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Acid sites in mesoporous Al-SBA-15 material as revealed by solid-state NMR spectroscopy

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Abstract

The nature of acid sites in Al-SBA-15 materials with various Si/Al ratios was studied by various NMR techniques including ^{27}Al, ^{29}Si, ^{1}H, ^{31}P MAS (magic-angle spinning), and some double-resonance methods such as ^{1}H/^{27}Al transfer of population in double resonance (TRAPDOR). XRD and ^{27}Al NMR results indicate that Al has been successfully incorporated into the framework of SBA-15 materials by post-synthesis method. The bridging hydroxyl groups (SiOHAl) associated with Brönsted acid sites are invisible either in ^{1}H MAS or in ^{1}H/^{27}Al TRAPDOR spectra of the dehydrated Al-SBA-15 materials. However, after the adsorption of basic probe molecules, such as trimethylphosphine oxide (TMPO), trimethylphosphine (TMP) and acetone, ^{31}P MAS and ^{13}C CP MAS NMR experiments strongly support the presence of Brönsted acid sites. NMR results suggest that Brönsted acid sites in dehydrated Al-SBA-15 materials are in the form of terminal silanol groups in the vicinity of aluminum atoms that can be induced to generate the bridging hydroxyl groups by the adsorbed basic probe molecules. Although the acid strength of Al-SBA-15 materials detected by different probe molecules is different, it is comparable to that of microporous zeolites. It is noteworthy that no Lewis acid site can be found in the Al-SBA-15 materials.

Keywords: Solid-state NMR; Al-SBA-15; Zeolites; Brönsted acid sites; Bridging hydroxyl groups

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1. Introduction

Microporous zeolites with regular arrays of uniformly sized channels have been widely applied in many fields including adsorption, separation, ion exchange and catalysis in past decades [1]. However, their relatively small pores (with a diameter usually less than 2 nm) cannot admit large molecules, leading to the limitation of their application. The synthesis of mesoporous MCM-41 materials by Mobil researchers in 1992 with pore size in the range of 1.5–10 nm can satisfy the size requirement [2,3], but their relatively low hydrothermal stability and weak acidity would limit their practical application. In 1998, Zhao et al. synthesized a new type of mesoporous material SBA-15 with uniform two-dimensional hexagonal structure [4]. Compared with microporous zeolites, this material is characterized by larger pore sizes up to approximately 30 nm and allows bulky molecules to enter into the pores. It has higher hydrothermal stability and thicker pore wall (3.1–6.4 nm) compared with mesoporous MCM-41 materials. For these reasons, the discovery of SBA-15 provides a potential for the material as versatile catalysts and catalyst support for conversion of large molecules. Many investigations have indicated that Al-SBA-15 materials show much higher catalytic activity compared with Al-MCM-41 material [5,6]. Since pure siliceous SBA-15 materials lack acidity, active centers must be introduced into their framework (mesoporous wall). Generally, incorporation of heteroatoms, such as Al into microporous zeolites will introduce a charge imbalance in the framework which is balanced by protons, thus generating bridging hydroxyl groups (SiOHAl, Brönsted acid sites) on these materials. Two methods including direct

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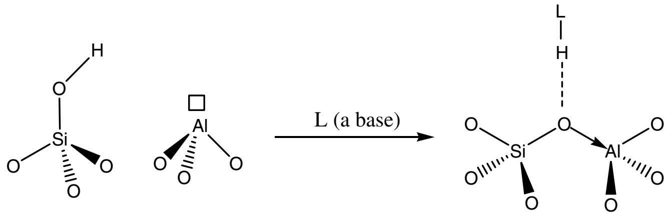

Scheme 1.

synthesis and post-synthesis have been developed to incorporate Al into the framework of mesoporous materials [7–12]. However, the direct synthesis approach seems infeasible for SBA-15 because most of aluminum precursors will dissolve in the strong acidic media (2 M HCl) during the synthesis procedure [4]. Several post-synthesis methods where aluminum was grafted onto the mesoporous wall with various aluminum sources have been developed without the mesoporous structure seriously destroyed [11,12].

In the case of zeolites, the introduction of Al into their framework will lead to the formation of bridging hydroxyl groups (Brönsted acid sites). However, whether the similar situation occurs in mesoporous materials still keeps argument. Some researchers assigned the hydroxyl vibration at about 3606 cm^{-1} in IR spectrum to the acidic bridging hydroxyl groups while others disagreed the assignment [13–17]. For example, Trombetta et al. argued that the Brönsted acid sites in mesoporous materials or aluminosilicates resulted from terminal silanol groups in the vicinity of aluminum atoms [16]. After the adsorption of a basic probe, such as pivalonitrile, the terminal silanol groups were induced to form the bridging hydroxyl groups (SiOHAl, shown in Scheme 1). In a previous study, we found that the bridging SiOHAl groups could only be observed for Al-MCM-41 materials by $^{1}H/^{27}Al$ TRAPDOR technique at low temperatures [18].

In this paper, we synthesized a series of Al-SBA-15 samples with various Si/Al ratios following the post-synthesis procedure described in the literature [11]. Using TMP, TMPO and acetone-2-^{13}C as probe molecules, we investigated the nature of acid sites in Al-SBA-15 samples with various solid-state NMR techniques. Our NMR experimental results indicate that the bridging hydroxyl groups are invisible in either ^{1}H MAS or $^{1}H/^{27}Al$ TRAPDOR spectra of the Al-SBA-15 materials in the absence of any basic probe molecules. Only after the adsorption of the basic molecules, the bridging hydroxyl groups can be detected by NMR, supporting the model raised by Trombetta et al. [16].

2. Experimental

2.1. Sample preparation

A purely siliceous SBA-15 samples was synthesized following the method described by Zhao et al. [4,12]. Two grams of amphiphilic triblock copolymer, poly(ethylene oxide)$_{20}$–poly(propylene oxide)$_{70}$–poly(ethylene oxide)$_{20}$ (average molecular weight 5800, Aldrich) was dissolved in 15 g of water with stirring. Followed by adding 60 g of 2 M HCl solution and then 4.25 g of tetraethyl orthosilicate (TEOS) with stirring for 2 h, the mixture was crystallized at 100 °C for 2 days in a Teflon lined autoclave. The molar composition of the reaction mixture was 1.00TEOS: 1.65×10^{-2} $EO_{20}PO_{70}EO_{20}$:6.95 HCl:140 H_2O. The solid product was then filtered, washed three times with distilled water, dried in air at room temperature and then calcined in air at 550 °C for 4 h to remove the template. Finally, a white powder was obtained.

The alumination procedure of SBA-15 followed the method reported in the literature [11]. Silica SBA-15 (1 g) was stirred in 50 ml of water containing various amounts (0.1344, 0.0672 and 0.0336 g) of sodium aluminate at room temperature for 20 h. The mixture was filtered, washed, dried at ambient temperature overnight and then calcined in air at 550 °C for 5 h. Finally, Al-SBA-15 samples with different Si/Al ratios (Si/Al = 10, 20, 40) were obtained. It should be noted that the Si/Al ratios of 10, 20 and 40 were calculated from chemical stoichiometric compositions used in the sample syntheses.

The XRD patterns of the Al-SBA-15 samples were performed on a Scintag PADX diffractometer equipped with a liquid nitrogen-cooled germanium solid-state detector using Cu Kα radiation.

For ^{1}H MAS NMR measurements, the Al-SBA-15 samples were placed into glass tubes that could be connected to a vacuum line. The samples were heated to 400 °C with a rate of 1 °C min^{-1} and then kept at that temperature for 12 h to remove water. For ^{31}P, ^{13}C NMR experiments of adsorbed molecules, the dehydrated samples were cooled to room temperature before a known amount of TMP or acetone was condensed and frozen inside the samples with liquid nitrogen. The adsorption procedure of TMPO was different from that of TMP. A known amount of dehydrated Al-SBA-15 sample was mixed with a CH_2Cl_2 solution containing TMPO in a glovebox before the mixture was stirred for about 3 h with an ultrasonic shaker, placed in the glovebox overnight, and then connected to a vacuum line to remove CH_2Cl_2 solvent. Prior to NMR experiments, the samples were packed into NMR rotors with a Kel-F endcap in the glovebox.

2.2. NMR spectroscopy

All NMR experiments were performed on a Varian Infinityplus-400 spectrometer equipped with a Chemagnetics triple-resonance 7.5 mm probe. The Larmor frequencies for ^{1}H, ^{27}Al, ^{13}C, ^{31}P and ^{29}Si are 400.12, 104.26, 100.61, 161.91 and 79.49 MHz, respectively. The chemical shifts were referenced to TMS for ^{1}H and ^{29}Si, to a 0.1 M $Al(NO_3)_3$ solution for ^{27}Al, to hexamethylbenzene for ^{13}C, and to an 85% H_3PO_4 solution for ^{31}P, respectively. A $\pi/12$ flip angle excitation pulse was used with a recycle delay of 0.5 s for ^{27}Al single pulse experiment. For ^{1}H,