^{1}H NMR Study of Hydroxy Groups in Mesoporous Molecular Sieve SBA-15

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Three types of hydroxy groups, which are attributed to single, hydrogen-bonded and geminal SiOHs in mesoporous molecular sieve SBA-15 are directly and quantitatively observed by ^{1}H ultrafast MAS NMR spectroscopy.

Since the first report of mesoporous molecular sieve, MCM-41,[1] there has been an extensive study of mesoporous materials. The unique characteristics of mesoporous molecular sieves, such as uniform mesoporous structure and large surface area, make the materials potential in catalysis, separation of large molecules, nanoelectronics, etc. However, early reported mesoporous molecular sieves suffer low thermal and hydrothermal stabilities, which limit their applications. In recent years a number of mesoporous molecular sieves with high thermal and hydrothermal stabilities were reported. For an example, the structure of SBA-15[2] may sustain up to 850 °C in air and in boiling water for 24 h.

The framework of mesoporous molecular sieve consists of amorphous silica. Because of large surface area a large fraction of silicon presents as SiOH on the internal surface. The high concentration of surface SiOH may be utilized to introduce catalytically active sites by grafting desirable species. In order to control the grafting process and the structure of active species at molecular level, it is crucial to precisely measure the concentration of SiOH. Single, hydrogen-bonded and geminal SiOH groups in MCM-41 were proposed based on the results of ^{29}Si MAS NMR,[3–6] FT–IR,[3,5,6] TPD[3] and TG[3]. However, none of these techniques can provide direct and quantitative information on the type and concentration of SiOH.

In the present study we apply for ^{1}H ultrafast MAS NMR spectroscopy to study SiOH in SBA-15. Our aim is to develop a new method to directly and quantitatively monitor the grafting process in mesoporous molecular sieves, in order to control the preparation of mesoporous catalyst at molecular level.

Synthesis of SBA-15 followed the recipe in literature.[2] The material was calcined in air at 773 K for 8 h to eliminate the surfactant. ^{1}H MAS NMR spectra were obtained at 500 MHz on a Bruker Avance DMX500 spectrometer with 10 s recycle delay at a spinning rate of 30 kHz using a Bruker probehead with 2.5 mm rotors. Haxamethylbenzene with known mass was used to calibrate the proton numbers in SBA-15. ^{29}Si MAS NMR spectra were acquired at 59.6 MHz on a Bruker Avance DSX300 spectrometer with 600 s recycle delay at a spinning rate of 3.5 kHz using a Bruker probehead with 7 mm rotors. Both ^{1}H and ^{29}Si chemical shifts were referenced to tetramethylsilane (TMS). All the dehydrated samples were packed into NMR rotors under dried nitrogen atmosphere in a glove box containing P_2O_5.

The XRD patterns of both as-synthesized and calcined SBA-15 exhibit strong and typical peaks of SBA-15.[2,7] Nitrogen adsorption and scanning electron microscopy measurements also indicate that both samples do not contain noticeable amount of amorphous materials. Therefore, all SiOH detected by ^{1}H and ^{29}Si MAS NMR mainly contribute from SBA-15.

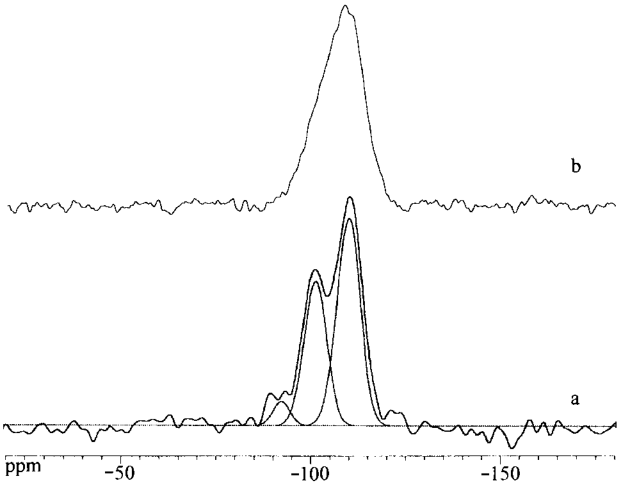


Figure 1. ^{29}Si MAS NMR spectra of (a) as-synthesized SBA-15 and (b) calcined SBA-15.

^{29}Si MAS NMR spectrum of as-synthesized SBA-15 (Figure 1a) shows three peaks at –92, –101, and –110 ppm with an intensity ratio of 0.091:0.57:1.00, assigned to Q^2 ($Si(OSi)_2(OH)_2$), Q^3 ($Si(OSi)_3(OH)$), and Q^4 ($Si(OSi)_4$),[3–6,8] respectively. Based on these data, the molecular formula of as-synthesized SBA-15 is $SiO_{1.77}(OH)_{0.45}$, i.e. ca. 40% of silicon atoms are SiOH. For a grafting process, a complete removal of surfactant is necessary, which is the best through calcination. However, the intensities of Q^2 and Q^3 decrease and the peaks of Q^2, Q^3 and Q^4 severely overlap (Figure 1b) after calcination. Similar to other mesoporous molecular sieves, it is very difficult to discriminate the type and concentration of different types of SiOH accurately from ^{29}Si MAS NMR spectra even with deconvolution.

^{1}H MAS NMR is, in principle, a very useful tool to study SiOH groups.[9] First, ^{1}H NMR measures the hydrogen atoms in SiOH groups directly. Second, ^{1}H NMR signals are much stronger than ^{29}Si ones. Third, the spin–lattice relaxation times of ^{1}H nuclei in mesoporous molecular sieves are normally in an order of seconds, whereas those for ^{29}Si nuclei are in an order of at least minutes. Therefore, the measuring time of ^{1}H NMR is much shorter than that of ^{29}Si NMR. However, due to the strong dipole–dipole interaction in solid, ^{1}H MAS NMR signals are normally very broad. Recently, with the development of NMR techniques, ultrafast MAS probehead becomes commer-

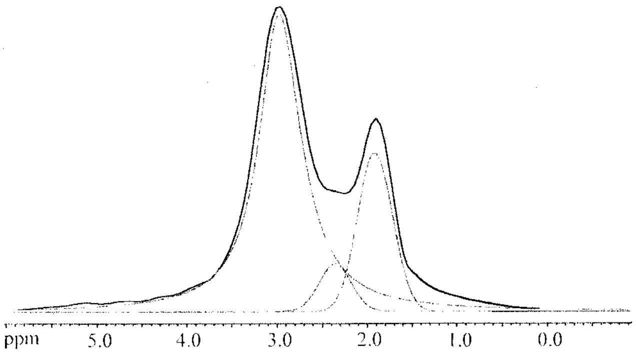
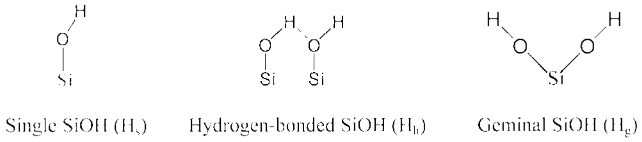


Figure 2. ^{1}H ultrafast MAS NMR spectrum of calcined SBA-15.



Scheme 1.

cially available. The maximum operating spinning rate of 30–35 kHz enables to remove the ^{1}H dipole–dipole interaction in mesoporous molecular sieves and to discriminate the SiOH groups in SBA-15 directly and quantitatively.

Figure 2 shows ^{1}H ultrafast MAS NMR spectrum of calcined SBA-15. There are two strong resonances at 3.0 and 1.9 ppm and a weak resonance at 2.4 ppm with an intensity ratio of 1.00 : 0.56 : 0.16. These chemical shifts are in the range of SiOH. In mesoporous molecular sieves, there are three possible SiOH groups, i.e. single (H_s), hydrogen-bonded (H_h) and geminal SiOH (H_g) groups[3–6] (Scheme 1). Among three SiOH groups, the concentration of H_g is the lowest. Therefore, the peak at 2.4 ppm may be assigned to H_g, corresponding to Q^2 site, which is difficult to be observed in the ^{29}Si MAS NMR spectrum of the calcined sample. Because the concentration of H_s is relatively high, some of adjacent H_s are expected to link together through hydrogen bonds to form H_h. However, H_s and H_h cannot be discriminated in the ^{29}Si MAS NMR spectrum as only one Q^3 peak is observed. As less electron density causes the chemical shift of proton to move to lower field, we may assign the peaks at 3.0 and 1.9 ppm to H_h and H_s, respectively. Using known-mass haxamethylbenzene as an external standard to calculate proton population, we obtain that the total number of hydroxy groups is 1.6×10^{21} g^{-1}, i.e. the numbers of H_h, H_g, and H_s are 9.3×10^{20}, 1.5×10^{20}, and 5.2×10^{20} g^{-1}, respectively. Fifteen percents of silicon in calcined SBA-15 is SiOH. Based on these data, the molecular formula of calcined SBA-15 is $SiO_{1.92}(OH)_{0.16}$. Although these three SiOH groups were proposed in MCM-41 based on several techniques,[3–6] the unique ^{1}H ultrafast MAS NMR offers unambiguously direct and quantitative results. The assignment is further supported by the ^{1}H ultrafast MAS NMR study of SBA-15 grafted with vanadium. As the grafting on an H_h site may occur further with other adjacent SiOH, the intensity of H_h peak decreases relatively more after grafting.

In conclusion, three types of SiOH groups, which are attributed to single, hydrogen-bonded, and geminal SiOHs, exist over SBA-15 surface. ^{1}H ultrafast MAS NMR can characterize quantitatively and directly the type and concentration of SiOH groups and, therefore, becomes an effective tool to monitor grafting process in mesoporous molecular sieves.

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