Pseudomorphic Amorphism after Zeolite-LTA at Acid Conditions: XRD, SEM and NMR characterization

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Linde Type A zeolites with Na ions (zeolite-LTA; $Na_{12}Al_{12}Si_{12}O_{48} \cdot 27H_2O$) were treated at acid conditions containing different concentration of hydrochloric acid (10–300 mM) and durations of 5–3000 min at room temperature. The obtained products were characterized by powder XRD, SEM, AFM, NMR, ICP analysis and nitrogen adsorption measurements. At lower concentration of HCl solution, the structure and original cubic morphology of zeolite-LTA was not destroyed, but at higher concentration and/or long duration zeolite-LTA was damaged and finally dissolved into solution. At 50–80 mM of HCl solution and/or duration of 40–280 min, noncrystalline pseudomorph after zeolite-LTA with Na cations was obtained. The material was amorphous one showing cubic shape in micron size. The cubic amorphous material was produced by sodium-hydrogen ion exchange and subsequent breakdown of the framework of zeolite-LTA. This material should be useful for eco-functional material such as adsorbent and catalytic substrate. Key words: Acid, Amorphism, Pseudomorph, Zeolite-LTA

1. INTRODUCTION

Zeolite is crystalline, hydrated aluminosilicate with exchangeable cations. The aluminosilicates portion of the structure is a 3-dimension open framework consisting of a network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all the oxygen. They have periodic and molecular-sized pores and channels in their unique structures [1]. They have high cation-exchange capacity, ion adsorption, and are of special interest for minimizing environmental pollution during municipal and industrial waste management [2-10].

More than 100 different species of natural and synthetic zeolites have been identified [11]. Among them, Linde Type A zeolite (zeolite-LTA) is one of the most important synthetic zeolites. Zeolite-LTA is distinguished from other zeolite by its Al/Si ratio of 1:1, which chemical formula is given as $Na_{12}Al_{12}Si_{12}O_{48} \cdot 27H_2O$. It has well-shaped cubic morphology with a few um. It has been extensively used in ion exchange, adsorption, catalysis, and especially used as a builder in laundry detergents. Its chemical behaviors in aqueous solutions have been extensively investigated [1, 9, 10]. The studies indicated that zeolite-LTA cannot be exchanged to the proton form in the presence of water without collapse of its crystalline framework, and especially in strong acid media it dissolves completely [1].

In this hydrolysis and degradation process of zeolite-LTA, the interesting phenomenon, that is,

amorphous pseudomorphism, was observed. Pseudomorphism is defined to be a phase transformation into another phase of different crystal structure or composition without any changes in the external form of the original phase [12, 13]. The product after zeolite-LTA with Na-cations at the controlled pH was analyzed to be completely amorphous upon the examination by X-ray diffraction and selected electron diffraction [14]. The results indicated that zeolite-LTA srtructure was disrupted even though electron micrograph showed little morphological change. Its formation mechanism was explained by two steps; the sodium-hydrogen ion-exchange and the subsequent release of silicic acid during the hydrolysis reaction of the framework. Same observations were appeared in our previous studies where zeolite-LTA with Na-ions was treated with HCl solution and hydrothermal condition [15, 16]. The nitrogen adsorption measurement suggested that the obtained glass after pseudomorphic transformation has mesopore at 1.9 nm.

The objectives of the present work are: (i) to study the dissolution, degradation and amorphous pseudomorphism after zeolite-LTA with Na-cations under various acid treatments conditions, by varying the concentration of HCl solution and duration, (ii) to characterize precisely the obtained solid after pseudomorphism by using XRD, SEM, AFM, NMR and nitrogen adsorption measurement.

2. EXPERIMENTAL

Synthetic zeolite-LTA with Na-cations was supplied as powders by Wako Pure Chemical Industries, Ltd. 1.0 g of zeolite-LTA with Na-cations was added to 100 mL aqueous solution containing different concentration of hydrochrolic acid (10-300mM). The reacted mixture (suspension of the powdered material in desired concentration of HCl solution) was stirred at room temperature for the desired durations of 5-3000 min, and then suspension was filtered with a 0.45µm membrane filter (Millipore, 0.45µm HA-type).

The ion concentration of the filtered solution was determined by inductive coupled plasma spectroscopy (ICP) (SEIKO HVR 1700). The pH of the solution was determined using a pH meter (Toa Dempa Kogyo HM-60V) before and after the treatment.

The reacted solid was separated, washed with 500 mL of distilled water and dried in an oven at 50°C for 12 hrs.

The obtained solid and initial zeolite-LTA were characterized by the powder X-ray diffraction (XRD) method with Cu Ka radiation (RIGAKU RINT 2200), by the scanning electron microscopy (SEM) (JEOL S-5500), by the atomic force microscopy (AFM) (SHIMAZU SPM 9500), and by the nuclear magnetic resonance (NMR) spectroscopy (JEOL EX-400). Nitrogen adsorption isotherm at -196°C was measured by the static volumetric system using a BELSORP 28SA (BEL JAPAN, Inc). Prior to the measurement, the solid sample was activated at 300°C under a reduced pressure for 12 hrs. Pore-size distribution was determined from the nitrogen adsorption isotherm by using Dollimore-Heal (D-H) method.

3. RESULTS AND DISCUSSION

3.1 Transformation of zeolite-LTA under various acid treatments conditions

The obtained solids and solution chemistry of the treated zeolite-LTA with Na-cations as function of concentration of hydrochrolic acid (10-150 mM) and durations (5-1000min) at room temperature were summarized in Table 1. The transformation-acid concentration-duration diagram for zeolite-LTA at room temperature was shown in Figure 1.

At lower concentration of HCl solution and shorter duration than a few ten minutes, the original crystallinty and the typical cubic morphology of zeolite-LTA were maintained (Figures 2a, b and 3a, b). ICP analyses indicated that there was selective release of Na-ion from zeolite-LTA, but negligible amount of Al and Si. The pH of the treated sample increased from that of the intial solution. The change of pH was compared with the increase of Na-ions in the treated solution. It suggested that the Na-ions in zeolite-LTA were exchanged by hydrogen ions in HCl solution during the acid treatment. At higher concentration of HCl solution more than 100 mM and longer duration, zeolite-LTA was dissoloved. After the treatment at 300 mM HCL solution, the zeolite-LTA was completely dissolved and made a clear solution. At higher concentration of 150 mM HCl and entire range of duration, and at 100-120 mM HCl and a few ten minutes durations, the zeolite-LTA dissolved and the precipitated amorphous gel appeared in the solution.

Table 1. Solid identifications and solution chemistry of the treated zeolite-LTA under various acid treatments conditions.

C _{HCI} (mM)	T (min)	pH before	pH after	Na(mM)	Al(mM)	Si(mM)	Solid Products
10	5	2.00	6.95	10.06	N. D.	0.02	N.D.C.
10	10	2.00	7.05	9,95	N. D.	0.03	N.D.C.
10	100	2.00	7.15	9.95	N. D.	0.08	N.D.C.
10	300	2.00	7.26	9.85	N. D.	0.17	N.D.C.
10	1000	2.00	7.42	10.38	0.01	0.35	N.D.C.
30	5	1.63	5.88	29.34	0.84	1.37	N.D.C.
30	10	1.63	6.00	29.31	0.67	1.17	N.D.C.
30	100	1.63	6.33	29.27	N. D.	0.98	N.D.C., G
30	300	1.63	6.51	29.87	N. D.	0.72	N.D.C., G
30	1000	1.63	6.76	30.31	N. D.	0.95	N.D.C., G
50	5	1.36	5.03	45.45	4.72	5.21	N.D.C.
50	10	1.36	5.33	47.65	5.20	5.88	N.D.C.
50	30	1.47	5.28	47.34	4.71	4.81	N.D.C.
50	100	1.47	5.57	46.51	4.85	5.08	N.D.C.
50	250	1.47	5.75	47.57	4.95	5.46	P.A
50	300	1.34	6.05	49.50	N. D.	2.11	P.A., G
50	1000	1.37	6.40	50.32	N. D.	1.73	D.C.N.C., G
60	5	1.33	4.29	52.43	7.69	8.29	N.D.C.
60	10	1.33	4.42	55.2 9	7.47	8.00	N.D.C.
60	30	1.29	4.55	56.09	7.79	8.08	N.D.C.
60	70	1.29	4.85	57.89	8.53	8.92	P.A
60	100	1.29	4.95	57.72	8.89	9.44	P.A
60	150	1.29	5.16	59.13	9.35	9.96	P.A
60	200	1.29	5.21	58.33	9.69	10.57	P.A
60	240	1.29	5.26	58.16	9.90	10.84	P.A
60	300	1.29	5.34	57.43	0.06	3.71	P.A., G
60	1000	1.32	5.42	60.64	N. D.	1.62	D.C.N.C., G
100	5	1.03	3.84	55.16	19.33	19.94	D.C.N.C.
100	10	1.03	3.86	58.81	20.63	21.16	D.C.N.C.
100	100	1.03	3.76	65.19	38.94	39.98	D.C.N.C.
100	300	1.03	3.70	66.87	53.27	54.47	D.C.N.C.
100	1000	1.03	3.59	68.59	8.52	7.59	D.C.N.C., G
120	5	1.01	3.75	58.77	26.00	27.10	D.C.P.L
120	10	1.01	3.74	61.19	28.33	29.54	D.C.P.L
120	100	1.01	3.63	66.45	53.01	54.84	D.C.N.C.
120	1000	1.01	3.41	66.94	61.34	62.94	D.C.N.C.
150	5	0.96	3.64	61.90	36.49	38.03	D.C.P.L
150	10	0.96	3.62	62.84	39.45	41.60	D.C.P.L
150	100	0.96	3.43	67.20	61.84	64.46	D.C.P.L
150	1000	0.96	3.32	66.43	64.17	65.07	D.C.N.C.

N.D.: not detected N.D.C.: no damage on cube D.C.P.L.: damaged cube with persisted LTA structure

D.C.N.C.: damaged cube in noncrystalline state



Figure 1. Transformation-acid concentration of HCl-duration diagram for zeolite-LTA at room temperature. •: pseudomorphic amorphism, : gel, \bigcirc : no damage on cube, \triangle : damaged cube with persisted LTA structure, \diamondsuit : damaged cube in noncrystalline state.

The treatments at 80 mM HCl for 40 min, 70 mM HCl for 40-80 min, and 60 mM HCl for 40-300 min, made the zeolite-LTA to be amorphous phase with the external shape of the original crystals of zeolite-LTA (Figure 2 c, and Figure 3c). The phenomenon is known as pseudmorphism: a phase is replaced by another phase of different crystal structure or composition without any change in the external form of the original phase. The noncrystalline pseudomorph after zeolite-LTA was characterized and discussed in detail in the next section.

At higher concentration of HCl and longer duration than those for the above region of the amorphous pseudomorph, the obtained solid was X-ray-amorphous aluminosilicate (Figure 2d) with precipitation of gel. The SEM observation revealed that the original cubic shape was damaged (Figure 3d).

ICP analysis for the release of Na, Si and Al form zeolite (Table 1) was compared with XRD, SEM observations and the change of pH after the treatment. Upon the acid treatments, the zeolite underwent significant changes for the degree of crystallinity and the chemical characteristics. The sharp decrease in the degree



Figure 2. XRD patterns of (a) zeolite-LTA with Na-ions, (b) the products treated by 10mM HCl for 10min, (c) 60mM HCl for 100min and (d) 1000min.



Figure 3. SEM images of (a) zeolite-LTA with Na-ions, (b) the products treated by 10mM HCl for 10min, (c) 100min, and (d) 1000min.

of crystallinity observed by XRD mesurement and the noticeable increase of the Na, Al and Si ions in the solution indicate that Na-H ion exchange was the trigger for the formation of amorphous aluminosilicate, and acid treatment resulted the congruent release of Al and Si from zeolite framework, and the precipitation of amorphous gel.

3.2 Characterization of pseudomorphs of amorphous zeolite-LTA

The noncrystalline pseudomorph after zeolite-LTA was confirmed by XRD and SEM, studies. After the acid treatment at the desired duration mentioned in the previous section, XRD patterns for zeolite-LTA (Figure 2a) was completely disappeared, but the amorphous broad peak was observed (Figure 2c). The original cubic morphology for zeolite-LTA was retained after the treatment (Figure 3c). These observations were compared with those in the previous studies [14-16]. AFM images also showed that no distinct change of surface morphology was occurred after the treatment (Figure 4).



Figure 4. AFM images of (a) zeolite-LTA with Na-ions, (b) the products treated by 60 mM HCl for 100 min.

The increase of Na-ion and pH in the filtered solution (Table 1) for the treated sample indicated that Na-H ion exchange played the main rule for the formation of noncrystalline pseudomorph after zeolite-LTA. The exchanged H ions in the zeolite framework interacted with Al-O-Si bond in the structure and then decomposed the bond. This mechanism was supported by NMR observations.



Figure 5. ²⁷Al NMR spectra of (a) zeolite-LTA with Na-ions, (b) the products treated by 60mM HCl for 100min.

In zeolite-LTA, Si and Al atoms are arranged alternately according to the Loewenstein rule. Therefore one sharp ²⁷Al MAS-NMR spectra for the four-coordinated aluminum Al(tet) was observed at 59 ppm (Figure 5a) for zeolite-LTA. After the formation of noncrystalline pseudomorph, ²⁷Al MAS-NMR spectra for

Al(tet), which was slightly broad at 56 ppm, coexisted with the spectra for the six-coordinated aluminum Al(oct) at 4 ppm (Figure 5(b)). The appearance of Al(oct) confirmed the decomposition of the bond in the framework. The change of Al(tet) to Al(oct) was also observed during protonation of zeolite-Y, which was obtained by calcinations of zeolite with ammonium ion at 550°C in air [17, 18]. During protonation, the dealumination from the framework of zeolite-Y was appreciably occurred, and played the important role of the change of aluminum coordination.

In the previous study, the formation of the additional pores with 1.9 nm was realized by the acid treatment and subsequent hydrothermal treatment of zeolite-LTA [16]. Unfortunately no distinct mesopore was recognized for the noncrystalline pseudomorph after zeolite-LTA in this study. Although the remaining the original micropore of about 0.5 nm was not determined because of the limitation of measurement condition for nitrogen adsorption, the obtained noncrystalline pseudomorph should be useful for eco-functional material such as adsorbent, catalytic substrate and may be applicable to membrane for ultrafiltration.

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