NMR study on the acidity of TS-1 zeolite

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The acidic properties of TS-1 and Silicalite-1 zeolites have been investigated by the solid-state MAS NMR technique capable of *in situ* sample pretreatment. As shown by a combination of the ^{31}P MAS NMR and ^{1}H MAS NMR techniques with trimethylphosphine, not only Brønsted acid sites but also Lewis acid sites exist in the TS-1 zeolites. Moreover, TS-1 zeolite is more acidic compared with Silicalite-1. The ^{1}H, ^{29}Si MAS NMR spectra and the resonance related to Brønsted acid species in the ^{31}P MAS NMR spectra demonstrate clearly that the presence of titanium in the framework results in the formation of a new hydroxy group, titanols, which is more acidic than silanols of Silicalite-1. The ^{31}P MAS NMR measurements also illustrate convincingly the existence of at least two different Lewis acid species on the TS-1 zeolites. The conversion of propylene oxide into methoxypropanol catalyzed by TS-1 or Silicalite-1 zeolite in methanol solution as a test reaction has also been described. With the increase of titanium in zeolite, TS-1 appears to have a higher activity during the reaction of propylene oxide to methoxypropanol.

KEY WORDS: TS-1 zeolite; solid-state MAS NMR; acidity.

1. Introduction

Great attention has been paid to the TS-1 zeolite since its synthesis in 1983, because of its excellent catalytic properties in selective oxidation of organic compounds as well as its environmentally benign characteristics [1,2]. In particular, it exhibits an exceptional catalytic activity for selective oxidation of alkene with hydrogen peroxide as the oxidant under mild conditions [3]. Generally, limited methoxyalcohol is always detected as well as epoxide during the oxidation of alkene. The former is considered to be the product formed by the ring opening of alkene oxide catalyzed by acidic species. Several studies have been published concerning the acid properties of TS-1, but there still exist two different points of views on the acidity of TS-1 zeolite, which have been under discussion for a long time [4,5]. Deo *et al.* [6] reported that there were no Brønsted and Lewis acid sites in the TS-1 zeolite at all. Although acidic species in TS-1 zeolite have been detected by IR with pyridine as a probe molecule, it is still considered that the Brønsted acid sites result from impurities such as aluminum, iron in the TS-1 zeolite and weak Lewis acid sites from TiO_2 (anatase). Meanwhile, Auroux *et al.* [7] inferred that TS-1 was very acidic compared with a Silicalite-1 sample. Thus, there remains a need to investigate whether Brønsted and Lewis acid sites will be produced upon the introduction of titanium into the zeolite framework. Recently, ^{31}P solid-state MAS NMR using alkylphosphine as basic probe molecules has emerged as a promising approach for evaluating the types of acidic sites in zeolites [8]. In this study, the ^{31}P MAS NMR characterization of trimethylphosphine (TMP) adsorbed on two well-synthesized TS-1 zeolites with different titanium contents and Silicalite-1 zeolite is demonstrated. Coupled with the ^{1}H, ^{29}Si MAS NMR results and a model reaction for acidity evaluation (propylene oxide to methoxypropanol), it provides an affirmative answer regarding the nature of the acidity of TS-1 zeolite.

2. Experimental

2.1 Synthesis and characterization

TS-1 samples (A and B) with two different levels of titanium content (the ratio of Si/Ti in the framework is 42.8 and 52.9 respectively) were provided by the BASF Corporation and were synthesized using the preparation method reported in the patent literature [9,10]. The structure of the obtained zeolites was checked by a D/max-γb type X-ray diffractometer (Rigaku) using monochromatic Cu K_α radiation (40 kV and 100 mA), with a scan speed of 5°/min in 2θ. UV–vis spectra were recorded on a JASCO V-550 spectrometer, with a scan range of 190–490 nm. The samples were treated at 813 K in air for 5 h before detection. The composition of the samples was checked by using an SRS 3400 X-ray fluorescence spectrometer.

2.2. NMR measurements

A special device for on-line treatment of zeolite samples has been designed and manufactured, which is

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functionally analogous to the CAVERN apparatus developed by Munson and co-workers [11,12]. By means of this device [13,14], the TS-1 and Silicalite-1 samples were heated at 673 K in vacuum (base pressure below 10^{-2} Pa) for 20 h for dehydration. Selective adsorption using trimethylphosphine (from Acros Organics) was performed by exposing the dehydrated sample to its saturated vapor pressure at room temperature for 30 min and then evacuated for a while to remove the physical adsorbates on the surface. After the treatment, the sample was filled *in situ* into a MAS NMR rotor, then sealed without exposure to air.

NMR spectra were obtained at room temperature on a Bruker DRX-400 spectrometer with a BBO MAS probehead, using 4 mm ZrO_2 rotors. ^{31}P MAS NMR spectra with high-power proton decoupling were obtained at 161.9 MHz, using a 2.0 μs pulse, a 2 s repetition time and 2048 scans. The samples were spun at 6 kHz and chemical shifts were referenced to 85% H_3PO_4. By varying the time between successive pulses, it was found that the samples had T_1 less than 0.3 s. ^{1}H MAS NMR spectra were obtained at 400.1 MHz using single-pulse experiments with a 3 μs pulse, a 4 s repetition time and 100 scans. ^{1}H MAS NMR spectra were recorded with samples spun at 8 kHz, and chemical shifts were referenced to a saturated aqueous solution of DSS.

2.3. *Conversion of propylene oxide to methoxypropanol*

The conversion of propylene oxide was carried out in a glass autoclave (50 ml) equipped with a condenser and a stirrer. 20 ml of a 10% (w/w) solution of propylene oxide (PO) in a mixture of water/methanol (50:50) containing 0.5 g catalyst was stirred at 50 °C for 5 h. Products were analyzed by gas chromatography using a Carbowax column (0.32 mm × 25 m). The temperature program is 5 min at 50 °C, with a ramp of 10 °C/min to 150 °C, and holding for 7 min. The temperature of the injector and detector is 250 °C.

3. Results and discussion

3.1. *XRD, UV–vis and XRF elemental analysis*

The X-ray powder diffraction patterns (XRD) of calcined TS-1 (samples A and B) and Silicalite-1 are shown in figure 1, which confirms that the synthesized materials have the MFI structure. No peak at 25.3° is found, indicating no TiO_2 (anatase) in the samples. There are no UV bands in the 280–400 nm UV range of the UV–vis spectra where the electronic transition of TiO_2 (anatase) should occur. These results eliminate the possibility that there are Lewis acid sites resulting from the TiO_2 (anatase). The results of elemental analysis shown in table 1 show that the ratio of Si/Ti is 42.8 in the framework of sample A and 52.9 in sample B. Iron is not detected in the samples. There is no aluminum in sample A. This result defies the viewpoint that Brønsted acid sites originate from impurities such as iron and aluminum in the TS-1 zeolite.

3.2. *^{31}P MAS NMR*

Trimethylphosphine (TMP) is a weakly basic molecule ($pK_a = 5.35$) with a diameter of 0.55 nm [15], which is

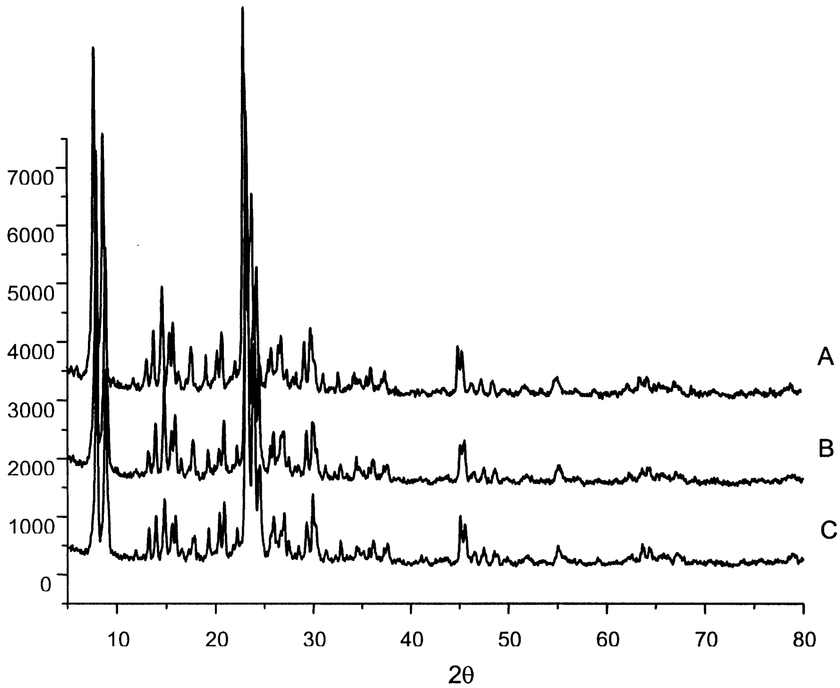


Figure 1. XRD of TS-1 zeolites with higher (A) and lower (B) content of titanium in the zeolite framework and Silicalite-1 (C).

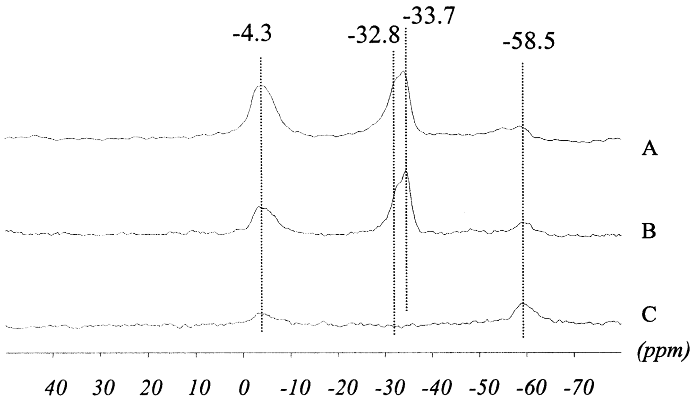


Figure 2. ^{31}P MAS-NMR spectra of $(CH_3)_3P$ in TS-1 with higher (A) and lower (B) content of titanium in the zeolite framework and Silicalite-1 (C).

suitable as a probe molecule for the pore size (0.55 nm) of TS-1 zeolite. Hence, it should be able to adsorb on both the internal and external surfaces, and be used as a probe molecule to characterize the acidity of the TS-1 zeolites. Figure 2 displays the ^{31}P MAS NMR spectra of TMP adsorbed on TS-1 zeolites (sample A and B) and Silicalite-1. The resonance centering at -4.3 ppm has been well characterized to be a $[(CH_3)_3P\text{-}H]^+$ complex arising from the interaction of $(CH_3)_3P$ with Brønsted acid sites in zeolites. The peak at -33.7 ppm is attributed to the Lewis-bonded trimethylphosphine, and the trace peak at -58.5 ppm is related to the remaining physisorbed phosphine [16]. Globally, and as expected, there should be no Brønsted acid sites occurring in the perfect TS-1 crystal because there is no charge on the framework. However, defects such as silanols and titanols are unavoidably formed during synthesis, which might result in acid centers. That the silanol stretching band was shifted down ($\Delta\nu = 330\,\mathrm{cm}^{-1}$) and strongly broadened was observed by FTIR spectra of the adsorbed basic molecule, which implied that the silanols of silicalite were weakly acidic, as are those of amorphous silica [17]. We can also obtain a weak signal of Brønsted acid sites derived from the ^{31}P MAS NMR spectrum of trimethylphosphine adsorbed on Silicalite-1. Thus, silanols are attributed to Brønsted acid sites in Silicalite-1. An intensity comparison among the ^{31}P MAS NMR spectra in figure 2 confirms that the Brønsted acid sites are sharply enhanced when titanium loads into the framework. Yet, because of the same acidic strength on the silanols of TS-1 as those of Silicalite-1 [18], as well as fewer silanols observed in TS-1 zeolites, which can be deduced from the signal of silanols (peak at -104.8 ppm) [19] in the ^{29}Si MAS NMR spectra shown in figure 3, the existence of another Brønsted acid species should be considered. The fact that the Brønsted acid sites increase with the titanium loading seems to confirm that other Brønsted acid species should be related to the titanium species. In other words, the presence of titanium results in the formation of a new hydroxy group, titanols, which are more acidic than those of silicalite. In conclusion, the Brønsted acid species in TS-1 zeolite are related to titanols and silanols.

There are several reports concerning the Lewis acid species of the materials containing titanium. Busca *et al.* [20] have tentatively identified two families of Lewis sites observed on the anatase surface as octahedral sites lacking two and one coordination valency respectively, *i.e.*, as tetracoordinated and pentacoordinated Ti cations by FTIR spectroscopy of adsorbed bases. Just one family of Lewis sites in the case of titanium silicalite samples was also detected by FTIR spectroscopy adsorbed with acetonitrile. They stated that titanium sites provided Lewis acidity corresponding to that of tetrahedrally-coordinated Ti ions able to expand the coordination sphere to octahedral or pyramidal [18], whereas the feature of twin peaks at -33.7 ppm in our spectra gives convincing evidence of the existence of at least two different Lewis acid species in TS-1 zeolites even though there is no anatase detected. Therefore, we consider that in addition to those tetrahedrally coordinated Ti ions except for the electron transferred from the probe molecule, the coordinately unsaturated Ti^{4+} ions also play a key role in Lewis acid species, which are formed from the dehydration of TiOH and SiOH when the sample is calcined under high temperature to remove the template. The intensity of Lewis acid sites in these two samples is enhanced a little with titanium loading. Meanwhile, no Lewis acid sites were found in

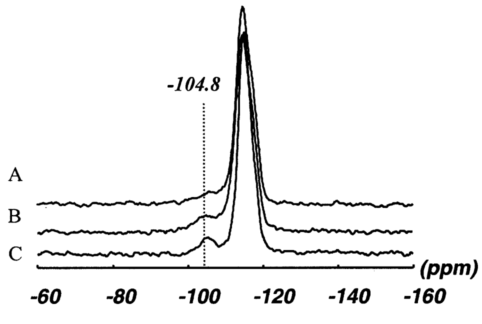


Figure 3. ^{29}Si MAS NMR spectra of TS-1 with higher (A) and lower (B) content of titanium in the zeolite framework and Silicalite-1 (C).

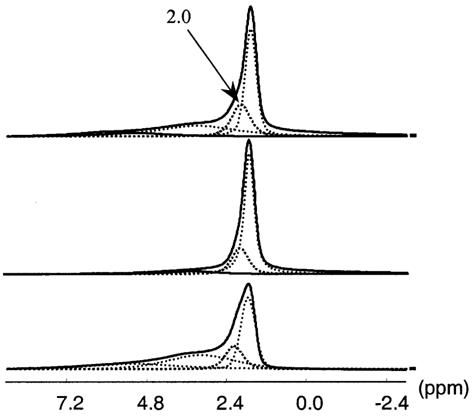


Figure 4. ^{1}H MAS-NMR spectra of TS-1 with higher (A) and lower (B) content of titanium in the zeolite framework and Silicalite-1 (C).

Silicalite-1. Overall, the total amount of acid sites increases with the titanium loading.

3.3 ^{1}H MAS NMR

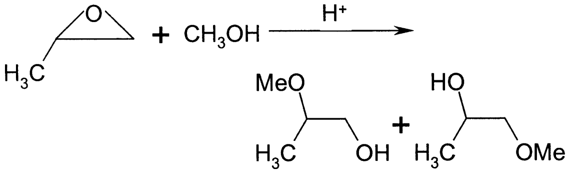
Proton NMR is an extremely useful tool for the characterization of surface acidity and hydroxyls. It contains information about Brønsted acidity and structure defects in zeolites [21]. The ^{1}H MAS NMR spectra of TS-1 (samples A and B) and Silicalite-1 are shown in figure 4. Curves A, B and C represent the ^{1}H MAS NMR spectra taken respectively from TS-1 samples A and B and from Silicalite-1. The results from deconvolution of the corresponding spectra are plotted simultaneously. Curve C of Silicalite-1 exhibits four proton resonance lines at 1.8, 2.0, 3.2 and 5.2 ppm. All these signals, except that at 5.2 ppm, correspond to silanol defects. The peaks at 1.8 and 2.0 ppm have previously been assigned to silanol moieties of silica [22]. The 3.2 ppm line can be ascribed to hydrogen-bonding silanols [22]. In addition, the peak at about 5.2 ppm is assigned to an extremely small amount of water molecules [23]. As with Silicalite-1, we also found three peaks at 1.8, 2.0 and 3.2 ppm in curves A and B of the TS-1 zeolites. From the comparison of the 2.0 ppm line among these three curves, the order of the intensity is $A > B > C$, which is in accordance with the decrease in titanium content. It is deduced that the peak at 2.0 ppm might be composed of both SiOH and TiOH resonance. Le Noc *et al.* [24] have reported that there might be a signal of TiOH at 1.8–2.0 ppm in the ^{1}H MAS NMR spectra of TS-1 zeolite. Combining their results with ours, we can conclude that some titanium from TiOH is responsible for the peak at 2.0 ppm in the ^{1}H MAS NMR spectra.

Table 1
Results of elemental analysis with XRF and conversion of PO to methoxypropanol.

Catalyst	SiO_2/TiO_2	SiO_2/Al_2O_3	Na/Ti	Conversion of PO (%)
TS-1 (sample A)	42.8	–	–	50
TS-1 (sample B)	52.9	182.5	0.097	26
Silicalite-1	–	–	–	12

3.4. Catalytic activity

Ring opening of propylene oxide is a well-known reaction catalyzed by acid and occurring under mild conditions.



The results shown in table 1 display the conversion of propylene oxide to methoxypropanol catalyzed by TS-1 zeolite and Silicalite-1 in methanol solution. The conversion of PO is 50 and 26%, respectively, catalyzed by TS-1 zeolite samples A and B. This result confirmed the existence of acid centers in the TS-1 zeolites. With the increase of titanium in TS-1 zeolite, it exhibits much more activity towards the conversion of propylene oxide, indicating that there are more Brønsted acid sites in zeolite. Moreover, we found that propylene oxide was also catalyzed by Silicalite-1, with a conversion of 12%, which indicates that there are Brønsted acid sites in Silicalite-1 too. This conclusion is in good agreement with the results deduced from the NMR spectra.

4. Conclusions

The combination of the selective adsorption of certain probe molecules and multinuclear MAS NMR is an excellent method to characterize the acidity of zeolites. ^{31}P MAS NMR spectra of trimethylphosphine adsorbed on samples and ^{1}H MAS NMR spectra confirm that both Brønsted and Lewis acid sites exist in the TS-1 zeolite. Brønsted acid sites are related to the silanols and titanols. An additional shoulder at −33.7 ppm in the ^{31}P MAS NMR spectra also convinces us that there are at least two different types of Lewis acid species in the TS-1, which are related to the coordinatively unsaturated and saturated titanium ion respectively in the framework. TS-1 zeolite is very acidic compared with Silicalite-1, since only very few Brønsted acid sites were detected in the latter. Ring opening of propylene oxide was carried out catalyzed by TS-1 or Silicalite-1 zeolite. With the increase of titanium in the zeolite, the catalyst appears to have a higher activity during the reaction of propylene oxide to methoxypropanol. It also confirms that the acidity exists in TS-1 zeolite.

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