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Synthesis of New NiO–SiO_2–Sol Pillared Montmorillonite and Its Catalytic Activity in the Hydrogenation of Benzene[1]

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Abstract—NiO–SiO_2–sol pillared montmorillonite was synthesized using a novel method. Tetraethyl orthosilicate (TEOS) and hexahydrate nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) were intercalated into the interlayers of H-montmorillonite simultaneously with the intercalation of octylamine. Interlamellar hydrolysis of TEOS catalyzed by octylamine resulted in the siloxane-pillared montmorillonite. A new NiO–SiO_2–sol pillared montmorillonite was obtained after removing the organic compounds at 550°C. The nitrogen adsorption–desorption isotherm for the pillared sample revealed that a large number of micro- and mesopores were created between the silicate layers, giving rise to a large surface of 554 m^2/g and total porosity of 0.626 ml/g. The catalytic activity of the NiO–SiO_2–sol pillared montmorillonite was evaluated in hydrogenation of benzene.

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During the past few years, a number of microporous and mesoporous layered aluminosilicates have been developed as catalysts [1–3], due in part of their catalytic and molecular sieving properties. Probably the most popular of these systems are the so-called pillared intercalated clays. In general, pillaring is achieved by the intercalation of bulk inorganic (polyoxocations) [4–6] or organic precursors (metal alkoxides) [7–8] between the interlayers of clays. Pillaring processes involving metal alkoxide are facilitated by using of pre-swelling step, whereby the interlayer is exposed to quaternary ammonium [9–12]. In the present study, H-montmorillonite–octylamine–tetraethyl orthosilicate–Ni intercalation compounds were produced via one-step method. In this intercalation compound, the long chain amine octylamine appears to act as a gallery height expander and a base catalyst during tetraethyl orthosilicate (TEOS) hydrolysis and as ligands for nickel species. The interlayer pillared structure was systematically investigated by termogravimetry–differential thermal analysis (TG–DTA), X-ray diffraction (XRD), BET and transmission electron microscopy (TEM), along with a preliminary test of the hydrogenation catalytic activity.

EXPERIMENTAL

Materials

Tetraethyl orthosilicate, hexahydrate nickel nitrate and octylamine were purchased from Shanghai Chemical Reagent Company. All chemicals were of analytical purity and used without further purification. Ca-montmorillonite was purchased from the third Bentonite Chemicals Factory of ZheJiang province.

Synthesis of NiO–SiO_2–sol Pillared Montmorillonite

In the first step, H-montmorillonite was obtained by the ion exchange of Ca in montmorillonite by H^+ using 0.1 N HCl solution. Ca-montmorillonite (2 g) in deionized water (200 ml) was titrated slowly with 0.1 N HCl solution to a final pH 2.0 and then maintained at this value for 24 h. H-montmorillonite was recovered by filtering, washing with deionized water (until Cl^-, free) and drying in air at 60°C. In the second step, the pillaring solution was obtained by mixing octylamine (4 ml), TEOS (4.5 ml), and $Ni(NO_3)_2 \cdot 6H_2O$ (1.6 g) together. H-montmorillonite (2 g) was mixed with the pillaring solution for an 1 h and 10 ml deionized water was added to get a gel. The gel was dried at 70°C and calcinated at 550°C for 2 h to give the NiO–SiO_2–sol pillared montmorillonite.

Characterization

A simultaneous thermogravimetry-differential thermal analysis was performed on a TG/DTA PYRIS DIAMOND with a heating rate of 10°C/min under an ambient atmosphere. The crystallinity of the sample was evaluated by powder X-ray diffraction patterns obtained on an X-ray diffractometer ("Bruker D8 Advance") with CuK_α radiation under operation con-

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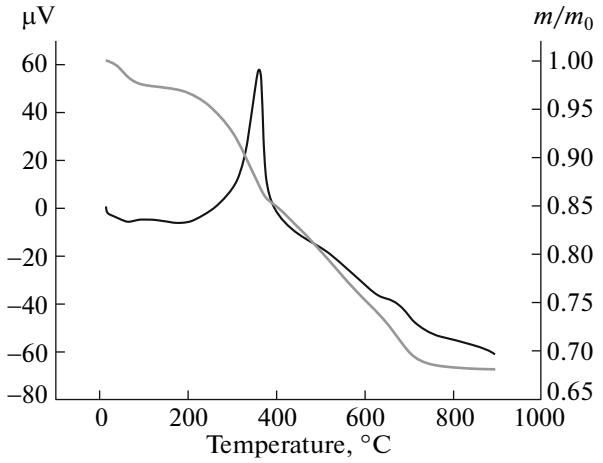

Fig. 1. TG and DTA curves of NiO–SiO_2–sol pillared montmorillonite precursor.

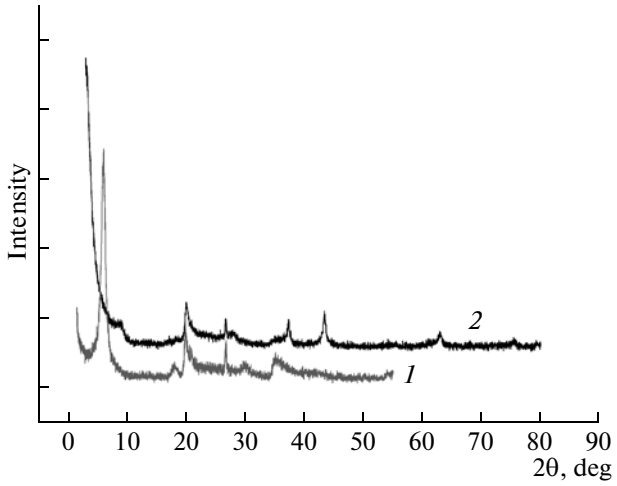

Fig. 2. XRD patterns of montmorillonite (*1*) and NiO–SiO_2–sol pillared montmorillonite (*2*).

ditions of 40 kV and 40 mA in the range $3° \le 2\theta \le 80°$. Transmission electron microscopy images were taken using JEM-2010 (HR). Surface areas and porosities were determined from the adsorption-desorption isotherms of N_2 at 77 K after degassing the samples at 393 K with a micromeritics ASAP 2020 apparatus.

Catalytic Activity

The hydrogenation of benzene was applied to evaluate the catalytic activity of the catalysts. The hydrogenation reaction was carried out in a microreactor (stainless steel U-shaped tube with inner diameter 4 mm) under atmospheric pressure. Hydrogen was employed as reductant gas and as carrier gas. The catalyst was reduced in situ under the hydrogen flow (30 ml/min) at 673 K for 2 h before the reaction was performed. A volume of 1 μl benzene was injected into the reactor containing 0.1 g catalyst each time. The product and reactant were analyzed by an on-line gas chromatograph equipped with thermal conductivity detector and data integrator. For comparison, γ-Al_2O_3–supported NiO catalyst with the same nickel loading was also prepared using the impregnation method.

RESULTS AND DISCUSSION

TG-DTA Analysis

TG and DTA curves for the air-dried gel are shown in Fig. 1, three-step weight losses were observed in the TG curve. The initial weight loss occurring below 100°C with a weak endothermic peak in the DTA curve can be assigned to desorption of water. The large weight loss in the temperature range of 180–400°C with an intense exothermic peak corresponded to the elimination of the organic matter (octylamine and residual ethyloxy groups from TEOS) between silicate layers. At higher temperature, an additional progressive weight loss with a weak endothermic peak at around 640°C can be attributed to dehydroxylation processes, both of the clay and the porous silica. An appropriate calcination temperature can be suggested as 550°C to remove the organic moieties completely.

XRD Patterns

The powder XRD patterns of pristine Ca-montmorillonite and NiO–SiO_2–sol pillared montmorillonite are shown in Fig. 2. The XRD patterns of montmorillonite generally show basal 001 reflection and two dimensional diffraction *hk* only; other *hkl* diffractions are usually not observed [13]. The NiO–SiO_2–sol pillared montmorillonite does not exhibit 001 reflections, indicating the delamination of the aluminosilicate layers [14]. The peaks at $2\theta = 37.7°$, 43.7°, and 63.3° could be readily assigned to (111), (220), and (311) lattice planes of cubic NiO crystals respectively (JCPDS78-0643). These peaks are rather broad, indicating that NiO crystals existed with nanosize.

TEM

According to TEM micrographs, as expected, the lamellar clay layers were delaminated and crystalline NiO particles were dispersed evenly in the matrix, which had an average diameter of 8 nm. The structure of the NiO nanoparticles was further confirmed by selective area electron diffraction (SAED) as shown in Fig. 3.

N_2 Adsorption-Desorption Isotherms

Figure 4 shows the adsorption-desorption isotherms of nitrogen for pristine montmorillonite and NiO–SiO_2–sol pillared montmorillonite. All these isotherms can be classified as the BDDT-type IV

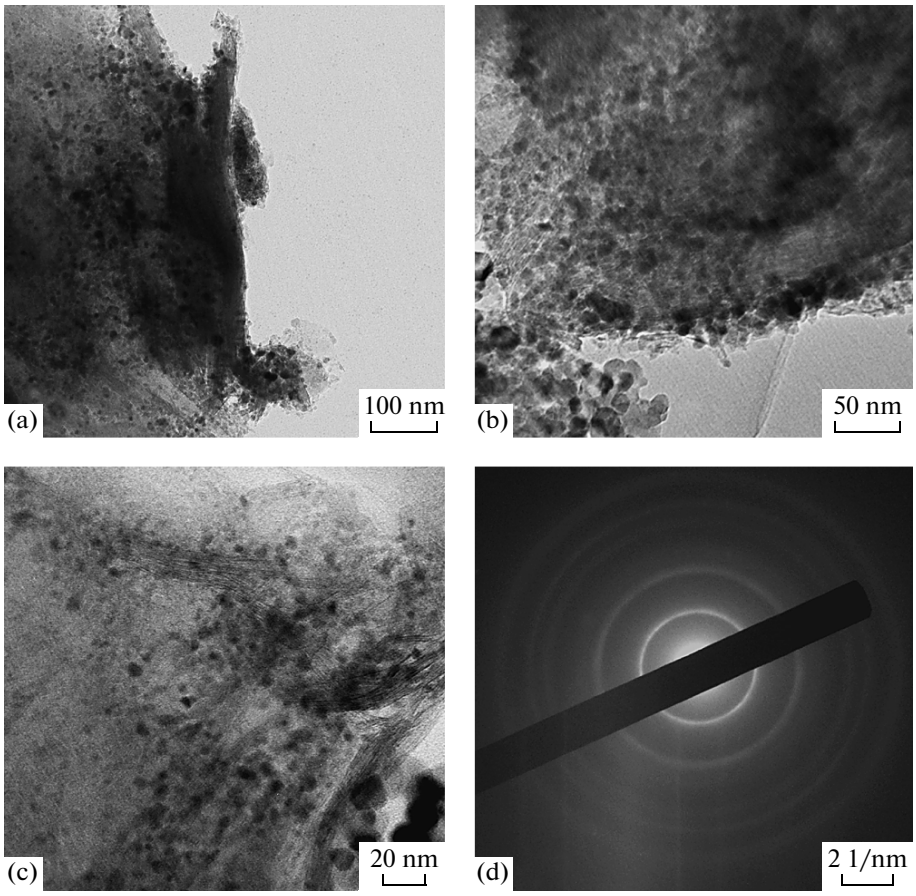

Fig. 3. TEM photographs (a–c) and SAED pattern (d) of NiO–SiO_2–sol pillared montmorillonite.

shape with a hysteresis loop, whose features correspond to type B in Boer's five types representing the presence of open slit-shaped or cylindrical pores formed in gallery regions [15]. The nitrogen uptake of NiO–SiO_2–sol pillared montmorillonite is substantially higher, compared with that of the pristine montmorillonite. The large hysteresis of the NiO–SiO_2–sol pillared montmorillonite indicates more mesoporosity, implying that the elimination of the organic moiety giving rise to mesopores in the interlayers. The values of BET specific surface areas, the t-plot external surface areas, the total pore volume of N_2 adsorbed at relative pressure $P/P_0 = 0.98$ (V_{tot}) and microporisity volume (V_{mic}), deduced from the t-plot, are listed in table. The pillared sample has higher S_{BET} arid V_{tot} compared with the values of the pristine montmorillonite, which can be attributed to the micro- and mesoporous structure of the NiO–SiO_2–sol pillared montmorillonite.

Catalytic Activity

Cyclohexane is found to be the only product for all the catalysts in the activity test, implying that the selectivity of benzene hydrogenation under the reaction temperature is almost 100%. The catalysis experiments revealed that in the reaction temperature range of 140–220°C, the catalytic activity of benzene hydrogenation over the NiO–SiO_2–sol pillared montmorillonite catalyst is higher than that over the γ-Al_2O_3–supported Ni catalyst. The benzene conversion rates as a function of reaction temperature over the catalysts are shown in Fig. 5.

Thus, NiO–SiO_2–sol pillared montmorillonite was synthesized using a novel method. Tetraethyl

Textural characteristics of pristine MMT and NiO–SiO_2–sol pillared montmorillonite

Sample	S_{BET}, m^2/g	S_{ext}, m^2/g	V_{tot}, cm^3/g	V_{mic}, cm^3/g
Pristine montmorillonite	80	73	0.103	0.015
NiO-SiO_2-sol pillared montmorillonite	554	107	0.626	0.383

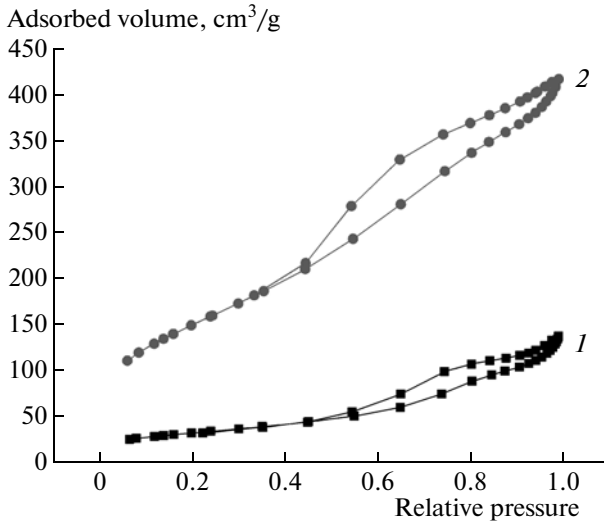

Fig. 4. N_2 adsorption–desorption isotherms of pristine montmorillnite (*1*) and NiO–SiO_2–sol pillared montmorillonite (*2*).

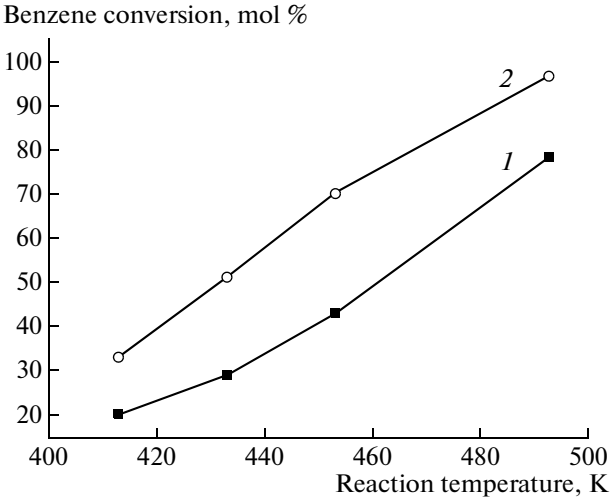

Fig. 5. Benzene conversion rate over Ni/γ–Al_2O_3 (*1*) and NiO–SiO_2–sol pillared montmorillonite (*2*).

orthosilicate and Ni^{2+} were intercalated into the interlayers of H-montmorillonite simultaneously with the intercalation of octylamine. Interlamellar hydrolysis of TEOS catalyzed by octylamine resulted in the siloxane-pillared montmorillonite. A microporous and mesoporous NiO–SiO_2–sol pillared montmorillonite was obtained after removing the organic compounds at 550°C. The nitrogen adsorption-desorption isotherms for the pillared samples revealed that a large number of micro; and mesopores were created between the silicate layers, giving rise to a large surface (554 m^2/g). The catalytic activity of benzene hydrogenation over the NiO–SiO_2–sol pillared montmorillonite catalyst was higher than that over the γ-Al_2O_3–supported Ni catalyst.

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