It can be seen that the N₂ adsorption, pore volume, and specific surface area of MMT and Ni/MMT are very low. However, the specific surface area increases from 10 m²/g for Ni/MMT to 76 m²/g for Ni/MMT-CTAB, and the pore volume increases from 0.04 cm³/g for Ni/MMT to 0.17 cm³/g for Ni/MMT-CTAB. In contrast, the specific surface area of Ni/MMT-Al₂O₃ is 64 m²/g, although that of MMT-Al₂O₃ is 113 m²/g. The pore volume of Ni/MMT-Al₂O₃ (0.08 cm³/g) is only about half that of Ni/MMT-CTAB. In addition, the micropore volume decreases from 0.05 cm³/g for MMT-Al₂O₃ to 0.02 cm³/g for Ni/MMT-Al₂O₃, and the mesopore volume and mesopore surface area are almost unchanged. This indicates that some micropores are blocked by Ni metal on the Ni/MMT-Al₂O₃ catalyst. However, only mesopores are observed for Ni/MMT-CTAB with the narrowest pore size distribution (Fig. 4(b)). This means that the pore size distribution of Ni/MMT is also improved by organic modification of MMT.

Table 2
Textural properties of different catalysts.

Catalyst	S_{BET}^a (m ² /g)	S_{meso}^b (m ² /g)	V_{pore} (cm ³ /g)	V_{micro}^b (cm ³ /g)	V_{meso}^c (cm ³ /g)	Pore diameter (nm)
MMT	9	7	0.05	—	0.05	20.9
Ni/MMT	10	10	0.04	—	0.04	15.5
Ni/MMT-CTAB	76	75	0.17	—	0.17	9.0
MMT-Al ₂ O ₃	113	27	0.11	0.05	0.06	3.7
Ni/MMT-Al ₂ O ₃	64	27	0.08	0.02	0.06	5.1

^a BET method. ^b t-plot method. ^c $V_{\text{meso}} = V_{\text{ads}, p/p_0=0.99} - V_{\text{micro}}$.

3.4. Promotion of activity of Ni/MMT by organic modification of MMT

We studied the activity of Ni/MMT, Ni/MMT-CTAB, and Ni/MMT-Al₂O₃ catalysts in the hydrogenation of naphthalene. The main hydrogenation products were tetralin and decalin, and no hydrocracking products were identified. Naphthalene conversion over the Ni/MMT-CTAB and Ni/MMT-Al₂O₃ catalysts was higher than that over the Ni/MMT catalyst (Table 3). The conversion of naphthalene obviously increases from 13.1% on Ni/MMT to 88.2% on Ni/MMT-CTAB, indicating the effect of organic modification of MMT. The use of Al₂O₃-pillared MMT as a support increases the activity of Ni/MMT by about 85% (the naphthalene conversion 24.2%). These results indicate that pillaring MMT with an organic compound (CTAB) or inorganic compound (Al₂O₃) increases the activity of the Ni/MMT catalyst, but the promoting of CTAB is much more effective than that of Al₂O₃. Moreover, we previously found that calcination in H₂ increased the activity of Ni/SBA-15 and 68.2% of conversion was achieved [21], which is lower than that obtained over Ni/MMT-CTAB.

3.5. Discussion

We have shown that organic modification of MMT (MMT pillared with CTAB) greatly enhances the catalytic activity of

Table 3
Catalytic hydrogenation activity over Ni/MMT catalysts.

Catalyst	Conversion (%)	Selectivity (%)	
		Tetralin	Decalin
Ni/MMT	13.1	98.3	0.7
Ni/MMT-Al ₂ O ₃	24.2	97.4	0.6
Ni/MMT-CTAB	88.2	99.4	0.6
Ni/SBA-15 ^[21]	68.2	93.6	6.4

Reaction conditions: the solution of naphthalene in *n*-dodecane (10.0 wt%) 10 g, catalyst 0.12 g, 300 °C, $p(\text{H}_2) = 5.0$ MPa, 2.0 h.

Ni/MMT. Specifically, we found that the effect on Ni/MMT with the organic modification of MMT is not based on the organophilic characteristics of CTAB, because the CTAB pillars are thermally decomposed during reduction of the catalyst. Therefore, the promoting effect of the organic modification of MMT is ascribed to interactions between the CTAB pillars and the Ni^{2+} ions introduced during impregnation. To investigate this interaction, we prepared a $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ + CTAB mixture and compared it with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{MMT-CTAB}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{MMT}$ samples. These samples show obvious color differences. An orange color appears after manual mixing of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and CTAB, the same color as the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{MMT-CTAB}$ sample. However, the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{MMT}$ sample remains pale blue, which is derived from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. This means that CTAB may complex with Ni^{2+} ions to form orange Ni-CTAB complexes. We performed UV-DRS measurements on $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{MMT}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{MMT-CTAB}$, MMT-CTAB, and the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ + CTAB mixture (Fig. 5) to determine whether Ni-CTAB complexation occurred in $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{MMT-CTAB}$. The UV band at around 390 nm for $\text{Ni}(\text{NO}_3)_2$ is observed for $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{MMT}$. New UV bands at around 335 and 440 nm ascribed to the orange Ni-CTAB complex appear, but the band at around 390 nm disappears for both $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{MMT-CTAB}$ and the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ + CTAB mixture. In contrast, the peaks at around 335 and 440 nm are not observed for MMT-CTAB and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{MMT}$.

Based on these results, a mechanism for catalyst promotion by organic modification of MMT in Ni/MMT catalysts is proposed, as shown in Scheme 1. Compared with that of MMT, the

Fig. 5. UV-DRS profiles of MMT-CTAB, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{MMT}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{MMT-CTAB}$, and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ + CTAB mixture.

basal spacing of MMT-CTAB is enlarged because the CTAB molecules are large. Nickel nitrate can then easily enter the MMT interlayers and the CTAB pillars can occlude Ni-CTAB complexes formed with the introduced Ni^{2+} ions during impregnation, which leads to greatly improved dispersion of Ni/MMT after reduction. The specific surface area and pore volume are greatly enhanced by the small Ni particles located

Scheme 1. Schematic diagram for promotion of Ni/MMT activity by using CTAB-pillared MMT as support.

Graphical Abstract

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

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The catalytic activity of Ni/MMT is greatly promoted by using CTAB-pillared MMT as a support. The CTAB pillars enlarge the basal spacing of MMT, and occlude and complex with the introduced Ni^{2+} ions during impregnation.

in the MMT interlayers. Moreover, there are no micropores in the Ni/MMT catalyst derived from CTAB-pillared MMT, which favors mass transfer of naphthalene and its hydrogenation products. In contrast, Al_2O_3 -pillared MMT has a high specific surface area as a result of the very small Al_2O_3 pillars located in the MMT interlayers. The Al_2O_3 pillars are small, so Al_2O_3 -pillared MMT contains micropores. Although more nickel nitrate can enter the Al_2O_3 -pillared MMT interlayers and Ni/MMT- Al_2O_3 dispersion is improved, some micropores are blocked by Ni metal particles. The specific surface area and pore volume of Ni/MMT- Al_2O_3 are therefore lower than those of MMT- Al_2O_3 . As a result, the hydrogenation activity of Ni/MMT is significantly promoted by using CTAB-pillared MMT as the supporting matrix, and the resulting catalyst is superior to the Ni/MMT- Al_2O_3 catalyst.

4. Conclusions

MMT pillared with CTAB greatly enhances Ni/MMT catalytic activity for naphthalene hydrogenation. The CTAB pillars are thermally decomposed during the reduction of the catalyst, so this promotion is not caused by the organophilic characteristics of CTAB-pillared MMT, but by interactions between the CTAB pillars and the Ni^{2+} ions introduced during impregnation. The CTAB pillars enlarge the basal spacing of MMT, and occlude and complex with the introduced Ni^{2+} ions. After reduction, the dispersion, specific surface area, and pore volume of the Ni/MMT catalyst are greatly improved. The obtained Ni/MMT catalyst exhibits excellent catalytic activity for the hydrogenation of naphthalene, not only much higher than those of Ni/pristine MMT and Ni/MMT- Al_2O_3 catalysts, but even higher than that of Ni/SBA-15. These results provide a new perspective on the preparation of highly active metal or metal oxide catalysts supported on clays.

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有机改性对粘土负载镍催化剂的促进作用及其萘加氢性能

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摘要: 以有机改性后的十六烷基三甲基溴化铵柱撑蒙脱石(CTAB-MMT)为载体, 采用浸渍法制备了Ni/MMT催化剂. 通过傅里叶红外光谱、X射线衍射、H₂程序升温脱附、N₂物理吸附以及紫外漫散射等物理化学手段对催化剂进行了表征; 并结合微型高压反应釜萘加氢反应, 评价了催化剂的加氢性能. 结果表明, 有机改性显著改善了Ni/MMT催化剂的金属Ni分散度和织构性质, 且所制催化剂表现出优异的萘加氢性能, Ni萘转化率达到88.2%, 不仅远高于未处理催化剂(13.1%)和Al₂O₃柱撑处理催化剂(24.2%), 而且高于Ni/SBA-15催化剂(68.2%). 鉴于CTAB有机柱撑体在催化剂还原过程因热解而消除, 其对催化剂所起的作用主要发生于浸渍过程, 提出了有机改性在浸渍过程对Ni/MMT催化剂的促进作用机制.

关键词: 镍; 有机蒙脱石; 高活性; 萘; 加氢

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