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Synthesis and Control of Pore-opening Size of Zeolite L by Chemical Method

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Zeolite L type of high purity and high crystallinity was synthesized from mono cationic system. As L type has one-demensional channels parallel to the C-axis, the authors tried to cotrol the pore-opening size by coating with SiO_2 phase. L type was dipped into the solution prepared from the hydrolysis of TEOS or TMOS. L type coated was characterized by XRD, IR spectra and adsorption of gas. This coating method did not cause the changes of the basic zeolite structure. L type was coated with SiO_2 phase and new Si-O-Si bond was formed on the framework. L type coated with the solution prepared with TEOS: C_2H_5OH: H_2O: HCl = 1:2:1:1/50 adsorbed more amount of N_2 gas than L type with TEOS: C_2H_5OH: H_2O: HCl = 1:2:2:1/50, in particular the internal adsorption of the former was larger than the latter. This suggested that as TEOS was hydrolyzed with the less amount of H_2O than the stoichiometric amount of hydrolysis (TEOS: H_2O = 1:2), the gel was constituted of the linear structure than of the three dimensional one. The compound of linear-like cluster was bound on the surface and around the pore opening. L type coated showed that the pore opening restrains the diffusion of C_6H_6 and N_2 molecules but allows to penetrate freely into the channel for H_2O molecules.

1. Introduction

Zeolite L crystals consist of channels of ε-D6R-ε units; ε-cage linked by double six oxygen rings, and the units crosslinked to other by oxygen bridges to form channels of 12-membered rings.$^{1)}$ The crystals consist of single-one-dimensional channels parallel to the C-axis and thier diameters are 0.71 nm.$^{2)}$ L type was synthesized for the first time by D. W. Breck$^{3)}$ and it was generally synthesized with Na-K-composited ions. In general, most of zeolites has been synthesized with NaOH as a source of base, Nishimura$^{4)}$ synthesized L type using only KOH as base, and SiO_2 sol, $KAlO_2$ solution. We also tried to synthesize L type of high purity and high crystallinity using K ion only, tetraethoxysilane (TEOS), $KAlO_2$ solution, KOH and H_2O.

As L type has characteristic one-dimensional channels of the circular windows, we suppose to be able to control the opening pore of overall crystals by only control the diameter of both edges of channels. Then application of the new shape-selective catalyst may be expected by the control of windows of the channels. The control of the shape selectivity and catalytic activity has considerably been developed by Niwa et al..$^{5-8)}$ Their methods were mainly based on using gas phase deposition on the crystals, namely CVD method. But there have been few researches to control directly the pore size of zeolites using the liquid and solid reaction.$^{9)}$

We tried to control the pore size of L type with SiO_2 by dipping of solid phase into the solution prepared by hydrolysis of TEOS or tetramethoxysilane (TMOS) at various conditions. L type coated was characterized by XRD, IR spectroscopy and gas adsorption methods.

2. Experimental

2.1 Synthesis of L type

L type was synthesized with TEOS, Al metal (99.99%), KOH and distilled H_2O. TEOS was distilled before use. KOH was analyzed by Warder method and evaluated the K content. Synthesis was performed using a fixed amount of starting materials as follows. The small pieces of Al were dissolved completely with KOH solution in the flask, and fixed H_2O and TEOS were added. After the mixture was stirred by an ultra sonic generator for 10 min, the flask was allowed to be stirred mechanically for 48 hr. at room temperature in order to age the reactant. To prevent evaporation, the flask was equipped with glass tube of which both ends were open, and heated in air oven at 100°C for fixed time. The solid phase was filtered off and washed with distilled H_2O until the pH of the washing was equal to 10.5 and then dried at 110°C for 24 hr.

2.2 Silica coating on L type

The dipping solution for coating was prepared as follows, TEOS or TMOS was hydrolyzed with C_2H_5OH, H_2O, and HCl solution at 50°C for 3 hr. The hydrolytic conditions were TEOS (or TMOS): C_2H_5OH: H_2O: HCl $=1:2:1:1/50$ or $1:2:2:1/50$ (mol.ratio) (TEOS: $H_2O=1:1$ or TEOS: $H_2O=1:2$).

L type of 3.0 g previously dried at 110°C for 24 hr. and cooled was added to the dipping solution at 50°C for 3 hr, with stirring. The solid phase was filtered off and exposed to saturated water vapor at room temperature for 24 hr, in order to complete the hydrolytic reaction. Then it was dried at 110°C for 24 hr.

2.3 Silica coating on LMS3A and gel preparation

In order to detect the characteristics of coating gel phase only, LMS3A without adsorbing N_2 gas at all was treated with the dipping solution derived from TEOS, in a similar manner as L type as a reference sample. The gels themselves that derived from TEOS or TMOS (TEOS: $H_2O=1:2$ or TMOS: $H_2O=1:2$) were characterized by N_2 gas adsorption.

2.4 Characterization of samples

Samples were dried at 110°C for 24 hr and cooled in the desiccator. The chemical composition of L type was analyzed by X-ray fluoresence spectroscopy (JEOL JSX-6057). The sample of 100 mg was mixed with TiO_2 (Anatase) of 20 mg as a internal standard, and was identified by powder X-ray diffractometry (XRD) using Thoshiba X-ray diffractometer model ADG 301 (CuKα, Ni filter, 30 kv, 20 mA G. M. detector). IR spectra were measured by the KBr wafer. Every wafer contained 1 mg of solid phase in 300 mg KBr. Spectra were recorded on a Hitachi infrared spectrometer model 260-50.

The adsorption of N_2 gas was subjected to volumetric measurements at the boiling point of liquid nitrogen and the adsorption of water and benzen vapor to gravimetric measurements at 25°C. The pretreatment of samples was carried out as follows. After being kept at 110°C for 24 hr, the sample was heated at 300°C for 2 hr, under atmospheric pressure, and degassed under vacuum (at 1.33×10^{-3} Pa) for 30 min, prior to the adsorption.

The monolayer capacity (Vm) was caluculated with the Langmuir or BET equation. The outer (Vm') and inner adsorption (Vc) were evaluated by fitting the Frenkel-Halsey-Hill equation[10,11] to the adsorption data.

3. Result and discussion

3.1 Synthesis of L type

L type was synthesized from clear solution that consists of TEOS, $KAlO_2$, KOH and H_2O. When the chemical compositions of starting materials was represented as $XK_2O \cdot Al_2O_3 \cdot YSiO_2 \cdot ZH_2O$, pure L type was formed in the range; $X = 12.5 - 17.5$, $Y = 25$, $Z = 1750 - 2625$. The range of formation was narrow considerably, and the optimum range was dependent on the concentration and the amount of the base.

In this experiment, the authors used L type of the highest crystallinity that was formed from the composition of the starting materials, $SiO_2/Al_2O_3 = 25$, $K_2O/SiO_2 = 0.65$, $H_2O/K_2O = 150$ (mol ratio), that is, $16.25\ K_2O \cdot Al_2O_3 \cdot 25\ SiO_2 \cdot 2437.5\ H_2O$. The results of XRD were in fair agreement with the reference.[12] The chemical compositions of the synthesized L type (SL) and the comercial L type (SK-45) are shown in Table 1. SL contained little Na_2O and CaO compared with SK-45, therefore L type could be synthesized with mono cationic system. SL was pure crystals as judged by XRD and chemical analysis.

Table 1. Chemical Composition of SL and SK-45

Sample	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	TiO_2
SL	10.25	1.62	1.67	0.02	0.01	0.00
SK-45	10.41	1.61	1.45	0.11	0.07	0.01

$(\text{mmol} \cdot g^{-1})$

3.2 XRD and IR spectra of the coating sample

XRD patterns and IR spectra of SL and SL coated with TEOS: $H_2O = 1:1$, or TEOS: $H_2O = 1:2$ are shown in Fig. 1 — Fig. 4 respectively. The numbers in the figures denote the times of dippig.

As shown in Fig. 1, Fig. 2, no changes of the angles (2θ) of XRD and of peak width indicate that this dipping method does not cause the changes of crystal structure. But the intensities of XRD were observed to become somewhat weak. These resuts reveal that SL is coated with much

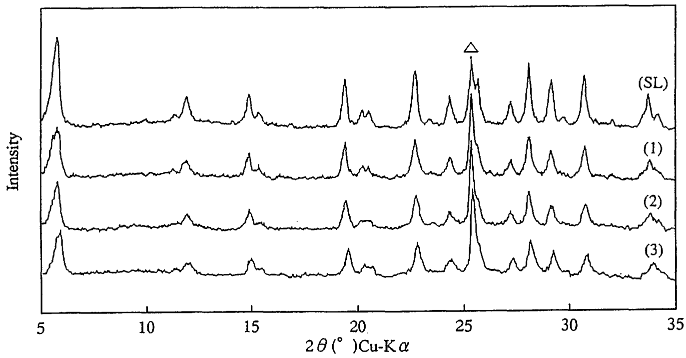

Fig. 1 X-ray diffraction patterns of Original (SL) and samples treated with TEOS: H_2O = 1:1. (SL); Original, Times of dip, (1); once, (2); twice, (3); three times, △; Internal standard (Anatase).

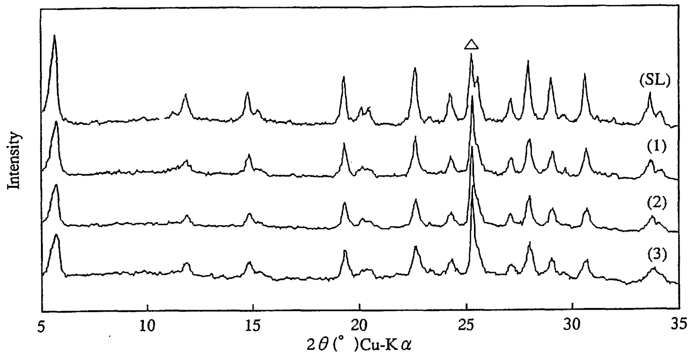

Fig. 2 X-ray diffraction patterns of original (SL) and samples treated with TEOS: H_2O = 1:2, (SL); Original, Times of dip, (1); once, (2); twice, (3); three times, △; Internal standard (Anatase).

SiO_2 gel at the first dipping, but with less amount of the gel by the dipping followed.

The systematic study by the IR spctra on the characteristics of zeolite frameworks related to the crystal structure was done by Flanigen and Khatami.[13] They pointed out that the mid-infrared region (1300 to 250 cm^{-1}) contained the fundamental vibrations of the framework. As shown in Fig. 3, Fig. 4, all fundamental vibrations of L type were observed in the spectra, 1160 cm^{-1} (very weak shoulder), 1080 cm^{-1} (strong), and 1015 cm^{-1} (strong) were assigned to asymmetric stretching mode←OT→ ←O (T: Si or Al). 767 cm^{-1} (medium weak), 721 cm^{-1} (medium weak), 642 cm^{-1} (very weak shoulder) were assigned to symmetric streching mode←OTO→. 606 cm^{-1} (medium), 580 cm^{-1} (very weak shoulder) were assigned to double ring vibrations. 474 cm^{-1} (medium strong), 435 cm (weak shoulder) were assigned to T-O bending mode. 375 cm^{-1} (very weak shoulder) was assigned to pore opening.

With increasing the times of dipping, the split of the strong bands at around 1100 cm^{-1} became

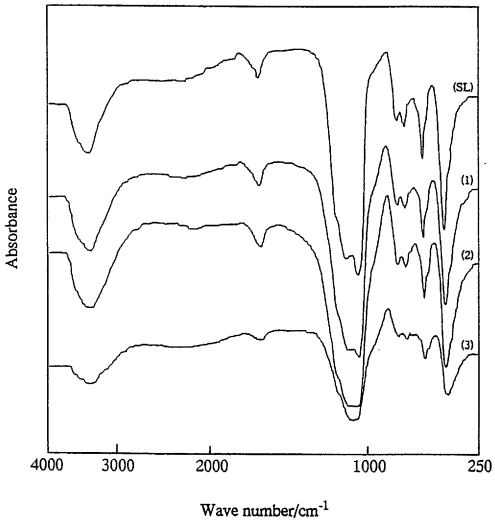

Fig. 3 IR spectra of SL and samples treated with TEOS: $H_2O = 1:1$. (SL); Original, Times of dip, (1); once, (2); twice, (3); three times.

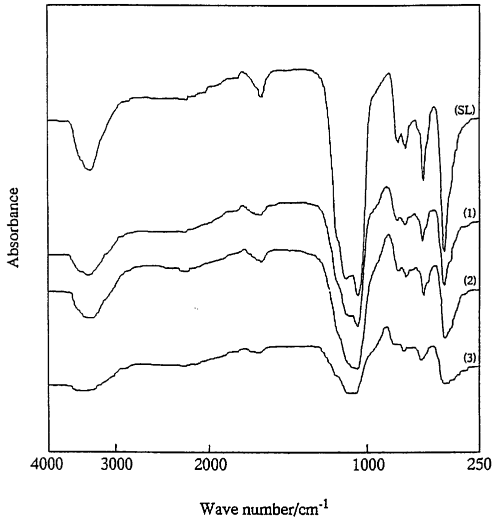

Fig. 4 IR spectra of SL and samples treated with TEOS: $H_2O = 1:2$. (SL); Original, Times of dip, (1); once, (2); twice, (3); three times.

obscure, and absorption intensity of overall spectra became weak and somewhat broad relatively. The band of Si-OH around 950 cm^{-1} enhanced relatively and band of T-O bending at 474 cm^{-1} became weak with the times of dipping.

These results sugest that SL are coated with SiO_2 gel and new SiO-Si bonds are formed on the framework. As a whole, SL coated with TEOS: H_2O = 1:2, compared with TEOS: H_2O = 1:1, revealed somewhat strong decrease of the absorbance. This result is related to the small difference of the amount of coating SiO_2 phase, and is attributable to the difference of the gel structure.

3.3 Adsorption of N_2 gas, H_2O and C_6H_6 vapor

The adsorption isotherms of SL coated with TEOS: H_2O = 1:1, TEOS: H_2O = 1:2 and TMOS: H_2O = 1:1 are shown in Fig. 5 – Fig. 7. The results of adsorption are shown in Table 2. As shown in Fig. 5 – Fig. 7, the amount of adsorption of SL coated was less than that of SL, whether

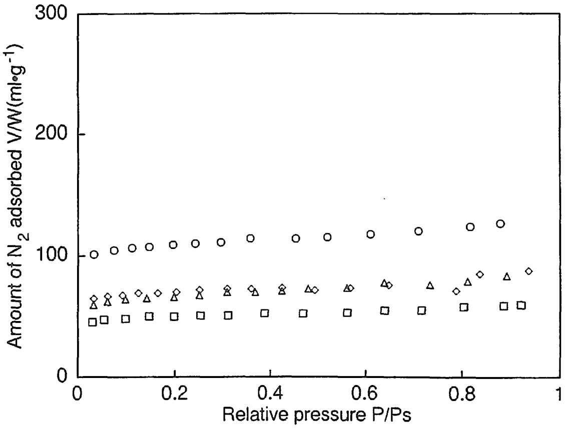

Fig. 5 Adsorption isotherms of N_2 gas at − 196°C, on SL and samples treated with TEOS: H_2O = 1:1. (○); SL, Times of dip, (□); once, (△); twice, (◇); three times.

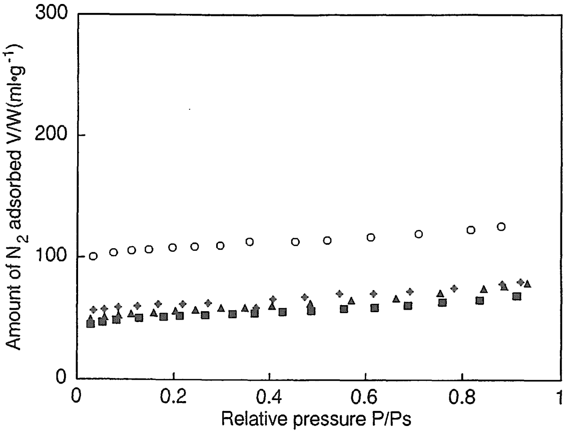

Fig. 6 Adsorption isotherms of N_2 gas at − 196°C, on SL and samples treated with TEOS: H_2O = 1:2. (○); SL, Times of dip, (■); once, (▲); twice, (◇); three times.

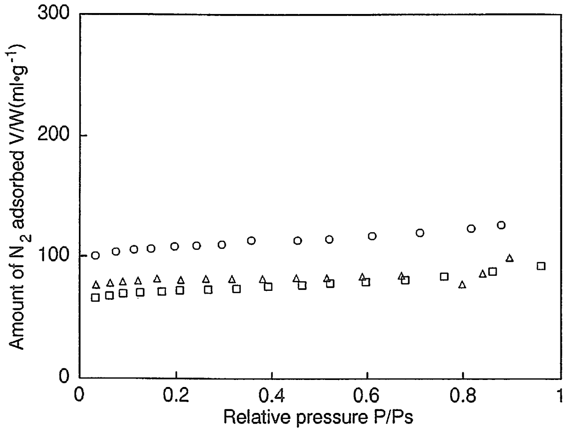

Fig. 7 Adsorption isotherms of N_2 gas at − 196°C, on SL and samples treated with TMOS: H_2O = 1:1. (○); SL, Times of dip, (□); once, (△); twice.

the dipping solution derived from TEOS or TMOS. The amount of adsorption of SL coated with solution derived from TEOS was less than TMOS, that is, the former decrease the amount to 45 − 49% and the latter 64% at the first dipping.

With increasing the times of dipping, both samples increased the amount of adsorption. If the outer adsorption of all samples is regarded as costant, increasing the amount of adsorption is dependent on the inner adsorption of SL. In the case of TEOS, the amount increased of SL coated with TEOS: H_2O = 1:1 is larger than TEOS: H_2O = 1:2. In order to clarify this result, the adsorption of the gel itself was measured. That is, LMS3A that can not adsorb N_2 gas was coated with TEOS: H_2O = 1:1 or TEOS: H_2O = 1:2 as a same manner as mentioned above. As shown in Fig. 8 and Fig. 9, the results revealed the opposite tendency. LMS3A coated with TEOS: H_2O = 1:2 adsorbed slightly larger amount than that coated with TEOS: H_2O = 1:1. In this case, the amount of adsorption also increased with times of dipping. Therefore, in the case of SL, the amount increased of adsorption with times of dipping depends on the effect of the gel structure only. In the case of LMS3A, the result revealed that the gel developed to the structure of three dimensional because TEOS: H_2O = 1:2 was advantageous for hydrolysis of TEOS than TEOS: H_2O = 1:1. Therefore the former adsorbed more than the latter.

On the other hand, SL coated with TEOS: H_2O = 1:1 adsorbed more than that with TEOS: H_2O = 1:2. This result was understood as follows, because TEOS was hydrolyzed with the less amount of water than the stoichiometric amount (TEOS: H_2O = 1:2), the gel may develop to the linear structure, not to three dimensional one. Then the linear cluster was bound on the SL surface.

A part of the opening pore of SL coated may be restricted with linear cluster of silica, so that the adsorption of N_2 gas decreased. But a part of the pore can be penetrated by N_2 molecules. In other words, the amount adsorbed of LMS3A coated is the adsorption of the gel itself and is dependent on the gel structure coated at the surfase, while the amount of adsorption of SL coated is

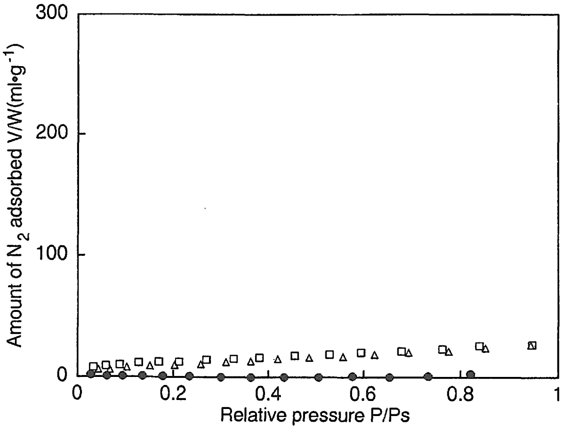

Fig. 8 Adsorption isotherms of N_2 gas at −196°C, on LMS3A and samples treated with TEOS: H_2O = 1:1. (●); LMS3A, Times of dip, (□); once, (△); twice.

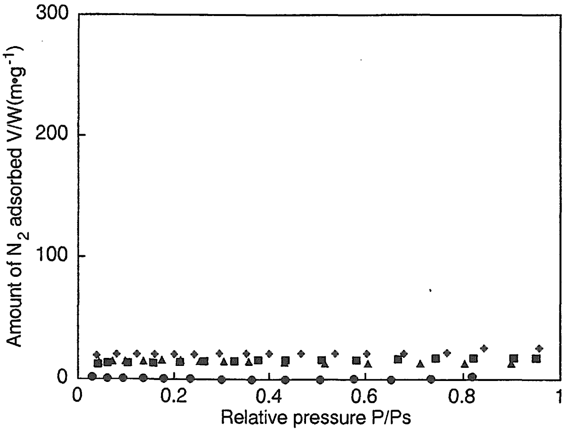

Fig. 9 Adsorption isotherms of N_2 gas at −196°C, on LMS3A and samples treated with TEOS: H_2O = 1:2. (●); LMS3A, Times of dip, (■); once, (▲); twice, (◆); three times.

influenced by both the coated gel structure and the changes of the pore structure of L type caused by coating gel.

The differences of the amount of coating are small in regard to the hydrolysis coditions, the differences of the inner adsorptions of the SL coated are dependent on the variance of the structure of coating phase. SL coated with TMOS: $H_2O = 1:1$ adsorbed more amount of N_2 gas than SL coated with TEOS.

This is the reason why TMOS hydrolyzes more rapidly than TEOS,$^{14)}$ and at the same condition, the gel derived from TMOS may be formed with three-dimensional-dense-gel structure.

Therefore SL coated with TMOS revealed the larger amount of inner adsorption, and the gel containes more micro pore structure. In this connection, the amount adsorbed of the gel derived from TMOS is larger than the gel derived from TEOS. The amount adsorbed decreased rapidly at the first dipping, and contrary to expectation the amount adsorbed increased slightly with times of dipping. This is considered that the degree of amount of coating is small on the coated surfase. This result is expected from the changes of intensity of XRD. At this experimental conditions, concerning of the effect of coating on the adsorption, inner adsorption is more influenced than the outer adsorption. The amounts of outer adsorption of SL coated are nearly same as original SL. There are slight changes among the values, but these values are regarded as constant. Therefore, the bond of SiO_2 cluster around the pore opening was mainly responsible for change of adsorption with the coating process.

The authors expected that SL was coated with one dimensional structure of SiO_2 of linear cluster when coating solution was prepared with H_2O-deficient condition, that is, TEOS: $H_2O = 1:1$, and this situation is favorable for the control of pore opening. On the other hand, when coating solution was prepared with stoichiometric amount of H_2O, that is, TEOS: $H_2O = 1:2$, the coating phase was formed with three dimensional SiO_2, these condition was not advantageous for the cotrol of the micro pore.

As shown in Fig. 10, Table 2 , the adsorption of C_6H_6 vapor revealed the same tendency as N_2 gas. But the amount of adsorption was small compared with N_2 gas.

As shown in Fig. 11 and Fig. 12 SL and SL coated revealed the same tendency of the adsorption of H_2O vapor. This results suggest that under this experimental conditions the pore opening of SL coated restrains the diffusion of C_6H_6 and N_2 molecules but allows to penetrate freely for H_2O molecules.

This method for coating on the zeolite surface from the liquid phase prepared by hydrolysis of TEOS or TMOS was very simple.

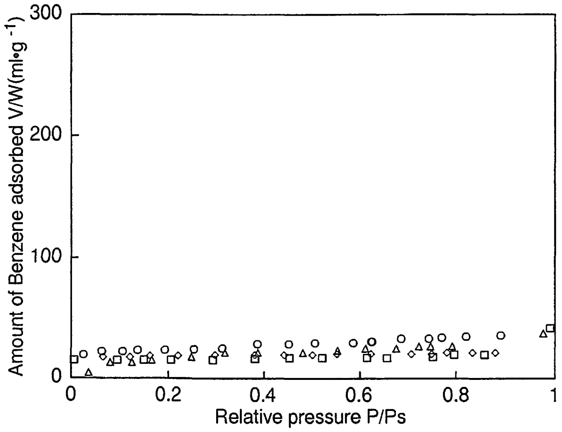

Fig. 10 Adsorption isotherms of C_6H_6 vapor at 25°C on SL and samples treated with TEOS: $H_2O =$ 1:1. (○); SL, Times of dip, (□); once, (△); twice, (◇); three times.

Table 2. Results of Adsorption

Samples	Vm a)	Vc b)	Vm' c)	$\mathrm{Vm_B}$ d)	$\mathrm{Vm_w}$ e)
SL	115	103	10	26	146
SK-45	119	115	4		
SL TEOS/H_2O=1/1					
dip once	56	46	10	16	157
dip twice	73	58	8	21	139
dip three times	75	65	5	24	153
SL TEOS/H_2O=1/2					
dip once	52	40	7		133
dip twice	58	42	12		135
dip three times	65	52	7		177
SL TMOS/H_2O=1/1					
dip once	73	64	8		
dip twice	85	78	2		
LMS3A	0	0	0		
LMS3A TEOS/H_2O=1/1					
dip once	10	6	6		
dip twice	13	7	6		
LMS3A TEOS/H_2O=1/2					
dip once	14	11	2		
dip twice	16	14	3		
dip three times	21	18	2		
LMS3A TMOS/H_2O=1/2					
dip once	15	12	4		

a) Vm; monolayer capacity (N_2 gas, ml·g^{-1})
b) Vc; inner adsorption capacity (N_2 gas, ml·g^{-1})
c) Vm'; outer adsorption capacity (N_2 gas, ml·g^{-1})
d) $\mathrm{Vm_B}$; monolayer capacity (C_6H_6 vapor, ml·g^{-1})
e) $\mathrm{Vm_W}$; monolayer capacity (H_2O vapor, ml·g^{-1})

Now the authors try to clear the behavior of the adsorption of various kinds of molecules with decreasing the amount of coating phase on SL.

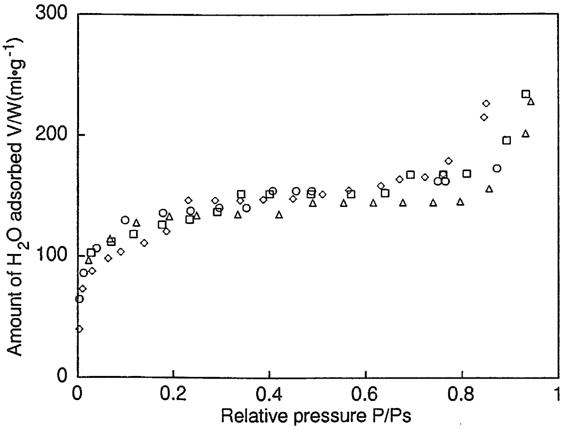

Fig. 11 Adsorption isotherms of H_2O vapor at 25°C, on SL and samples treated with TEOS: H_2O = 1:1. (○); SL, Times of dip, (□); once, (△); twice, (◇); three times.

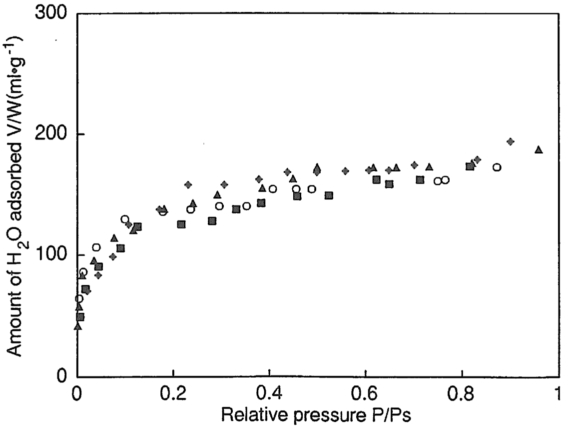

Fig. 12 Adsorption isotherms of H_2O vapor at 25°C, on SL and samples treated with TEOS: H_2O = 1:2. (○); SL, Times of dip, (■); once, (▲); twice, (◆); three times.

4. Conclusion

1. L type of high crystallinity and high purity was synthesized in the mono cationic system.

2. L type was coated with SiO_2 phase drived from two different conditions of hydrolysis of TEOS or TMOS, that is, TEOS or TMOS: H_2O = 1:1 and TEOS: H_2O = 1:2. The former absorbed larger amount of N_2 gas than the latter. This result may be caused by the difference of gel structure.

3. The former revealed larger inner adsorption than the latter. This suggested that when TEOS was hydrolyzed with less amount of water, the gel was constituted of linear structure than of

the three dimensional one.

4. L type coated showed that the pore opening restrain the C_6H_6 and N_2 molecules but allows to penetrate freely in to the channel for H_2O molecules.

5. This method of the control of pore-opening size is very simple, but moreover the conditions of hydrolysis and coating of hydrolyzed solution must be considered.

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