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A study of *n*-hexane hydroisomerization catalyzed with the $Pt/H_3PW_{12}O_{40}$/Zr-MCM-41 catalysts

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Abstract

A series of Zr-modified MCM-41 mesoporous materials with a variety of Si/Zr molar ratios were synthesized by the surfactant-templated method. Textural properties, crystalline structure and surface acidity were characterized by X-ray diffraction (XRD), low-temperature N_2 physisorption isotherms, solid-state nuclear magnetic resonance (MAS-NMR), UV–visible spectroscopy, and Fourier-transform infrared (FTIR) spectroscopy of pyridine adsorption techniques. Both the as-made and the calcined materials show the typical MCM-41 structure with hexagonal mesochannels. The structural regularity varies with zirconium content in the materials. A proper amount of zirconium ions incorporated into the Si framework may noticeably improve the structural order, but high zirconium content leads to the reduction of the structural regularity. The mean pore diameter of the materials increases from 2.8 to 3.0, 3.8 and 4.5 nm as the Si/Zr molar ratio decreases from 25 to 15, 8 and 4, respectively. Meanwhile, the surface area and pore volume diminish with the increase of zirconium content. As $H_3PW_{12}O_{40}$ (referred as HPW) is dispersed on the Zr-MCM-41 materials, the Brönsted acidity is greatly enhanced: from four to eight times. Three forms of heteropolyanions: (i) bulk-like HPW particles, (ii) highly dispersed HPW clusters with deformed Keggin structure and (iii) HPW species with partially fragmented Keggin structure, are adopted by the HPW deposited on the Zr-MCM-41 solids, due to the different interactions between the heteropolyacid species and the support. The 1 wt.%Pt/25 wt.%HPW/Zr-MCM-41 catalysts show high activity for the *n*-hexane hydroisomerization reaction, with 100% selectivity to isohexanes at temperatures below 260 °C. Increasing the zirconium content generally leads to a higher *n*-hexane conversion but it lowers the selectivity to hexane isomers that might be related to the different pore diameter distribution and surface density of the Brönsted acid sites.

Keywords: Zr-MCM-41; Heteropolyacid; *n*-Hexane; Hydroisomerization; Catalyst

1. Introduction

The Si-based MCM-41 materials have large potential applications in the fine chemical industry, adsorption and separation processes, heterogeneous catalysis and in the petroleum refinery industry [1–5]. However, Si-based MCM-41 lacks Brönsted acidity and it exhibits only mild Lewis acidity, which is much weaker than that of microporous zeolites [6]. In acidic catalyzed reactions, such as the isomerization of hydrocarbons, when Si-MCM-41 is used either as catalyst or as catalyst support, its acidity needs to be enhanced [7].

Through two approaches, the surface acidity of the Si-MCM-41 materials can be enhanced: the first is the framework modification by incorporation of foreign ions like Al^{3+} and Zr^{4+} into the Si framework [8–10], and the second is surface grafting by the introduction of strong acid groups like SO_4^{2-} or heteropolyacids [3,11–15].

In the present work, the enhancement of the surface acidity of Si-MCM-41 by simultaneous modifications of the surface

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and the framework is reported. Our aim was to introduce zirconium ions into the Si framework during the synthesis procedure and to disperse a heteropolyacid, $H_3PW_{12}O_{40}$, onto the surface of the Zr-MCM-41 support. After impregnation with a given amount of H_2PtCl_6, a series of 1 wt.%Pt/25 wt.%HPW/Zr-MCM-41 (referred as Pt/HPW/Zr-MCM-41) catalysts can be obtained.

The textural properties including surface area, average pore diameter and pore size distribution of the Zr-MCM-41 solids were measured by the low-temperature N_2 physisorption method. The crystalline structures of the resultant mesoporous solids and Pt/HPW/Zr-MCM-41 catalysts were studied by using XRD, ^{31}P MAS-NMR and UV–visible spectroscopic techniques. The surface acidity of both, the Zr-MCM-41 support and the catalysts, were determined by using the *in situ* FTIR of pyridine adsorption method. The catalytic activity and selectivity of the catalysts were evaluated in the reaction of *n*-hexane isomerization in the presence of hydrogen at different conditions.

2. Experimental

2.1. Preparation of the Zr-MCM-41 supports

The Zr-MCM-41 solids were prepared using tetraethylorthosilicate (TEOS) as Si precursor and zirconium-*n*-propoxide (70% in propanol) as Zr source, along with cetyltrimethylammonium chloride (CTACl) as synthesis template. The typical preparation procedure of a Zr-MCM-41 sample with a molar ratio of Si/Zr = 25 is as follows: First of all, two solutions were prepared, the first solution was made by adding 1.77 ml of zirconium-*n*-propoxide and 22.8 ml of TEOS with stirring; the second solution was made by adding 11.3 g of CTACl into 110 ml of hot water (around 50 °C) with stirring, followed by the addition of 110 ml of $NH_3{\cdot}H_2O$ (28 wt.%). Then, the first solution was added, drop by drop, into the second solution. During the addition, the mixture was vigorously stirred for about 2 h, until a gel was formed. The resultant gel was loaded into a stoppered Teflon bottle without stirring and kept at 100 °C for 48 h. After cooling to room temperature, the resulting solid product was recovered by filtration and was washed for four times with 500 ml deionized water. The white solid obtained was dried in air at 80 °C for 24 h. Finally, the sample was calcined at 600 °C for 6 h in air. The heating rate was 1 °C/min. The samples were referred as Zr-MCM-41-*n*, where molar ratio *n* = Si/Zr = 25, 15, 8 and 4.

2.2. Preparation of the catalysts

The Zr-MCM-41 supports were first impregnated with 20 ml of a methanol solution containing a given amount of $H_3PW_{12}O_{40}$. The solvent was removed at 40 °C in a vacuum evaporator until dryness. Afterwards, the 25 wt.%HPW/Zr-MCM-41 solids were impregnated with 20 ml of a water solution containing H_2PtCl_6. The solvent was evaporated at 80 °C in a vacuum evaporator until a dried material with 1 wt.%Pt was obtained. The amounts of the $H_3PW_{12}O_{40}$ and the H_2PtCl_6 used depend upon the amount of the support. The dried catalysts were calcined at 300 °C in air for 2 h.

2.3. X-ray diffraction analysis

The low-angle X-ray diffraction patterns of the samples were measured in a D-500 SIEMENS diffractometer with a graphite secondary beam monochromator producing a monochromatic Cu Kα radisation, and the evaluation of the diffractograms was made by DIFFRAC/AT software. The scanning was made from 1.5° to 10°, with a 2θ step size of 0.02° and a step time of 2 s. In order to avoid the problem of illuminated area at low 2θ angles, all the samples were measured using the same sample holder. In this way, the hexagonal reflection (1 0 0) positions as well as the intensities are directly comparative. Position correction was made using the NIST standard reference material 675.

2.4. N_2 adsorption isotherms measurements

The specific surface area, pore volume and pore size distribution of the samples were measured in a Digisorb 2600 equipment by using low-temperature N_2 physisorption isotherms. Before the measurement, the sample was evacuated at 350 °C under vacuum condition. The surface area was calculated using the BET method based on the adsorption data within the partial pressure P/P_0 range from 0.01 to 1. The mesopore volume was determined from the N_2 adsorbed at a $P/P_0 = 0.4$.

2.5. Solid-state nuclear magnetic resonance (^{31}P MAS-NMR)

Solid-state ^{31}P MAS-NMR spectra were recorded on a Bruker 400 MHz spectrometer at a frequency of 79.49 MHz, 7.5 kHz spinning, using pulses at 90 s intervals and 4 mm zirconia rotors. The number of accumulations was 500. All the measurements were carried out at room temperature. For the ^{31}P analysis, H_3PO_4 was used as standard reference to obtain the chemical shift of the solid materials.

2.6. The diffuse reflectance UV–visible spectroscopic analysis (UV–vis)

The UV–vis diffuse reflectance spectra of the samples were collected on a Varian Cary 1G UV–visible spectrometer with an attached diffuse reflectance apparatus at room temperature after pre-treatment at 300 °C for 2 h. Scan control conditions: average time, 0.10 s; data interval, 1.00 nm; scan rate, 600 nm/min; absorption mode; wavelength range, 190–900 nm.

2.7. FTIR spectroscopy of pyridine adsorption

To evaluate and analyze the strength and types of acid sites, pyridine adsorption on the samples was performed on a 170-SX Fourier-transform infrared (FTIR) spectrometer at different temperatures, ranging from 25 to 400 °C. Before pyridine