Hydrothermal Synthesis of Calcium Silicate of ZSM-5 Structure in Alkali-Metal-Cation-Free Conditions

Kiyomi Okabe,* Kenji Matsuzaki,† and Hiroyuki Hagiwara
Surface Chemistry Division, National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305
†Maruzen Petrochemical Co., Ltd., Hatchobori, Chuo-ku Tokyo 104
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Synopsis. Crystalline calcium silicate of ZSM-5 structure was hydrothermally synthesized by using an excessive amount of tetrapropylammonium bromide (TPABr) as an organic base and without using any alkali metal ions in the low pH range. The acidity caused by Ca was verified by IR, NH_3-TPD, and methanol conversion.

Calcium silicates, such as tobermolite and xonotolite, are known to be cement minerals, and have pore structures with a diameter of a few Å.[1] However, they do not have any acidic sites, owing to the high Ca-content, and have never been regarded as catalysts. On the other hand, magnesium silicate, such as sepiolite, has ion-exchangeable protons, and is used as a catalyst for methanol conversion.[2] It is expected that calcium silicate would be used as a catalyst if a small amount of calcium happened to be occluded in a silica matrix and had any acidity. In this respect, the possibility of the hydrothermal synthesis of crystalline calcium silicate with a low Ca-content was examined in alkali-metal-ion-free conditions.

Colloidal silica (Cataloid SI-30) containing 30 wt% SiO_2 was purchased from Catal. Chem. Ind. Co. A trace amount of Al (Al_2O_3/SiO_2=0.0003) was detected in the colloidal silica by X-ray fluorescence spectrometry (XRF). Appropriate amounts of aqueous solutions of calcium hydroxide and of tetrapropylammonium bromide (TPABr) were added to the colloidal silica, and stirred to form gel. A gel mixture without any alkali metal ions was autoclaved to be crystallized at a temperature range from 403 to 473 K. The crystals were washed with distilled water, dried, and calcined in air at 773 K for 15 h to remove the organic additive. The excessive amount of Ca was removed by ion exchange with an aqueous solution of ammonium chloride (5 wt%) followed by calcination at 773 K. The crystallinity was checked by X-ray diffraction (XRD) using Cu $K\alpha$ radiation, and the Ca-content was determined by XRF. The acidity of the catalysts was evaluated by methanol conversion, the FT-IR spectra of adsorbed pyridine, and the temperature programmed desorption of ammonia (NH_3-TPD). Methanol conversion was carried out at T_r=773 K and LHSV= 1 h^{-1}, as described previously.[3] The desorption of NH_3 was performed at a heating rate of 10 K min^{-1} in a He flow[4] by recording M/e=16—18 using a mass-filter.

Although pure xonotolite was obtained from a gel mixture of Ca/Si=1 without using TPABr at 473 K for 24 h, the addition of TPABr (TPABr/SiO_2=0.1)[5] and a decrease of the Ca/Si ratio provided a poorly crystalline phase similar to that of ZSM-5. The detailed hydrothermal conditions were examined in order to obtain the phase of higher crystallinity. An excessive amount of TPABr (TPABr/SiO_2=1) and the prolonged hydrothermal time to 7 days improved the crystallinity, which is contoured in Fig. 1 with the Ca/Si ratio range of the gel mixture (Ca/Si*) from 0.02 to 0.5 and the hydrothermal temperature (T_h) range from 403 to 473 K. The numerals in the figure denote relative XRD peak intensities of the crystals at 2θ=23.2° The highest crystallinity was obtained with Ca/Si*=0.02 and T_h=403—423 K. Under these hydrothermal conditions, the pH of the filtrate was almost neutral, as listed in Table 1. The crystallinity

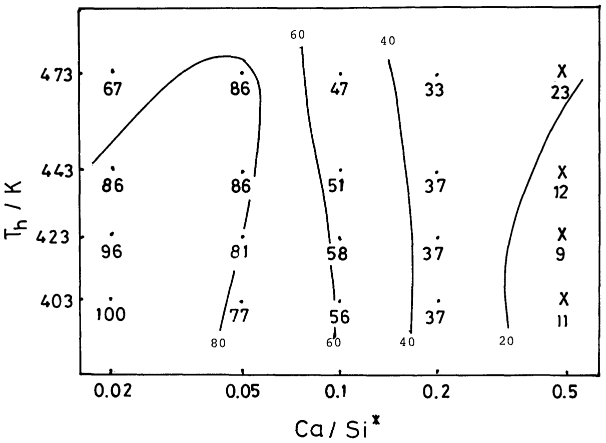

Fig. 1. Crystallinity of calcium silicates. Numerals denote relative XRD intensities. X stands for the formation of xonotolite, as a by-product.
Ca/Si*: Ca/Si atomic ratio of gel mixture.

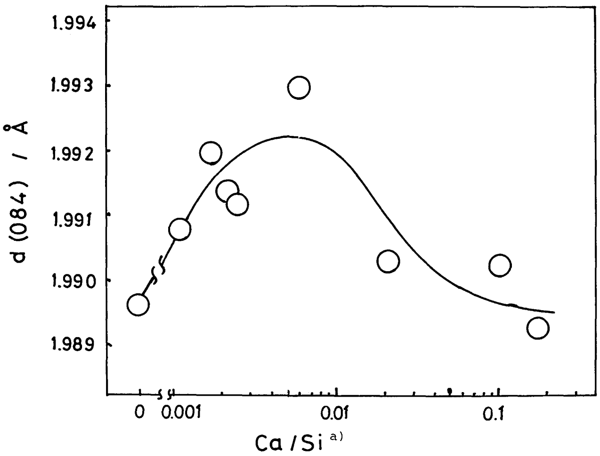

Fig. 2. Spacing $d(084)$ of calcium silicates. a) Atomic ratio determined by X-ray fluorescence spectrometry (XRF).

Table 1. Aluminum and Calcium Contents of Calcium Silicates,a) and pH of Filtrate of the As-Synthesized Silicates

Hydrothermal Temperature (T_h)/K	Ca/Si*=0.02b)			Ca/Si*=0.05b)			Ca/Si*=0.1b)		
	Al/Si	Ca/Si	pH	Al/Si	Ca/Si	pH	Al/Si	Ca/Si	pH
473	<0.001	0.002	7	<0.001	0.01	8	<0.001	0.01	8
443	<0.001	0.003	7	<0.001	0.03	9	<0.001	0.08	9
423	<0.001	0.003	8	<0.001	0.04	9	<0.001	0.07	9
403	<0.001	0.003	7	<0.001	0.02	9	<0.001	0.09	9

a) Determined by X-ray fluorescence spectrometry (XRF). b) Ca/Si atomic ratio of the starting gel mixture.

Table 2. Methanol Conversion over Silicate Catalystsa)

Catalyst	Ca/Sib)	Al/Sib)	Conv. %	DMEc) Yield %	Selectivityd) (C-%)				
					C_2—C_5 Olefin	C_1—C_5 Paraffin	BTXe)	C_6+f)	CO CO_2
Ca-silicate	0.003	<0.001	100.0	0.0	79.7	3.0	3.8	13.3	0.1
Ca-silicate	0.04	<0.001	80.3	22.6	33.9	4.1	0.2	55.4	6.4
Ca-silicate	0.07	<0.001	77.1	39.6	26.7	4.9	0.2	65.2	3.1
Silicalite	<0.001	<0.001	7.0	1.0	(4.8)	(7.3)	(5.9)	(81.9)	(0.1)
ZSM-5	<0.001	0.02	100.0	0.0	46.6	23.0	18.5	11.8	0.1

a) Reaction conditions: T_r=773 K, LHSV=1 h^{-1}. b) Determined by X-ray fluorescence spectrometry (XRF). c) DME=dimethyl ether. d) Selectivity in effective conversion3) (=conversion—DME yield). e) BTX=benzene, toluene and xylene. f) Including carbonaceous deposit.

decreased drastically at Ca/Si*=0.05—0.1, and the pH of the filtrate increased. Xonotolite was additionally formed at Ca/Si*=0.5. The XRD patterns, SEM images and pore size distributions estimated by the adsorption characteristics of hexane isomers6) suggest that the hydrothermal products with high crystallinity obtained at Ca/Si*<0.05 have ZSM-5 structure.

The spacing *d*(084) of the products was precisely determined by XRD with *d*(200) of Si metal as an internal standard. The result is illustrated in Fig. 2. The spacing of the products was slightly expanded with Ca-content, only when Ca/Si ratio determined by XRF (X-ray fluorescence spectrometry) was less than 0.01, suggesting the possibility that a part of Ca is occluded in the silica matrix in these cases.

Table 1 lists the Ca- and Al-contents of the crystals after removing most of the excessive amount of calcium from the surface. The amount of Al-impurity in the silicates was almost invariable under the hydrothermal conditions. The Ca content of the highly crystalline products was less than that of the starting gel mixtures.

In order to elucidate the acidity, some of the hydrothermal products synthesized at 423 K were tested as the catalysts for methanol conversion (Table 2). The calcium silicate of Ca/Si=0.003 showed high activity and high selectivity for light olefins at 773 K. Silicalite containing the same amount of Al-impurity was not active and methanol was decomposed. By increasing the Ca content in the starting gel, the activity and selectivity for light olefins decreased. Zeolite H-ZSM-5 of Al/Si=0.02 was more active than the calcium silicates, and showed high selectivity for BTX (benzene, toluene, and xylene) and paraffins at lower temperature range.

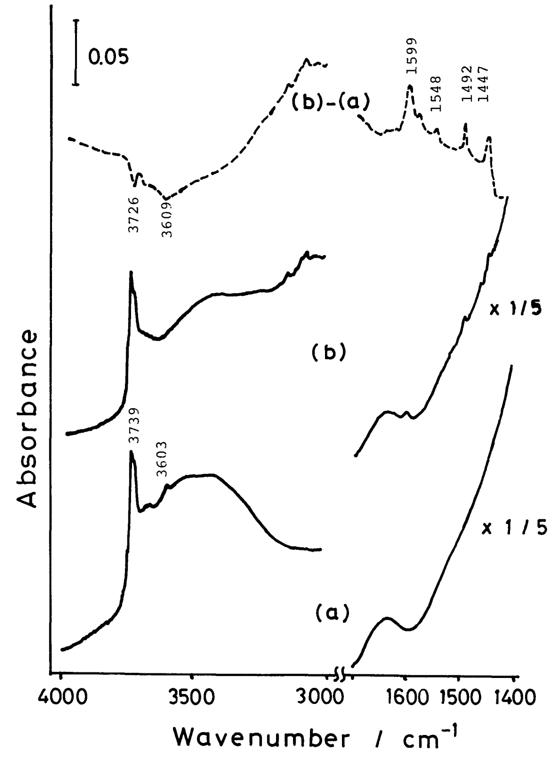

Fig. 3. FT-IR spectra of calcium silicate (a) before and (b) after pyridine adsorption.

Zeolite ZSM-5 modified with alkaline earth metal salts has been reported to be an excellent catalyst for methanol conversion to light olefins.7) The high selectivity for light olefins is ascribed to the acidic Al sites being weakened by modification. The reaction results described above suggest that the calcium silicate of low Ca-concentration also has some weak

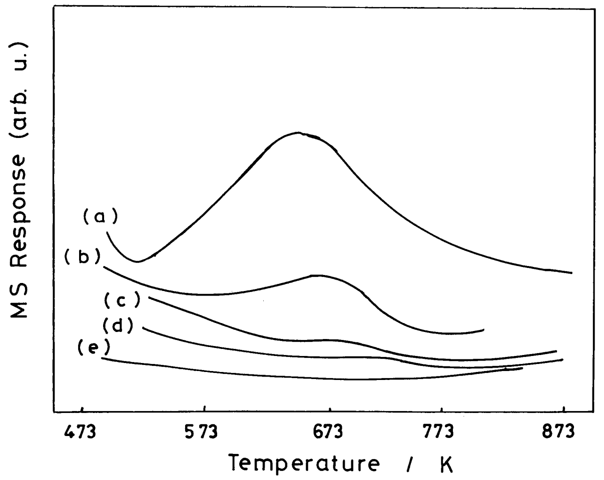

Fig. 4. NH_3-TPD spectra of (a) ZSM-5 (Al/Si=0.02); (b) Ca-silicate (Ca/Si=0.003); (c) Ca-silicate (Ca/Si=0.04); (d) Ca-silicate (Ca/Si=0.07); and (e) silicalite.

acidic sites, even if the amount of Al-impurity is negligibly small.

The FT-IR spectra of the calcium silicate of Ca/Si=0.003 before and after pyridine adsorption are depicted in Fig. 3. A weak OH band at 3603 cm^{-1} was diminished by introducing 0.4 kPa of pyridine at room temperature and following evacuation at 373 K for 5 h, indicating that the silicate has a small amount of Brønsted acid sites. A new peak at 1447 cm^{-1} after the introduction of pyridine indicates that the Ca-silicate does have some Lewis acid sites.[8]

The acidity was also verified by NH_3-TPD spectra as shown in Fig. 4. The calcium silicate of Ca/Si=0.003 showed broad desorption peaks from 473 to 723 K. The desorption amount above 573 K was estimated at 42 $\mu mol\ g^{-1}$ from the peak area, which was much higher than the acidity ascribed to Al-impurity. By increasing the Ca-content of the starting gel mixture (Ca/Si*), the desorption amount decreased. Silicalite did not show an NH_3-desorption peak above 573 K. These results suggest that calcium silicate with low Ca-content only has weak acid sites. The reason for the decrease in the acid sites by increasing Ca/Si* has not yet been well explained.

It is not yet clear whether Ca is substituted for Si in the lattice of the silicate or not. The expansion of spacing *d*(084) and the evidence for acidity may suggest the possibility for the occlusion of Ca somewhere in the calcium silicate lattice, only when the Ca-content is extremely low. A further characterization of Ca is now in progress and will be reported in later.

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