

Synthesis of low silica zeolites under the water with alcohols and the surface characterization of gaseous adsorption

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ABSTRACT

Low silica zeolites are synthesized generally by sol-gel method in water. In this study, efforts were made to prepare low silica zeolites from sodium aluminate and sodium silicate, in the presence of alcohols, at 373 K under an atmospheric pressure. It was of our special interest to investigate how the addition of various alcohols into water affects the type of zeolites synthesized during crystallization process for different reaction times (2, 6, 24, 120 hours). Five different types of zeolites were identified during zeolite synthesis process: ZeoliteA, ZeoliteX, Sodalite, Na-Pc, and Analcime. The zeolites synthesized at designated reaction times were characterized by X-ray diffraction (XRD), N₂ and H₂O vapor adsorption/desorption. The results indicated that zeolite Na-Pc was preferentially synthesized in solely water solvent, whereas in solvent containing alcohols ZeoliteX and ZeoliteA appeared at the early stage of crystallization process, subsequently transforming to Analcime through intermediates of Sodalite and Na-Pc. It was presented that Na-Pc possessed peculiar surface characteristics, which were suggested from a stepwised H₂O isotherm and hysteresis loop in N₂ isotherm, both of which were not recognized on other types of zeolites synthesized in the present study.

INTRODUCTION

Zeolites contain crystalline tectoaluminosilicates that are constructed from TO₄ tetrahedra (T=Si, Al). Each apical oxygen atom is shared between two adjacent tetrahedral giving a framework ratio of O/T=2 as shown in **Figure 1**.

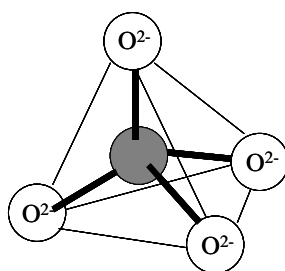


Figure 1 Unit of TO₄ (A center is ether Si⁴⁺ or Al³⁺)

According to Flanigen's notation, the frameworks ratios of Si/Al are divided into three kinds of zeolites. Low-silica zeolites are defined as having 1 Si/Al 2, intermediate-silica zeolites contain 2 Si/Al 5 and high-silica zeolites with Si/Al 5 [1, 2].

Generally low silica zeolites are synthesized in a solvent of water. **Table 1** is a list of literature review relating low silica zeolites synthesized in water [3-6]. There is no information available for the description of pressure except that zeolites synthesis was carried out in either open or closed system. Moderate synthetic condition (< 423K) prefers

to form ZeoliteX and ZeoliteA and then they change their forms to Na-Pc and Analcime, depending upon the severances of experimental conditions of temperature (See, Ref. 7)). It should be noted that Analcime can be formed only above the temperature of 423K when water is solely used as solvent [3, 8].

Table 1 Synthetic conditions of low silica zeolites prepared in water

| Crystal Phase | Silicate source | Aluminate source | Gel Composition [mol] | Reaction system | Heating Temperature [K] | Heating Time [hours] | References |
|---------------|-----------------|------------------|---|-----------------|-------------------------|----------------------|------------|
| zeoliteX | Sodium silicate | Sodium aluminate | $XNa_2O-Al_2O_3-YSiO_2$ (X=2-4, Y=2-6) | Closed | 333-383 | 2-3 | [3] |
| zeoliteX | Sodium silicate | Sodium aluminate | $XNa_2O-Al_2O_3-YSiO_2$ (X=3.9-14.4, Y=3.0-14.5) | * | 323-393 | 1.5-11days | [4] |
| ZeoliteA | Fumed silica | Sodium aluminate | $XNa_2O-Al_2O_3-YSiO_2$ (X=2-4, Y=1-3) | Closed | 333-383 | 2-3 | [3] |
| ZeoliteA | Silica gel | Sodium aluminate | $XNa_2O-Al_2O_3-YSiO_2$ (X=1.4-4.5, Y=1.5-3.0) | -* | 298-423 | 2.5-14days | [5] |
| Na-Pc | Fumed silica | Sodium aluminate | $XNa_2O-Al_2O_3-YSiO_2$ (X=2-4, Y=2-6) | Closed | 383-473 | 2-3 | [3] |
| Na-Pc | Sodium silicate | Sodium aluminate | $0.97Na_2O-Al_2O_3-3.04 SiO_2$ | Open, closed | 348-423 | 6-16 | [6] |
| Analcime | Fumed silica | Sodium aluminate | $XNa_2O-Al_2O_3-YSiO_2$ (x=3-4, Y=4-10) | Closed | 423-473 | 2-3 | [3, 8] |

-*: Not described in the corresponding references

There has been a little work done on zeolite preparation in the presence of organic solvents in water. Dutta et al [9] used a mixture of water and ethanol as solvent to synthesize low silica zeolites at the temperature range of 363-368K up to 10hours under autogeneous pressure in a closed system. They reported that ZeoliteA, ZeoliteX, ZeoliteY were formed at the low ratios of ethanol (<50%; volume per volume), and that Sodalite and Cancrinite were crystallized at the high ratios (>50%; volume per volume). It is mentioned that formation of Cancrinite has not been reported, within author's knowledge, under relatively low temperature of 373K in solely water solvent.

In this study, the work done by Dutta et al [9] has been extended to a series of alcohols (methanol to decanol) with prolonged reaction times up to 120hours in open system. The zeolites obtained at different reaction times were characterized by X-ray diffraction (XRD), N₂ and H₂O vapor adsorption/desorption isotherms.

EXPERIMENTAL

In this study, aluminate solutions and silicate solutions were mixed together to obtain silicaalumina gels. These gels were reacted then to synthesize zeolites at 373K for a series of reaction time in an open system. The diagram of zeolite preparation is presented in **Figure 2**. In the case of zeolites formed in solely water, aluminate solution was first

prepared by dissolving NaAlO_2 (Kanto Chemical Co.) in 20ml of water. Silicate solution was also prepared by dissolving both of Na_2SiO_3 powder (Junsei Chemical Co.) and sodium hydroxide (Junsei Chemical Co.) in 20ml of water. Then, the solutions of aluminate solution and silicate solution were mixed to obtain silicaalumina gels. The gels were homogenized at room temperature, and heated at 373K for a designated time of 2, 6, 24, 120 hours in order to synthesize zeolites. After the reaction, the zeolite samples were cooled to room temperature, filtered and washed by distilled water until pH of the filtrate became below 10. These samples were then dried in air at 373K overnight and kept in a desiccator over Drierite until they were used for further studies.

As another type of solvent, a mixture of water and alcohol was used to synthesize zeolites. It is noted in this case that each of aluminate solution and silicate solution was prepared by adding 10ml of water and 10ml of alcohol, instead of 20ml of water as seen in **Figure 2**. Rest of the procedure was same as described on zeolites prepared in water. In this study, a number of alcohols were used from methanol to decanol.

Synthesized zeolite samples are identified by listing the type of solvent, and length of time reacted, e.g., a zeolite treated solely in water for 6 hours is reported as (W6h), and a zeolite treated in a mixture of water with ethanol for 24 hours is as (Et24h).

The zeolite samples were examined using X-ray diffraction (Rigaku, rint1200) and

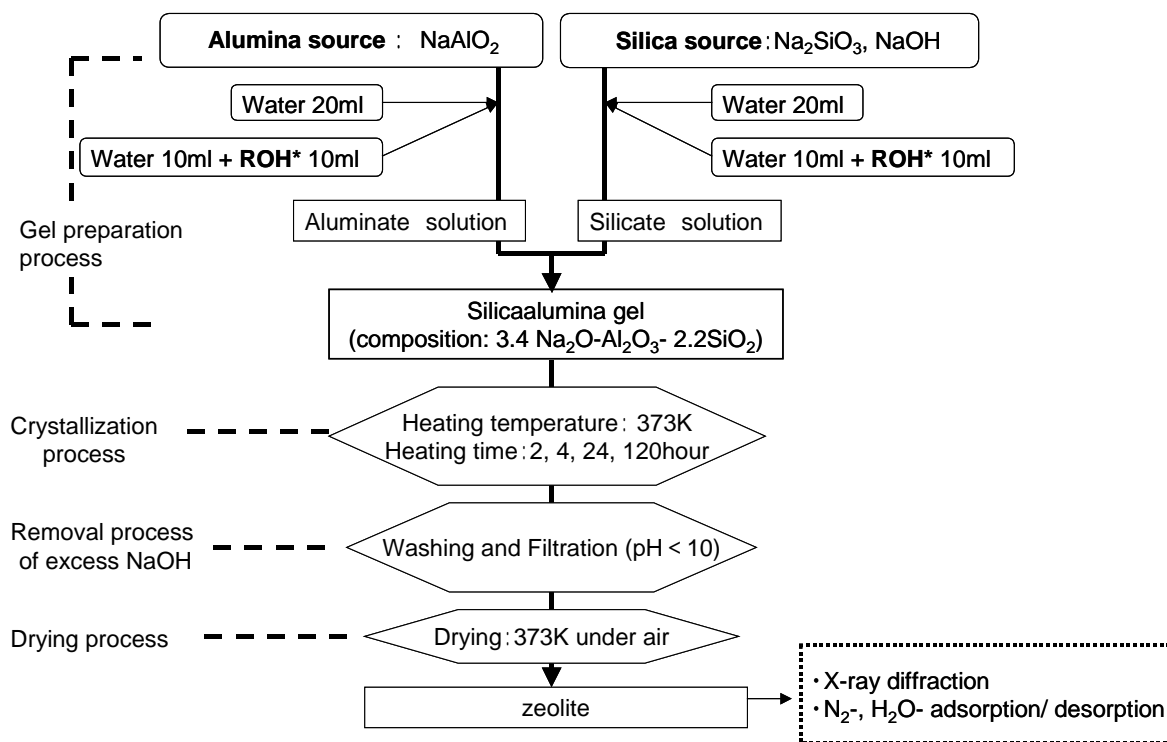


Figure 2 Flow chart of zeolites synthesis performed in water and in water/alcohol mixture. Silicaalumina gel was prepared by following two methods; (A): water was used as solvent to prepare silicaalumina gel, and (B): water and alcohols (ROH*: alcohols [methanol ~ decanol]) were used as solvents to prepare silicaalumina gel.

Automatic gas and vapor adsorption measurement (BEL JAPAN, INC, BELLSORP-18PLUS). The X-ray diffraction (XRD) spectra were obtained using CuK radiation in the 2 θ range of 5-60 ° to identify crystal phases.

RESULT AND DISCUSSION

Type of Zeolites Formed in Presence of Alcohols: The components of zeolites identified by X-ray diffraction are listed in **Table 2**.

Table 2 Zeolites synthesized in aqueous alcoholic solutions

| | Solvents [ml] | | Heating time [hours] | | | |
|---------------|---------------|----------|----------------------|-------------|--------------------|-----------------|
| | Water | Alcohols | 2 | 4 | 24 | 120 |
| Water [W] | 40 | None | X, Na-Pc | Na-Pc | Na-Pc | Na-Pc |
| Methanol [Mt] | 20 | 20 | Sodalite | Sodalite | Sodalite | Na-Pc |
| Ethanol [Et] | 20 | 20 | Sodalite | X, A | Sodalite | Analcime |
| Propanol [Pr] | 20 | 20 | X, A | X, A | X, A, Na-Pc | Na-Pc |
| Butanol [Bu] | 20 | 20 | X, Sodalite | X, Sodalite | X, Na-Pc | Analcime |
| Pentanol [Pe] | 20 | 20 | X, A | X, A | Na-Pc, Analcime | Analcime |
| Hexanol [He] | 20 | 20 | X, A | X, Sodalite | Na-Pc, Analcime | Analcime |
| Heptanol [Hp] | 20 | 20 | X, Sodalite | X, Sodalite | Na-Pc, Analcime | Analcime |
| Octanol [Oc] | 20 | 20 | X, A | X, Na-Pc | Na-Pc, Analcime | Analcime |
| Nonanol [No] | 20 | 20 | X | X, Sodalite | Analcime | Analcime, Na-Pc |
| Decanol [De] | 20 | 20 | X, Sodalite | X, Sodalite | X, Na-Pc, Analcime | Analcime |

The interpretation of the data is not easy, but some important remarks can be made. In water, ZeoliteX and Na-Pc were formed first, while Na-Pc was only the component even after 120 hours of reaction time. However, ZeoliteX and ZeoliteA appear predominantly in the presence of alcohols at the early stage of reaction with time, and they are converted to Sodalite or Na-Pc. As the heating time increased further, Analcime became a stable component. It is inferred that Sodalite and Na-Pc were transformed to Analcime, the formation of which has not been yet reported at a moderate condition: at 373K and under an atmospheric pressure.

N₂ and H₂O Isotherms on Zeolites: Adsorption and desorption isotherms are obtained in N₂ (77K) and H₂O vapor (298K) on the zeolites prepared in this study and commercially available zeolites of MX and .MA. The MX is X type zeolite (ZeoliteX) and the .MA is A (ZeoliteA) type zeolite. Characteristic values of zeolites measured by N₂ and H₂O adsorption are listed in **Table 3**, and the isotherms on selected samples (MX and W6h) were presented in **Figure 3**. It is mentioned that W6h sample, thus Na-Pc, showed the hysteresis loop in N₂ isotherm, implying the presence of mesopores. None of other

zeolites indicated hysteresis in N₂ adsorption/desorption isotherms. The W6h sample also showed a peculiar phenomenon, which was recognized as stepwised H₂O adsorption isotherm. It is not clear at this moment that this stepwise adsorption is originated from heterogeneous surface characteristics or mesopores present on the zeolite surface.

Table 3 Results of N₂ and H₂O adsorbed on Zeolites

| Samples | Zeolite type | Amount of N ₂ Adsorbed at P/ P ₀ = 0.9 [ml/g] | Amount of H ₂ O Adsorbed at P/ P ₀ = 0.9 [ml/g] | N ₂ BET surface area [m ² /g] |
|---------|--------------|---|---|---|
| MX | ZeoliteX | 211 | 492 | 818 |
| MA | ZeoliteA | 3.14 | 302 | <1 |
| W6h | Na-Pc | 54.9 | 337 | 52.9 |
| Et24h | Sodalite | 69.7 | -* | 102 |
| Oc120h | Analcime | 6.64 | 6.1 | <1 |

*Not measured

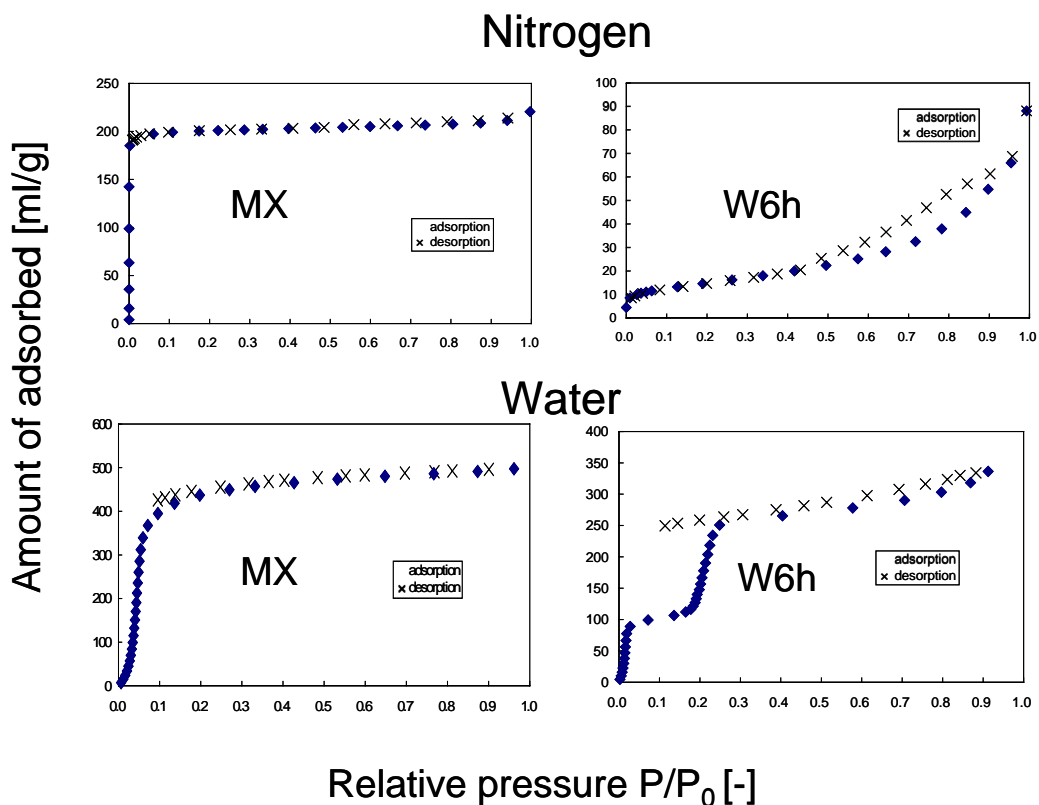


Figure 3 Nitrogen (77K) and water (298K) isotherms on MX and W6h

CONCLUSION

In this study, efforts were made to prepare low silica zeolites from sodium aluminate and sodium silicate, with/without the presence of alcohols, at 373 K under an atmospheric pressure. The zeolites synthesized at designated reaction times were characterized by X-ray diffraction (XRD), N₂ and H₂O vapor adsorption/desorption. It was found that Na-Pc was preferentially synthesized in solely water, while five different types of zeolites were identified during zeolite synthesis process in alcohols: ZeoliteA, ZeoliteX, Sodalite, Na-Pc and Analcime. In alcohols, except in methanol and propanol, Na-Pc and Sodalite were seemingly transformed to form Analcime. It was also found that Na-Pc possessed peculiar surface characteristics, which were recognized from a stepwise H₂O isotherm and hysteresis loop in N₂ isotherm.

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