Solid state NMR study of acid sites formed by adsorption of SO₃ onto γ-Al₂O₃

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Detailed structure of Brønsted acid sites on the surface of SO₃/Al₂O₃ catalyst has been proposed based on ¹H/²⁷Al TRAPDOR NMR results and the acidity of the catalyst has also been characterized by NMR probe molecules.

Sulfated metal oxide (SO_4^{2-}/MO_x, M = Zr, Ti, Fe, Al) catalysts have received a great deal of attention because of their strong Hammett acidity and high activity for the isomerization of paraffins, specifically n-butane, at low temperatures.[1–5] In the past 20 years, numerous studies have been devoted to characterization of their physicochemical properties and catalytic performance in various chemical reactions. However, a number of issues regarding the structure of sulfated species on the catalyst surface, the acid strength and the detailed structure of most acidic centers, which play a key role in high catalytic performance, are still the matter of open debate. At present, for example, there are at least ten theories on the formation of strong acid sites on SO_4^{2-}/ZrO_2 catalysts, but none of them have been generally accepted.[6] Solid state NMR has proved to be a powerful technique for investigating the structure of acid sites on various solid acid catalysts.[7] Recently, Haw *et al.*[8] studied the acid sites formed by adsorption of SO₃ onto ZrO₂ and SiO₂ using NMR and theoretical calculations. In this communication, we report multinuclear solid state NMR studies on the acidity of an SO₃/Al₂O₃ catalyst.

SO₃/Al₂O₃ was prepared by adsorption of SO₃ gas onto the surfaces of activated γ-Al₂O₃ in an autoclave at 573–593 K for 4 h, followed by calcination in flowing air at 673 K for 2 h. Prior to NMR experiments, the samples were placed in glass tubes and dehydrated at 623 K under a pressure below 10^{-2} Pa for 5 h on a vacuum line. 50 Torr of trimethylphosphine (TMP) was introduced into the activated catalysts and equilibrated for 1 h, then degassed for 1 h at room temperature. A known amount of [2-¹³C]acetone (0.2 mmol g⁻¹) was introduced and frozen on the activated catalysts by liquid N₂. Finally, the samples were flame sealed. The sealed samples were transferred into a ZrO₂ rotor (tightly sealed by a Kel-F cap) under a dry nitrogen atmosphere in a glove box.

All the NMR experiments were carried out at 9.4 T on a Varian Infinityplus-400 spectrometer. ¹H MAS NMR spectra were recorded with a spin echo pulse sequence. The ¹H/²⁷Al TRAPDOR experiment was performed according to the method of Grey *et al.*[9] Single pulse ³¹P MAS NMR experiments with ¹H decoupling were performed with a 8 s recycle delay. ¹H → ¹³C CP/MAS spectra were recorded with a 2 ms contact time and a 2 s recycle delay. Spatially selective composite pulses[10] were combined with conventional CP pulse sequences in order to effectively suppress weak signals (background) from the spinning module.

The ¹H NMR spectrum of parent γ-Al₂O₃ is shown in Fig. 1a. In amorphous γ-alumina, there are three types of OH groups:[11] a terminal OH group attached to a single tetrahedral or octahedral Al (OHAl_T or OHAl_O), a bridging OH coordinated to two octahedral Al (OH2Al_O) or to one tetrahedral Al and one octahedral Al (OHAl_O Al_T) and a bridging OH attached to three octahedral Al (OH3Al_O), giving rise to ¹H signals at *ca.* 0, 2.5 and 4.3 ppm,[12] respectively. Similar assignments can be made

for the 0.3 and 2.2 ppm signals and the shoulder peak at the high frequency of the 2.2 ppm signal in our ¹H NMR spectra. After loading SO₃ gas onto the surface of γ-Al₂O₃ (Fig. 1b), there are some changes in the corresponding spectrum. First, the peak at 2.2 ppm slightly shifts to 2.4 ppm and it dominants the whole spectrum, while the intensity of the 0.3 ppm signal considerably decreases, suggesting that acidic SO₃ gas reacts preferentially with the basic terminal OH groups (OHAl_T or OHAl_O). Second, a new signal at 11.2 ppm emerges in the spectrum of SO₃/Al₂O₃. In order to reveal the nature of these signals, we carried out the ¹H/²⁷Al TRAPDOR experiment. As shown in Fig. 1c, under Al irradiation, the signals at 0.3, 2.4 and 4.3 ppm are significantly suppressed, while the intensity of the 11.2 ppm signal remains almost unchanged (see Fig. 1c and Fig. 1d), indicating that the hydroxyl groups corresponding to the 11.2 ppm signal are not in close proximity to Al. Thus, we tentatively attribute the 11.2 ppm signal to hydroxyl groups connected to S atom, as shown in Scheme 1A. There are two equilibrium configurations for the surface sulfated species. Because the proton in the surface species is a relatively large distance away from Al, no obvious TRAPDOR effect can be observed for the 11.2 ppm signal. Finally, a peak at 4.3 ppm can be observed in the corresponding ¹H NMR spectrum. Since this signal shows a strong TRAPDOR effect, it should arise from the most acidic bridging OH group (OH3Al_O).[13] However, by careful spectral deconvolution and integration, we found that the integrated intensity of this peak (including its spinning sidebands) is increased by 1.7 times compared with that of the shoulder peak
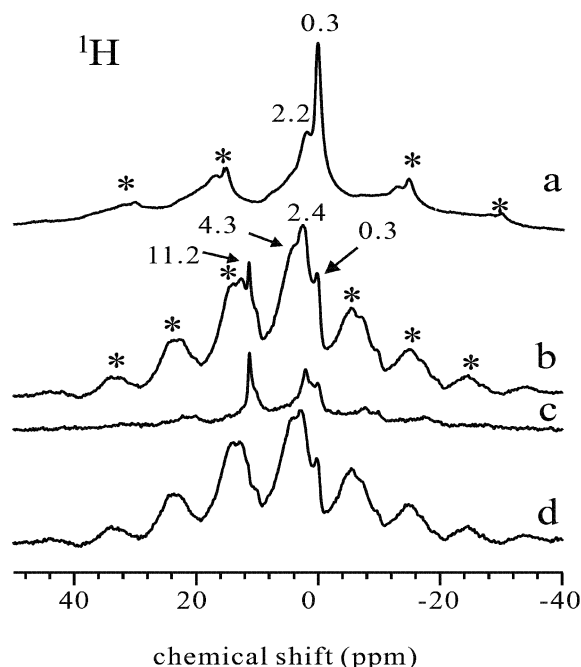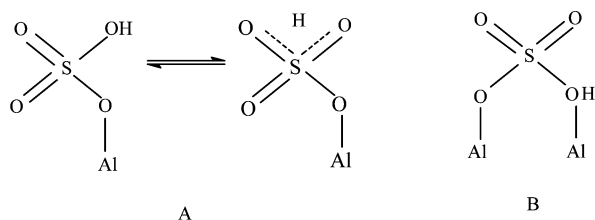

Fig. 1 ¹H spin echo spectra of (a) γ-Al₂O₃ (without Al irradiation), (b) SO₃/Al₂O₃ (without Al irradiation), (c) SO₃/Al₂O₃ (with Al irradiation), (d) difference spectrum of (b) and (c). Asterisks denote spinning sidebands.

Scheme 1

in the ^{1}H NMR spectrum of the parent γ-Al$_2$O$_3$ sample, implying that at least part of this signal arises from the contribution of other bridging hydroxyls, such as S–OH–Al shown in Scheme 1B, which should also have a strong TRAPDOR effect.

Trimethylphosphine (TMP) is an effective probe molecule to study the acidity of catalysts. It is well accepted that the formation of TMPH[+] due to the interaction of TMP with Brønsted acid sites will give rise to a ^{31}P resonance at about −2 to −4 ppm, while TMP molecules bound to Lewis acid sites will result in ^{31}P resonances in the range from −32 to −58 ppm.[14] Only one major peak at −51 ppm is present in the ^{31}P MAS NMR spectrum (Fig. 2a) of TMP adsorbed on γ-Al$_2$O$_3$. According to its chemical shift, we attribute it to the TMP bound to Lewis acid. While in the ^{31}P spectrum of TMP adsorbed on SO$_3$/Al$_2$O$_3$ catalyst (see Fig. 2b), the signal at −51 ppm shifts to −49 ppm with a shoulder peak at −53 ppm. This suggests that a slight variation in the distribution of Lewis acid strength occurs, probably due to the interaction between SO$_3$ with Lewis acid sites on the surface. The appearance of the signal at −3

Fig. 2 ^{31}P single pulse with ^{1}H decoupling MAS spectra of TMP adsorbed on (a) γ-Al$_2$O$_3$, (b) SO$_3$/Al$_2$O$_3$. The weak signal at 34 ppm in (a) is due to trimethylphosphine oxide; ^{13}C CP/MAS NMR spectra of [2-^{13}C]acetone (0.2 mmol g^{-1}) adsorbed on (c) γ-Al$_2$O$_3$ and (d) SO$_3$/Al$_2$O$_3$. The broad peaks between 120 to 180 ppm in the ^{13}C spectra are due to the background of spinning module. Asterisks denote spinning sidebands.

ppm indicates the formation of Brønsted acid sites on the surface of SO$_3$/Al$_2$O$_3$, corresponding to the hydroxy groups only connected to S or the bridging S–OH–Al hydroxys (see Scheme 1). Obviously, TMP can not discriminate between the two different types of surface sulfated species.

SO$_4^{2-}$/Al$_2$O$_3$ was previously classified as a solid superacid because of its strong Hammett acidity ($H_0 < -14$).[3] [2-^{13}C]A-cetone is a useful NMR probe molecule for measuring the relative acid strengths of solid acids.[15] Fig. 2c and 2d show the ^{13}C CP/MAS spectra of [2-^{13}C]acetone (0.2 mmol g^{-1}) adsorbed on γ-Al$_2$O$_3$ and SO$_3$/Al$_2$O$_3$, respectively. Acetone can react with the Lewis acid on the surfaces of γ-Al$_2$O$_3$. As displayed in Fig. 2c, the signals at 217 and 71 ppm are due to the formation of diacetone alcohol from the [2-^{13}C]diacetone reaction.[16] Other bimolecular and trimolecular reactions lead to products such as mesityl oxide (210 ppm) and mesitylene (34 ppm). Fig. 2d shows the ^{13}C CP/MAS spectrum of acetone adsorbed on the SO$_3$/Al$_2$O$_3$ catalyst. Apart from the signals of the above products, the new signal at 228 ppm is probably due to the unreacted acetone adsorbed on Brønsted acid sites. The large chemical shift indicates that the acid strength of the SO$_3$/Al$_2$O$_3$ catalyst is slightly stronger than that of zeolite HZSM-5, where adsorbed [2-^{13}C]acetone gives rise to a ^{13}C resonance at 223 ppm,[15] but still weaker than that of 100% H$_2$SO$_4$, in which the isotropic ^{13}C shift of [2-^{13}C]acetone is *ca.* 245 ppm. However, in this case, the NMR probe molecule is unable to distinguish the acid strengths of the various types of Brønsted sites.

In summary, the acidity of SO$_3$/Al$_2$O$_3$ has been studied by multinuclear solid state NMR. The adsorption of SO$_3$ on the surface of γ-Al$_2$O$_3$ introduces two different kinds of Brønsted acid sites, and their acid strengths are slightly stronger than that of zeolite HZSM-5, but still weaker than that of 100% H$_2$SO$_4$. The results can help us to understand the nature of acid sites on sulfated metal oxides and the corresponding catalytic reaction happening on these kinds of catalysts.

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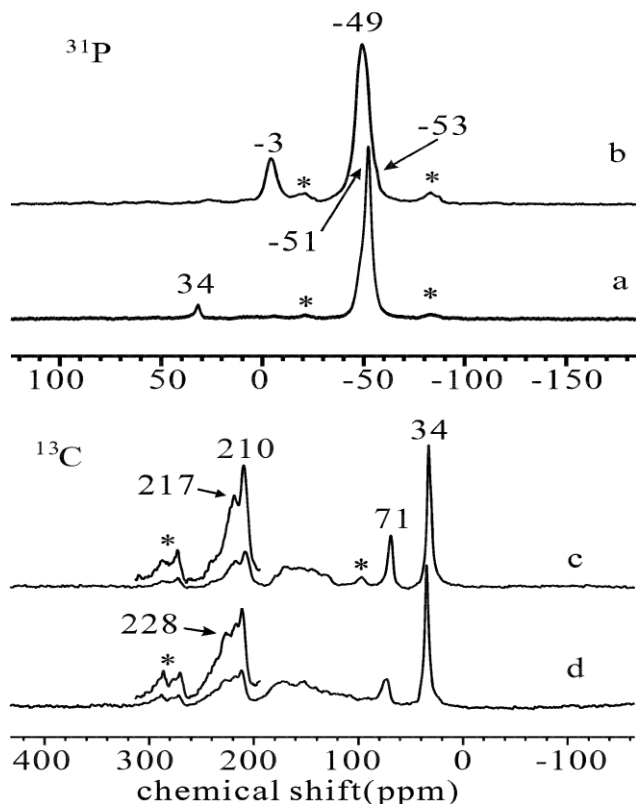16 A. I. Biaglow, R. J. Gorte and D. White, *J. Catal.*, 1994, **150**, 221.