Alcohol and Seed-assisted Synthesis of OSDA-free High-silica ZSM-5

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Zeolites are widely used as heterogeneous catalysts in industrial chemical processes, because of their strong acidity and shape selectivities. The synthesis of OSDA-free high-silica ZSM-5 has been one of the most difficult challenges for environment-friendly and simplified preparation of catalysts.

In this work, we synthesized ZSM-5 zeolites by exclusively TPAOH, Na cations (OSDA-free), and Na cations with alcohols, pentaerythritol (PET) and *tert*-butylalcohol (TBO), to investigate how the distribution of Al atoms in the **MFI** structure is governed by the types of organic species in the synthetic gel.

ZSM-5 zeolites were synthesized by referring to our previous work [1]. The [TPA] and [PET, Na] samples were synthesized from the mother gels with the molar compositions of 1 SiO_2/0.025 Al_2O_3/0.25 TPAOH /20 H_2O, 1 SiO_2/0.020 Al_2O_3/0.50 PET/ 0.25 Na /20 H_2O. The high-silica [TPA], [TBO, Na], and [Na] samples were synthesized from the mother gels with the molar compositions of 1 SiO_2/0.0125 Al_2O_3/0.16 TPAOH /40 H_2O, 1 SiO_2/0.0125 Al_2O_3/0.16 TBO/0.16 Na /40 H_2O and 1 SiO_2/0.0125 Al_2O_3/0.16 Na /40 H_2O and designated as [TPA_high Si/Al], [TBO, Na], and [Na], respectively. The mother gels of [TPA_higi Si/Al], [TBO, Na] and [Na] were stirred at 80 °C for 1 h, Na-ZSM-5 with Si/Al ratio of 50, 5 wt% of SiO_2 in gel, was added before crystallization, and then hydrothermally treated at 473 K for 1 day.

The high-resolution ^{27}Al MAS NMR spectra of the proton-type ZSM-5 samples were obtained on a JEOL ECA-600 spectrometer (14.1 T) equipped with an additional 1 kW power amplifier. The ^{27}Al chemical shift was referenced to $AlNH_4(SO_4)_2 \cdot 12H_2O$ at −0.54 ppm, and samples were spun at 15 kHz by using a 4 mm ZrO_2 rotor. Figure 1 shows the ^{27}Al MAS NMR spectra of a series of ZSM-5 zeolites with different Al locations. The spectra of all the samples consist of the broad peak ranging from 45 to 65 ppm attributed to the framework Al atoms. They were divided into five peaks at around 52, 53, 54, 56, and 58 ppm and designated as a, b, c, d, and e, respectively. The proportions of these peaks are listed in Table 1. Note that there are significant differences in the proportion between [TPA] and [PET, Na]; the proportion of d was low and that of c was high for [TPA] compared to [PET, Na]. It is considered that the chemical shift in the ^{27} Al MAS NMR spectrum of the **MFI**-type zeolite is shifted to higher magnetic field as the mean T–O–T angle is increased [2, 3]. The difference in the proportion would be caused by the different distribution of Al atoms over 12 distinct T-sites of the MFI structure.

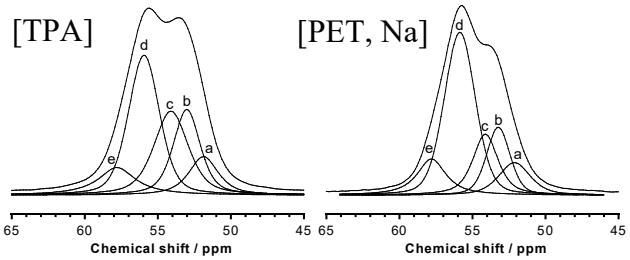

Fig.1 Curve fittings of the ^{27} Al MAS NMR spectra of [TPA] and [PET, Na].

Table 1 Relative peak area of the ^{27} Al MAS NMR spectra

	Relative peak area / %				
	e	d	c	b	a
Chemical shift / ppm	58	56	54	53	52
[TPA]	11	35	25	20	10
[PET, Na]	12	46	16	15	11

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