Structural Change and Cobalt Fixation in the Hydrothermally Synthesized Zeolite Phases from a Si–Al–Co Hydrous Oxide

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A series of Co-zeolite samples were synthesized at 170–200 °C, controlling the reaction between a Si–Al–Co hydrous oxide and NaOH solution. With increase of the reaction time, and NaOH concentration, synthesized phase changed in the sequence of MOR, PHI, and ANA with Na. The results of chemical analysis and FT-IR spectra of each phases showed that NaOH concentration in the initial slurry and the architecture of zeolite affected Co fixation in the zeolite structure.

Recently, Co-containing high silica zeolite attracted attentions for its selective NO reduction activity. Therefore Co distribution in the zeolite structures has been studied.[1] In previous studies, it has been considered that in the structure of high silica zeolites, Co forms cationic complex with alkyl amine and anchors to negative charge sites of Al in the framework.[1–3] In the synthesis process of high silica zeolite, the added alkyl amines have been considered to be important to form precursors for zeolite-structures.[4] However, when the synthesized zeolite is used for catalysis, the organic template has to be removed from the cage of zeolite.[5] In the studies of template-free syntheses of zeolites, Itabashi et al. (1986) synthesized mordenite (MOR) in Na–Si–Al system from a mixture of amorphous silica and sodium aluminate solution. They recommended that the composition of the obtained MOR changed not only depending on the SiO_2/Al_2O_3 ratio (SAR) of the starting composition, but also depends on the concentration of sodium.[6,7] Recently, Machado et al.[8] synthesized MFI and MOR from an alumino silicate by template-free method. They described that first the MFI was crystallized and then was changed to MOR structure with either increase of the reaction time or the temperature.[8] From those studies, it seems that the composition and the phases of the products will be changed to aluminum-rich with increase of the reaction time and temperature of hydrothermal syntheses.

In this study, with the aim to examine the phase relationships and Co-incorporation in the zeolite matrix during the hydrothermal syntheses, a series of Co-containing zeolites (MOR, PHI, ANA) were synthesized from Si–Al–Co hydrous oxides by mainly controlling the reaction with the NaOH solution. The relationship between the Co fixation in the zeolite architecture and the conditions of syntheses was discussed.

The hydrous oxide was prepared by adding cataloid SI30 (Colloidal Silica, Catalysts & Chemicals IND. Co., LTD. $Na_2O < 0.38\%$) to $AlCl_3.6H_2O$ and $CoCl_2.6H_2O$ solution, and precipitated by NH_4OH. The resulted hydrous oxide was washed and mixed with a NaOH solution uniformly. Hydrothermal treatments of the slurries were carried out in the Teflon container without stirring. The phases of the synthesized samples were characterized by XRD, XPS, FT-IR, UV–vis, SEM-EDS, and TEM.

Table 1. Hydrothermal conditions and the products in the syntheses

Run No.	Compositions of the initial slurries			Hydrothermal treatment		Products identified by XRD
	Hydrous oxides (Si–Al–Co ratio)	conc. of Si/ mol/L	conc. of NaOH/ mol/L	Temp. /°C	Time /h	
1	1–0.15–0.05	2	1.25	200	48	MOR
2			1.40		48	MOR
3			1.50		24	MOR + PHI
4			2.00		4	PHI
5			2.00		24	ANA
6			5.0		12	ANA
7			1.40		116	ANA
8	1–0.15–0.05	2	1.50	170	48	MOR
9			1.50		54	MOR + PHI
10			2.00		24	PHI
11	1–0.0375–0.0125	3	2.00	200	24	MOR
12	1–0.025–0.025					MFI + MOR
13	1–0.025–0.075					MOR + Cristobalite

The hydrothermal condition for the syntheses and the resulted phases as determined by powder XRD patterns are listed in Table 1. Concentration of the slurry for syntheses of mordenite were relatively high and it needed much higher NaOH concentration in comparison to that reported in previous studies.[7,8] The color of the initial slurries and the synthesized zeolite samples were changed from pale pink to blue depending on the NaOH concentration and the reaction time. By SEM-EDS, it is observed that even without stirring, particles were well crystallized and the size and composition of each particle in a sample seemed to be almost uniform. A scheme of the phase relationships between the samples (Runs No. 1–7) is shown in Figure 1. Figure 1 shows that the structural change of solid phase in the sequence of mordenite (MOR), phillipsite (PHI), analcime (ANA) not only depends on the concentration of NaOH, but also on the reaction time. SAR of the obtained samples analyzed by SEM-EDX were 10–13 for MOR, 7–9 for PHI, 5–7 for ANA and gradually decreased from that of starting composition with the progress of the reaction between solid phases and NaOH. In Figure 2, under the condition of low NaOH concentration (a), and in the case of short time synthesis (b), the obtained samples had small polycrystalline particles, which suggests the crystallization in the solid phases as observed in the crystallization of clay minerals from glass.[9] With the increase of NaOH concentration, depending on the dissolution of the hydrous oxide, the secondary growth of more Al-rich phases took place with Na. The phase and SAR of the synthesized samples changed to Al-rich with reaction time, which means that low SAR phase were unstable and Na and Al uptake in the solid phase was gradually

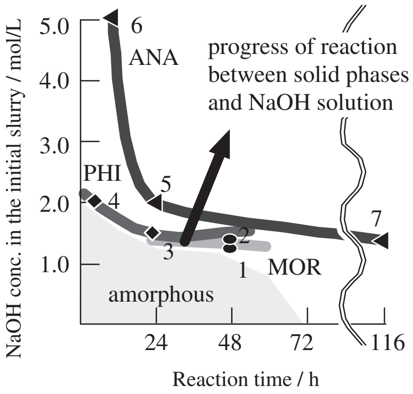

Figure 1. A scheme of the phase relationships with the variation of NaOH concentration and the time of the hydrothermal treatment of the hydrous oxide (Si–Al–Co = 1–0.15–0.05) at 200 °C. The numbers beside the circles are the run number listed in Table 1.

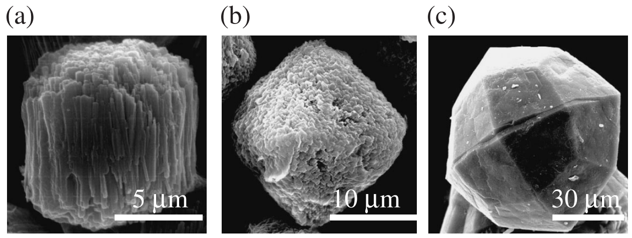

Figure 2. SEM photographs of the particles of synthesized Co-zeolite samples listed in Table 1. (a) MOR (No. 1), (b) PHI (No. 4), (c)ANA (No. 5).

prompted by the interaction with NaOH in the slurry. When the starting SAR of the hydrous oxides were increased (Run No. 11–13), the obtained phases were changed in the sequence of MFI and MOR as reported previously.[8] However, an increase of Co/Si ratio in the starting composition seemed not to promote the crystallization of zeolite (Run No. 13) and Co/Al ratio in the product was not increased.

In the sample from the same hydrous oxide (Runs No. 1–7), Co/Al ratio was 0.11 for Cs-exchanged MOR, 0.21 for Ca-exchanged PHI, and 0.30 for Ag-exchanged ANA. Compared to the Co contents before the cation-exchange treatments, only 60 and 30% of cobalt remained in the PHI and MOR, respectively. After stirring with 0.1 N HCl twice (each for 24 h), Co-content in MOR was almost dissolved out. In ANA, which was synthesized under higher pH condition, Co-content was almost unchanged even after 4 times treatments with HCl. More than 80% of Co was remained. O(1s) binding energy of XP spectra and STEM observation reveals that Co contents were still inside the structure of the HCl-washed ANA without precipitations of Co oxide. Thus, it seems that cobalt was fixed in the structure in the course of the phase change.

UV–vis spectra of as-synthesized (AS-) zeolite samples suggest that Co-species are dominantly inside the 8-ring cavities (Figure 3).[2] Intensity ratio of the bands at 15300, and 16400 to 18500 cm^{-1} increase with the progress of reaction and the phase change from MOR, PHI to ANA. Because the peaks of Co-oxides were 15200 cm^{-1} for Co_3O_4 and near 17900 cm^{-1} for CoO, the increase in intensity ratio of the band at 15300 to 18500 cm^{-1} seems to suggest the oxidation of Co^{2+} to Co^{3+}.

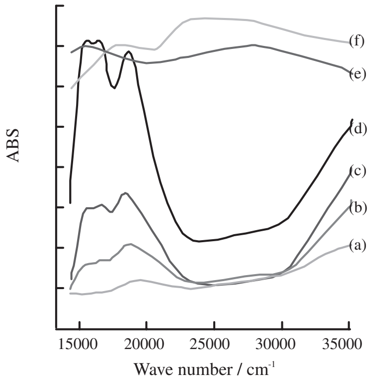

Figure 3. UV–vis spectra of Co zeolite phases: Co-exchanged H-MOR (640HOA) from TOSOH co.(a), as-synthesized (AS-) MOR of No. 1 (b), AS-PHI of No. 4 (c), AS-ANA of No. 5 (d), and Co oxides: Co_3O_4 (e), CoO (f).

In FT-IR spectra, the absorption band at 969–914 cm^{-1} attributed to Co perturbation[10] was observed after heating the sample at 500 °C in AS-MOR of No. 1, however, in the case of AS-MOR synthesized under relatively high NaOH concentration, the absorption could be obtained before calcination. El-Malki et al. reported that in the case of Co^{2+}-exchanged MFI, Co^{2+} cation exhibits blue color after dehydration and make large size complexes with ammonia and oxygen; part of them were oxidized to Co^{3+} releasing the ammonia ligands, increasing the interaction with the zeolite framework.[3] Z. Gabelica and S. Valange described that the structural state of metal contents in the metallosilicates depends on the formation of $(Si(Al)–O–M)^{n+}$ type oligomers releasing the amine content from the amino metal complex ion in basic media during the syntheses,[1] which was also observed in the early stage of synthesis of Fe-smectite.[11] The same type of polymerization and oxidation of Co^{2+} should occurr also in the step of hydrothermal treatment of the slurry of Si–Al–Co hydrous oxide. Thus, it can be considered that Co-amino complex anchored to Al site of gel structure. It should be caged in the zeolite structure during the hydrothermal treatment, in which the pore size of zeolite structure became smaller with the phase change. The caged Co-complex was gradually fixed to the framework leaving the ammonia with oxidation prompted by NaOH.

From above all, it was revealed that the rate of the interaction between hydrous oxide and NaOH solution in the synthesis plays the important role in the formation of different zeolite architecture and Co-fixation.

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