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Short Communication

Catalytic reforming of n-heptane over Pt/Al-HMS catalysts

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ABSTRACT

Pt catalysts supported on Al-HMS materials were prepared and characterized by XRD, NH_3-TPD, TGA and pyridine-adsorbed FTIR techniques. Catalytic performance of samples was investigated for reforming of n-heptane and compared as a function of Al content. TPD measurements showed that the acidity of Al-HMS materials enhanced with the increasing Al content. Results showed that the ratio of BrÖnsted/ Lewis acidic sites decreased with the increasing Al content. The catalytic evaluation revealed that Pt/Al-HMS catalysts had a high activity for conversion of n-heptane. The distribution of products was described based on the nature of the acidic sites.

1. Introduction

Catalytic reforming of alkanes which is the conversion of conventional petroleum light naphta feeds (C_6 and C_7 hydrocarbons) into branched aliphatic hydrocarbons and aromatics has been studied extensively in the last two decades because at the same time the requirements to the gasoline quality are toughened [1,2]. It has been widely accepted that this reactions are achieved over bifunctional catalysts consisting of noble metal particles supported on a matrix which contains acid sites [3]. The major reactions promoted by bifunctional catalysts are hydrogenation, dehydrogenation, isomerization, cyclization and hydrocracking [4]. Pt/Al_2O_3-Cl is the commercial monometallic reforming catalysts. Owing to environmental concerns, the Pt/Al2O3-Cl catalyst is not the best choice for this reaction because it requires continuous regeneration with chlorine in order to regain the catalyst acidity, which may cause severe corrosion problems. In addition, this kind of catalyst is very sensitive to water and sulfur in the inlet stream. Their use is, however, characterized by high hydrogenolysis activity at high temperatures. In the last decade, researchers paid more attention to hydroconversion of alkanes over solid acid catalysts with large pore diameter including mesoporous molecular sieves in order to prepare new catalysts for the conversion of heavier hydrocarbons [5–11]. Among them, Al-containing mesoporous molecular sieves which possess the acidic sites and good hydrothermal stability are favored. HMS is a hexagonal mesoporous silicate with a particular wormlike pore structure. It has a simple preparation method and cheap primary alkylamines and can be used as a modified support in catalytic reactions. However, no studies have so far been reported in the open literature on the use of Al-HMS for reforming of n-alkanes. In this work, we have investigated the catalytic activities of Pt catalysts supported on Al-HMS for the reaction of n-heptane reforming.

2. Experimental

2.1. Materials and methods

The HMS and Al-HMS materials were synthesized by sol–gel method similar to Pinnavaia and coworkers [12], Mokaya and Jones [13]used TEOS (Merck) as the silica source, aluminum isopropoxide (Merck) as the aluminum source and dodecylamine (Merck) as the surfactant. The samples by the various Si/Al ratios were obtained by taking appropriate amounts of aluminum isopropoxide and TEOS for Si/Al ratio of 5, 10, 20, and 35 following the procedure. Each solid product was separated by filtration and dried at 110 °C overnight and calcined at 540 °C for 6 h in the flowing air.

(0.6 wt %) Pt catalysts were prepared by impregnating the support with appropriate concentration of H_2PtCl_6 (Merck) using HMS or Al-HMS (Si/Al = 5, 10, 20, 35) as the support. After evaporation of the solvent and drying, the Pt catalysts were calcined in flowing air at 300 °C for 4 h. The prepared catalysts are named Pt/Al-HMS(x) that x is Si/Al ratio. Also, in the order to investigate metal loading on the catalytic performance 0.3 and 0.9 wt %Pt/Al-HMS-35 catalysts were prepared.

2.2. Characterization of catalysts

The mesoporous materials were characterized by XRD using STOE diffractometer. The acidity measurement of HMS and Al-HMS materials

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was evaluated by TPD of ammonia in a TPD/TPR analyzer (2900 Micromeritics). To evaluate and analyze the type of acidic sites, pyridine adsorption on the samples was performed on a Fourier-transform infrared spectrometer (170-SX). The level of coke laid down on the surface measured by thermogravimetric analysis (TGA) equipment using a STA503 M instrument.

2.3. Catalytic evaluation

The catalytic conversion of n-heptane in the presence of hydrogen was carried out at the temperature range of 450–550 °C, LHSV = 2 h^{-1}, and P = 1 atm in a continuous fixed-bed microreactor packed with 1.0 g of catalyst. After the treatment of catalyst in a H_2 flow (60 ml min^{-1}), n-heptane was fed into the reactor. Hydrogen was also introduced in the optimized amount of H_2/C_7 molar ratio for our samples in order to obtain the best selectivity of desired products (H_2/HC = 5). The performance of the catalysts was tested after 0.5 h time on stream (TOS) at noted temperatures for each experiment. Also, the catalytic performance of all samples was investigated at 500 °C for 5.5 h time one stream. The reaction products were analyzed by online gas chromatography (Shimadzu 8A) equipped with a TCD detector.

3. Result and discussion

3.1. Characterization

The XRD diagrams of the HMS and AlHMS(*x*) materials are similar to those reported in literatures [12,13], as shown in Fig. 1. There is a single broad reflection that can be assigned to a lattice with the short-range hexagonal symmetry. The increase of Al content in the samples results in a broadening of this peak, indicating that incorporation of Al is associated with an increasing lattice disorder. The NH_3-TPD results for acidic properties are shown in Table 1. TPD profile of pure HMS shows no evident peak, indicating that HMS material has no acid sites (not shown here). There is one asymmetric broad peak in the range of 150–500 °C on TPD profiles of Al-HMS samples, attributed to the distribution of acid site from weak to strong acid sites (not shown here). Maximum of desorption peak is in the range of 250–300 °C corresponded to the medium acid sites. Details of Table 1 (second column) indicate that the number of acidic sites of Al-HMS increases with the decrease of Si/Al ratio. Results also indicate that maximum of the TPD diagram shifts to the high temperatures with the decrease of Si/Al ratio. It means that the strength of acid sites increased with the increasing Al content. The type of acid sites (Lewis acid and Bronsted acid) was also studied by FT-IR spectra of pyridine adsorption. It is well known that the vibration bands in the 1400–1650 cm^{-1} regions of the IR spectrum of the chemisorbed pyridine could be distinguished between the BrÖnsted and Lewis acid sites [14,15]. The infrared spectra of the pyridine-adsorbed Al-HMS (not shown here) revealed three peaks at ca 1449 and 1540 cm^{-1} due to pyridine adsorbed on Lewis and BrÖnsted acid sites, respectively and near 1480 cm^{-1} corresponded to Lewis and BrÖnsted (L + B) sites. It is observed that the intensities of bands for adsorbed pyridine on BrÖnsted and Lewis acid sites increased with the increase of Al content. The infrared spectra of all the samples were recorded at room temperature. BrÖnsted to Lewis pyridine ratio (B/L) was obtained by measuring the integrated absorbance of bands for BrÖnsted and Lewis acid-site chemisorbed pyridine and by using the correlation developed by Emeis for porous aluminosilicates (1.67 cm/μmol for the 1545 cm^{-1} band characteristic of pyridine on a BrÖnsted acid site and 2.22 cm/μmol for the 1455 cm^{-1} band of pyridine on a Lewis acid site) [16]. The B/L acid site ratio decreases with increasing Al content. It is in agreement with this fact that the tetrahedrally coordinated framework aluminum (potential BrÖnsted acid site) decrease with increasing Al content while octahedrally extra framework aluminum (potential Lewis acid site) increases [17,18]. The number of BrÖnsted and Lewis acid sites was calculated from the NH3-TPD results by using the B/L ratios (Table 1).

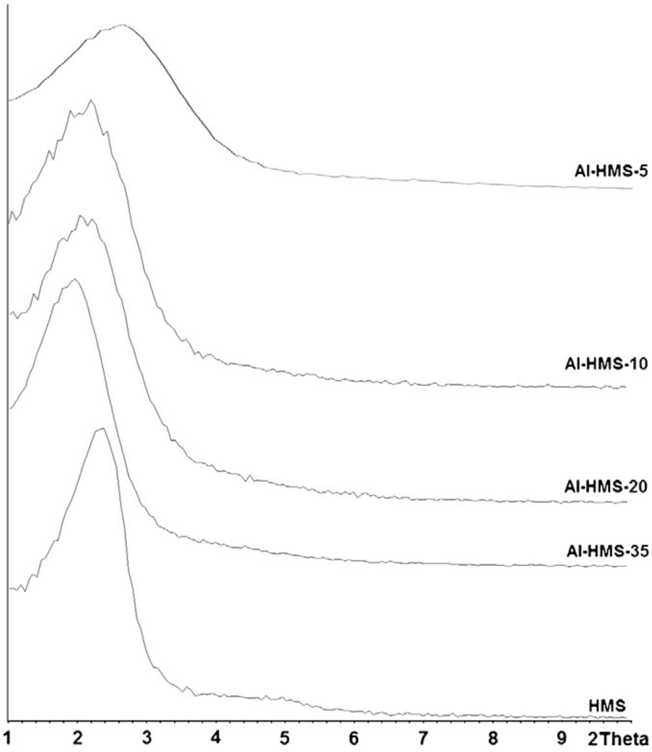

Fig. 1. XRD patterns of HMS and Al-HMS with different Si/Al ratio.

Table 1
Acidic properties of mesoporous supports.

Sample	Peak Temperature of TPD (°C)	Acidity (mmol NH_3/g)	B/L	BrÖnsted acidity (mmol NH_3/g)	Lewis acidity (mmol NH_3/g)
Al-HMS-35	258.9	0.426	1.8	0. 277	0.153
Al-HMS-20	270.8	0.845	1.37	0.489	0. 355
Al-HMS-10	278.4	1.398	1.06	0.720	0.677
Al-HMS-5	287.1	1.556	0.86	0.719	0.837

3.2. Hydroconversion of n-C7

In order to make an evaluation of the activity of catalysts, n-heptane hydroconversion was performed over mesoporous catalysts between 450 and 550 °C. The major products obtained were classified into (1) hydrogenolysis, (2) hydrocracking, (3) C_7 isomers and (4) aromatic products.

The activity and selectivity of various products over Pt/HMS and Pt/Al-HMS catalysts are given in Fig. 2(a–e). It can be seen that Pt/Al-HMS(*x*) catalysts are highly active for conversion of n-heptane (Fig. 2a). Fig. 2 shows that n-heptane conversion linearly increased with increasing reaction temperatures. The highest conversion for n-heptane appeared for the Pt/Al-HMS-10 catalyst. It was observed that the catalytic activity does not follow that the surface acidity variation may be due to the fact that catalytic activity are influenced by more activity-determining factors including textural properties, metallic function and others. The selectivity of isoheptanes as a function of temperature is presented in Fig. 2b. It can be seen that the isomerization selectivity depends on the reaction temperature. For all samples, the isomerization selectivity decreases with the increasing temperature in agreement with the fact that isomerization and