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Significance of Silicate Source for Controlling Pentasil Zeolite Phase Synthesized from Organic-Free System

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High resolution ^{29}Si NMR spectra of silica sols and water glass in addition to a wide survey of hydrothermal zeolite syntheses from them with no aid of organic templates brought forth such a view that pentasil zeolite phases to be formed are controlled at the aging stage of room temperature in the liquid phase. Pure ZSM-5 crystals were synthesized at high yields, only when a small-sized silica sol(10 — 20 nm) was used, indicating that appropriate amounts of silicate species(Q^2 and Q^3) are required to react with aluminate at room temperature in the alkaline solution.

In zeolite syntheses, silicate raw materials are selected carefully, because different zeolitic phases are often synthesized from different silicate sources in spite of a common starting composition being adopted.$^{1)}$ As for the organic-free system of pentasil zeolite synthesis, only the silica sol with a limited particle size(10 — 20 nm) gives pure ZSM-5 crystals; mordenite is formed in place of ZSM-5 with use of the large sols(35 — 55 and 70 — 90 nm).$^{2)}$ It is important to elucidate the reason why the silicate sources affect the zeolite phase, as the mechanism of zeolitization is closely related to this size effect. On the ground of high resolution ^{29}Si NMR studies at room temperature and hydrothermal zeolite syntheses, we have found that the silicate species dissolved in the solution are dependent on the silicate sources and that the sort of pentasil zeolites to be formed is determined in the liquid phase at the aging stage of room temperature.

^{29}Si NMR spectra were measured on a JEOL GX-270 NMR spectrometer at 53.69 MHz;$^{3)}$ the gated decoupling mode was adopted to avoid the Nuclear Overhauser effect(NOE). Sufficient signal-to-noise ratios were obtained by accumlating 500 — 800 FID decays. ^{29}Si chemical shifts were referred to the chloroform solution of tetramethyl silane(TMS/$CHCl_3$ = 1/3 in volume) sealed in a 5 mm glass tube as the internal standard inside the 10 mm teflon sample tube.

Starting compositions were varied systematically for zeolite synthesis within the molar ratio ranges of $10.0 \leqq SiO_2/Al_2O_3 \leqq 100$ at constant $OH^-/SiO_2 = 0.27$ and

H_2O/SiO_2 = 45.9. The aqueous solution of sodium aluminate and sodium hydroxide was added gradually to the silicate source (SiO_2 = 0.29 mol)4) and stirred for 1 h at room temperature, followed by heating without agitation in a stainless steel autoclave under hydrothermal conditions at 190 ± 2 °C for 48 h.

Alkaline silicate solutions were prepared with sodium hydroxide and silica sols, with the compositions of H_2O/SiO_2 = 45.9 and OH^-/SiO_2 = 0.27(SiO_2 = 14.33 mmol) kept constant. The ^{29}Si NMR measurements were started after the sample solutions were prepared and stirred for 1 h at room temperature. D_2O(20 vol%) was always added in order to lock the NMR magnetic field.

The water glass gave five ^{29}Si NMR resonance peaks(Fig. 1); Marsmann5) and Engelhardt6) observed them similarly for the sodium silicate solutions and assigned to the monomeric SiO_4(Q^0) and oligomeric species(Q^1 — Q^4). No Q^0 — Q^2 peaks were utterly found in the NMR spectra of both S-20L and SI-80P silica sols in contrast to the water glass. A broad band appeared around -112 ppm was also assigned to the Q^4.7)

After the silica sols dissolved in the sodium hydroxide aqueous solution were kept for 1 h at room temperature, the NMR spectra of the S-20L sol gave four additional peaks of Q^0 — Q^3, whereas weak Q^0, Q^1,and Q^2 peaks appeared from the SI-80P sol(Fig. 2).8) As no NOE was operative in the present NMR conditions, the peak intensities should correspond to the amounts of dissolved silicate species. In contrast to the large-sized silica sol SI-80P, the species containing the branching group Q^3(designated Q^3 species hereafter) were yielded from the small-sized silica sol S-20L. As reported previously,9) it is reasonable that small-sized silica sols dissolve more easily.

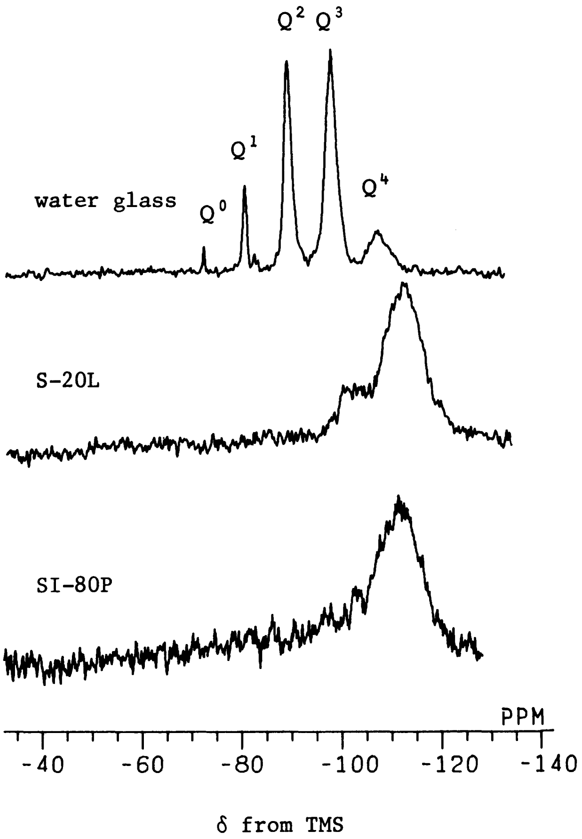

Fig. 1. ^{29}Si NMR spectra of water glass and silica sols with different particle sizes.

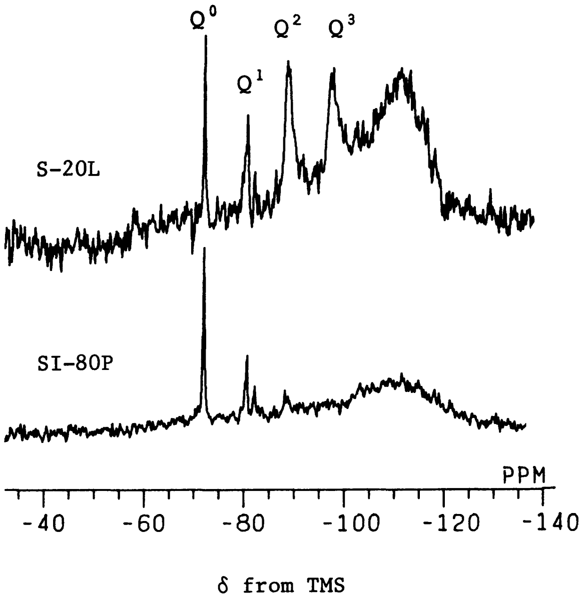

Fig. 2. ^{29}Si NMR spectra of silica sols with different particle sizes in alkaline solution, taken after 1 h from dissolution at room temperature.

New information is added by the present NMR study that dissolved silica species inherited from the silicate source are different in the aqueous solution, being affected by the particle size. It is quite interesting that the concentrations of the Q^2 and Q^3 species are increasing in the order of SI-80P < S-20L < water glass, since these NMR peaks have been related[10] to the secondary building units with the double rings and to the zeolite crystallization.

Three kinds of silicate sources gave different zeolitic phases with each other from a common starting composition under the same hydrothermal conditions(Fig. 3). At the starting ratio of SiO_2/Al_2O_3 = 40.0, for example, a pure mordenite phase was obtained from the SI-80P sol, whereas the water glass produced a mixture of ZSM-5 + mordenite + α-quartz, and the S-20L sol gave the coexisted phases of ZSM-5 and mordenite. The minimum SiO_2/Al_2O_3 ratios necessory to form the ZSM-5 phase increased in the order of water glass < S-20L < SI-80P.

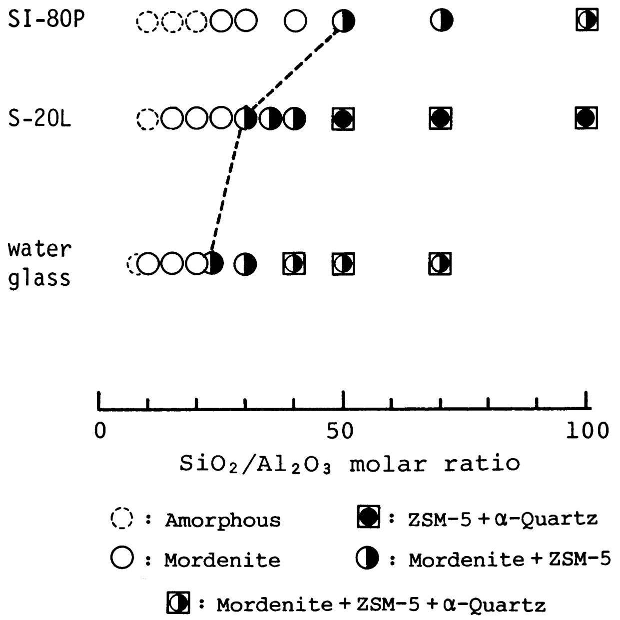

Fig. 3. Zeolite synthesized under hydrothermal conditions of 190°C for 48 h by using colloidal silica sols and water glass at various starting SiO_2/Al_2O_3 ratios.

Since the water glass itself contains the Q^2 and Q^3 species in the solution sufficiently, the minimum amount of these species requisite to ZSM-5 formation is fulfilled with the lowest starting SiO_2/Al_2O_3 ratio among the three kinds of silicate sources. The small-sized silica sol S-20L can afford the Q^2 and Q^3 species more in the alkaline solution than the large-sized SI-80P, which causes the lower minimum SiO_2/Al_2O_3 ratio of the former. As far as the determination of ZSM-5 phase is concerned, the aging stage of room temperature is more important than the period prior to zeolite crystal growth at elevated temperature,[2] because silica sols dissolve thoroughly to give water-glass-like solutions regardless the particle sizes under the severe hydrothermal conditions(190 °C, pH > 13).[9]

Pure ZSM-5 crystals were successfully synthesized at high yields only from the S-20L sol,[11] whereas contaminations with mordenite were inevitable for the water glass under the same starting compositions and hydrothermal conditions(Table 1).[12] Provided

Table 1. Zeolite Crystals Synthesized by Using Silica Sol and Water Glass at Various SiO_2/Al_2O_3 Starting Ratios in Organic-Free System[a)]

Silicate source	Synthesis period/h	SiO_2/Al_2O_3 molar ratio 20.0	25.0	30.0	40.0	50.0	70.0
sol S-20L	24	M(g)	A	Z(t)	Z(t)	Z(g)	Z(g)
	36	M(g)	M(t)	Z(t)	Z(t)	Z(g)	Z(g) +Q(t)
water glass	24	M(g)	Z(t)	Z(m)	Z(t) +M(t)	Z(t)	A
	36		M(m) +Z(t)	Z(t) +M(t)	Z(t) +M(m)	Z(m) +M(t)	Z(t) +M(t) +Q(t)

a) Z: *ZSM-5*, M: *mordenite*, Q: *α-quartz*, A: *amorphous*, g: *good*, m: *medium*, t: *trace*.

that the appropriate amounts of the Q^2 and Q^3 species were required to react with aluminate at room temperature in the alkaline solution. One should carefully choose the silicate source in order to synthesize pure ZSM-5 zeolite at high yields from the organic-free system.

References

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2) F.-Y. Dai, M. Suzuki, H. Takahashi, and Y. Saito, Proc. 7th Int. Zeol. Conf., Tokyo(1986), p.223.
3) The NMR detection was performed at the conditions of the observed range of 8 KHz, pulse intervals of 6 s and pulse width of 10 μs.
4) The silicate sources adopted are water glass(SiO_2 24.3%, Na_2O 8.12%, and Al_2O_3 0.023%(% in weights) of reagent grade), silica sol S-20L(SiO_2 20.3%, Na_2O 0.04%, and Al_2O_3 0.024%; particle size of 10 — 20 nm) and SI-80P(SiO_2 40.8%, Na_2O 0.43%, Al_2O_3 0.030%; 70 — 90 nm), supplied from Catalysts & Chemical Industry, Co. Ltd.
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8) It is ascertained that no obvious changes of these spectra within 3 h after the NMR measurement was started.
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11) The starting compositions were SiO_2/Al_2O_3 = 50 — 70, Na_2O/SiO_2 = 0.13 — 0.18, and H_2O/SiO_2 = 45.9.
12) As for the SI-80P sol, a trace amount of ZSM-5 was obtained at most in addition to large quantities of mordenite, when the SiO_2/Al_2O_3 ratios of 50.0 and 70.0 were adopted and heated at 190 °C for 24 h; the degree of crystallization of mordenite reached maximum at the period of 60 — 72 h, whereas the ZSM-5 phase disappeared.

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