

# Synthesis of Co-Silicalite-1 from a Layered Silicate

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**Abstract**—Co-Silicalite-1 ( $\text{Co}_{2.3}\text{Si}_{9.7}\text{O}_{192}$ ) was synthesized from  $\text{Co}^{2+}$  ion exchanged magadiite. The characteristics of Co-Silicalite-1 were investigated by using X-ray powder diffraction, IR spectroscopy, surface area measurement,  $\text{NH}_3$  temperature programmed desorption, and electron microprobe analysis. The measurements indicate that  $\text{Co}^{2+}$  ions replace  $\text{Si}^{4+}$  ions in the Silicalite-1 framework. The orthorhombic framework structure of calcined Co-Silicalite-1 has been determined.

**Key words:** Silicalite-1, Cobalt Substitution, Layered Silicate, Magadiite, Acidity

## INTRODUCTION

The synthesis of transition metal-incorporated molecular sieves is a fascinating area in molecular sieve science since metal incorporation leads to many interesting catalytic properties. In particular, transition metal incorporated ZSM-5 molecular sieves have attracted much attention due to their specific catalytic activity and selectivity [Ko and Ahn, 1998]. For example, cobalt and manganese incorporated ZSM-5 molecular sieves have been proved to be effective catalysts for the selective catalytic reduction of  $\text{NO}_x$  by methane with excess oxygen [Cowan et al., 1995]. Cobalt incorporation into the molecular sieve has been reported in the literature. However, cobalt substitution with a uniform and high content into the tetrahedral framework site is still a problem. Conventional synthetic methods using ethoxide or chloride metal sources have led to the successful substitution of Ga, Ti and B into zeolite frameworks. However, these methods are not generally applicable to the syntheses of most transition metal-substituted frameworks because most of transition metals are easily precipitated as insoluble hydroxides at high pH.

In order to avoid a hydroxide precipitate, synthetic routes at lower pH are required. Recently, Round et al. [1997] synthesized cobalt-substituted Silicalite-1 in an aqueous, slightly acidic, fluoride medium using tetrahalometallate compounds as sources of cobalt. Another report of the synthesis of cobalt-substituted ZSM-5 included descriptions of its formation only in a very narrow range of OH/SiO<sub>2</sub> ratio [Inui et al., 1996].

Layered silicates such as kanemite ( $\text{NaHSi}_2\text{O}_5 \cdot \text{H}_2\text{O}$ ), magadiite ( $\text{Na}_2\text{Si}_{14}\text{O}_{29} \cdot 11\text{H}_2\text{O}$ ), makatite ( $\text{Na}_2\text{Si}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$ ), and ilerite ( $\text{Na}_2\text{Si}_8\text{O}_{17} \cdot x\text{H}_2\text{O}$ ) were proposed as good precursors to synthesize framework materials. Yanagisawa et al. [1988] reported the synthesis of mesoporous silicas from a layered silicate, kanemite. Inagaki et al. [1994] have proposed a folded sheets formation mechanism of highly ordered mesoporous materials, FSM-16 (Folded Sheets Mesoporous materials), from kanemite. Pál-Borbély et al. [1997, 1998]

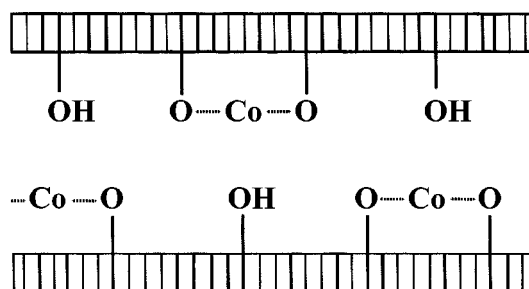


Fig. 1. Proposed structure model of  $\text{Co}^{+2}$  ion exchanged magadiite.

have synthesized MFI, MEL and FER type zeolites by recrystallization of magadiite.

Proton or transition metals can easily exchange for sodium ions that reside between the layers of layered silicate [Hatsushika et al., 1996]. The proton-exchanged silicates (silicic acids) have reactive silanol groups on their interlayer surface that orient in a crystallographically regular manner on the interlayer surface. They are sufficiently acidic to allow proton transfer to an amine group. These "layered silicic acids," which also contain transition metals as shown in Fig. 1, are expected to be good precursors for the synthesis of metallosilicates. If such is the case, a sole source should provide all the components that are required for the synthesis of metallosilicates. Recrystallization of such a precursor may not require the transport process mediated in the conventional synthesis by the liquid phase.

We report here the synthesis and characterization of cobalt isomorphously substituted Silicalite-1 prepared from  $\text{Co}^{2+}$  ion exchanged magadiite. By stabilizing  $\text{Co}^{2+}$  ions between the layers of silicates, it is possible to prepare a framework material where the cobalt ions are present in the tetrahedral framework sites.

## EXPERIMENTAL

### 1. Starting Materials

#### 1-1. Na-magadiite

Na-magadiite was prepared by the reaction of NaOH with SiO<sub>2</sub> under hydrothermal conditions. NaOH (97%, 4.8 g) was dissolved

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in 105 ml of deionized water and 45 g of colloidal silica (Ludox HS-40) was added to the solution dropwise over 30 min. The gel, of composition  $\text{Na}_2\text{O} : 5\text{SiO}_2 : 122\text{H}_2\text{O}$ , was stirred at room temperature for 1 h, transferred to a teflon-lined autoclave, and heated under autogenous pressure at 160 °C for 24 h.

#### 1-2. H-magadiite

H-magadiite was prepared by acid titration of Na-magadiite. A suspension of Na-magadiite in water was stirred for 1 h. The suspension was then titrated with 0.1 N HCl to a final pH of 2.0 and allowed to remain for an additional 4 h with stirring at this pH. The H-magadiite was recovered by filtering, washing with deionized water, and drying at 40 °C. The chemical composition was  $\text{Na}_{0.1}\text{H}_{1.9}\text{Si}_{14}\text{O}_{29}$  as determined by inductively coupled plasma (ICP) spectrometer and atomic absorption spectrophotometer.

#### 1-3. $\text{Co}^{2+}$ Ion-exchanged Magadiite

Ion exchange of H-magadiite by cobalt chloride was performed by using a normal batch method at 80 °C. The ion exchange reaction proceeded rapidly. The final chemical composition was  $\text{Co}_{0.2}\text{H}_{1.6}\text{Si}_{14}\text{O}_{29}$  as determined by electron microprobe analysis.

#### 2. Recrystallization of Ion-exchanged Magadiites

0.1 g of  $\text{Co}^{2+}$  ion-exchanged magadiite was suspended in 5 ml of 0.1 M tetrapropylammonium hydroxide solution. The molar ratio of the mixture was fixed to  $1(\text{Co}_{0.2}\text{H}_{1.6}\text{Si}_{14}\text{O}_{29}) : 0.29\text{TPA} : 163\text{H}_2\text{O}$ . The reaction mixture was heated under autogenous pressure in a teflon-lined autoclave for 72 h at 160 °C. The product was washed with water and ethanol, and then dried at 40 °C. X-ray powder diffraction data confirmed that the highly crystalline MFI structure had been synthesized. Furthermore, scanning electron microscopy analysis showed very homogeneous elongated prismatic crystals, 20–30  $\mu\text{m}$  in length.

For comparison, another hydrothermal treatment has been tried by using a mixture of tetrapropylammonium hydroxide,  $\text{CoCl}_2$  and H-magadiite as a silica source instead of  $\text{Co}^{2+}$  ion exchanged magadiite to synthesize Co-Silicalite-1. However, the product obtained after hydrothermal treatment for 72 h at 160 °C was found to remain amorphous.

#### 3. Characterization

X-ray diffraction patterns were obtained by using a Rigaku D/Max-IIA diffractometer with Cu K $\alpha$  radiation. IR spectra were recorded at a frequency range between 400–1400  $\text{cm}^{-1}$  on a Perkin Elmer 1600 M-80 spectrometer. Nitrogen BET surface areas were determined by using a Micromeritics ASAP 2000 analyzer. All samples were outgassed at 200 °C under vacuum for 2 h. The  $\text{NH}_3$  TPD was obtained on a Micromeritics TPD/TPR 2900 analyzer. Electron-probe microanalysis was carried out on samples by using Philips, CM 30 scanning transmission electron microscopy. Chemical analyses were performed by a Jarrell-Ash Poliscan 61E inductively coupled plasma (ICP) spectrometer and a Perkin-Elmer 5000 atomic absorption spectrophotometer.

### RESULTS AND DISCUSSION

#### 1. Synthesis

The synthesis of Co-Silicalite-1 from cobalt ion exchanged magadiite is easily achieved in the conventional synthetic range of ZSM-5 or Silicalite-1, although a prerequisite condition for the synthesis of highly pure Co-Silicalite-1 is to avoid cobalt hydroxide precipi-

tate in the basic media. In the Co-Magadiite-TPAOH- $\text{H}_2\text{O}$  system, Co-Silicalite-1 is crystallized within 48 h in the temperature range of 160–200 °C. However, when cobalt ions are not sufficiently exchanged into magadiite layers or they change into hydroxide forms during ion exchange, Co-Silicalite-1 is not synthesized.

To understand further whether it is necessary to use cobalt ion-exchanged magadiite as a silica source to synthesize Co-Silicalite-1, another hydrothermal treatment has been tried by using a mixture of tetrapropylammonium hydroxide,  $\text{CoCl}_2$  and H-magadiite. The products obtained after hydrothermal treatment using the slurry of tetrapropylammonium hydroxide,  $\text{CoCl}_2$  and H-magadiite were amorphous to X-ray diffraction. These results imply that only when cobalt ions are protected from basic media by being present between the Layers, they can be incorporated into the framework during the hydrothermal treatment.

#### 2. X-ray Diffraction

Fig. 2 shows the X-ray powder diffraction patterns of calcined Silicalite-1 and Co-Silicalite-1. The X-ray powder diffraction pattern of Co-Silicalite-1 corresponds to that of MFI framework and does not reveal the presence of extra phases related to cobalt oxide species as shown in Fig. 2(b). However, Co-Silicalite-1 is different from Silicalite-1 in the lattice symmetry. All the peaks from the X-ray powder diffraction patterns of Co-Silicalite-1 could be indexed on the basis of the orthorhombic lattice symmetry. Two singlet peaks at two theta 24.38° and 29.26° are observed for Co-Silicalite-1 instead of doublets, which are observed for Silicalite-1. This is ascribed to a change of symmetry from monoclinic to orthorhombic by incorporation of metal into the framework of Silicalite-1. Morphology, symmetry and cell parameter of zeolites are known to depend on the amount of defects (generated by subtracting some adjacent Si atoms) in different synthesis methods. Also, the orthorhombic/monoclinic phase transition of MFI framework has been frequently reported in the literature, which has been caused by the temperature variation [Mentzen and Sacerdote-Peronnet, 1993], sorption of mol-

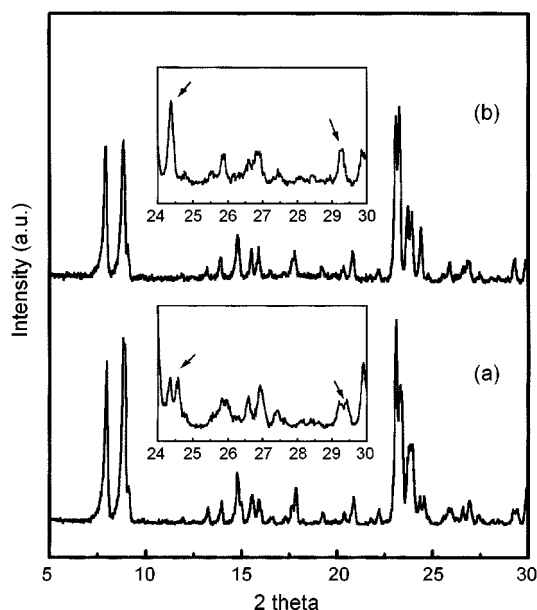


Fig. 2. X-ray powder diffraction patterns of calcined (a) Silicalite-1 and (b) Co-Silicalite-1.

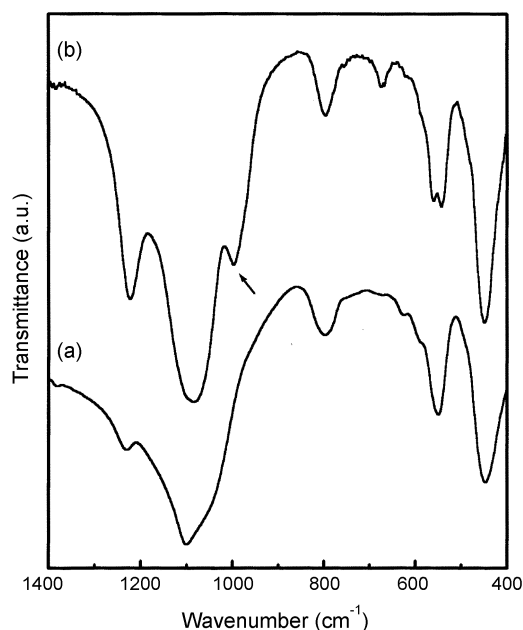


Fig. 3. Infrared spectra of (a) Silicalite-1 and (b) Co-Silicalite-1.

ecules [Mentzen, 1992], the effect of different synthesis conditions [Marra et al., 1994; Kim et al., 2000] or by the isomorphous substitution of other elements [Taramasso et al., 1983; Chapus et al., 1994]. Therefore, the observed changes between Co-Silicalite-1 and Silicalite-1 indicate the incorporation of cobalt into the Silicalite-1 framework. A similar phenomenon has been observed for TS-1 in comparison to Silicalite-1 [Taramasso et al., 1983].

### 3. IR Spectroscopy

The substitution of cobalt into Silicalite-1 framework is also confirmed by IR spectrum. Recently, Round et al. [1997] synthesized Co-Silicalite-1 in fluoride medium using  $(\text{NPr}_4)_2(\text{CoBr}_4)$  and reported that the incorporation of cobalt into Silicalite-1 framework resulted in additional peaks around  $1000 \text{ cm}^{-1}$  in the IR spectrum of Co-Silicalite-1. As shown in Fig. 3(b), the IR spectrum of Co-Silicalite-1 synthesized from cobalt ion-exchanged magadiite also exhibits an additional band at  $995 \text{ cm}^{-1}$ , which is not present in the IR spectrum of pure Silicalite-1. This is due to the substitution of cobalt into the Silicalite-1 framework. The band created by metal substitution in the Silicalite-1 is known as the stretching vibration mode of  $\text{Si-O}^-$  perturbed by heavy metal in a neighboring position [Khouw and Davis, 1995].

### 4. Acidity and BET Surface Area Measurements

The acidic properties of Co-Silicalite-1 were studied to examine the intrinsic acidity caused by the incorporation of Co instead of Si into the framework. The strength and amount of the acidic sites were investigated by temperature-programmed desorption of  $\text{NH}_3$ . As shown in Fig. 4(b), the  $\text{NH}_3$  TPD profile of Co-Silicalite-1 exhibits two peaks near  $180^\circ\text{C}$  and  $350^\circ\text{C}$ , which correspond to weak acid sites and relatively strong acid sites, respectively [Inui et al., 1996]. The strong acid sites are attributed to the formation of a new Si-O-Co linkage, which gives rise to a net negative framework charge. However, weak intensity in the TPD profile of ammonia for Co-Silicalite-1 implies that the number of strong acid sites would be small.

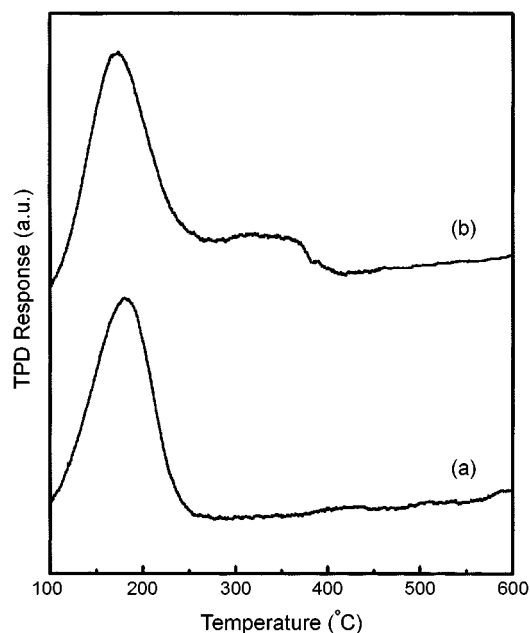


Fig. 4. TPD profiles of ammonia for (a) Silicalite-1 and (b) Co-Silicalite-1.

The BET surface areas for Co-Silicalite-1 and Silicalite-1 are  $439$  and  $412 \text{ m}^2/\text{g}$ , respectively. The large surface area indicates that Co-Silicalite-1 was synthesized in the pure phase.

### 5. Chemical Analyses

The chemical composition of as-synthesized Co-Silicalite-1 was determined to be  $\text{Co}_{2.3}\text{Si}_{93.7}\text{O}_{192}$  by electron microprobe analysis. The Si/Co ratio in the Co-Silicalite-1 ( $\text{Co}_{2.3}\text{Si}_{93.7}\text{O}_{192}$ ) synthesized by using our method in this work is similar to that ( $\text{Co}_{2.9}\text{Si}_{92.9}\text{Zn}_{0.1}\text{O}_{192}$ ) reported in the literature [Round et al., 1997].

The Si/Co ratio in Co-Silicalite-1 is lower than that of the corresponding layered silicates precursor ( $\text{Co}_{0.2}\text{H}_{1.6}\text{Si}_{14}\text{O}_{29}$ ), indicating that most of cobalt species in the precursor participate in the crystallization of Co-Silicalite-1.

## CONCLUSION

We have synthesized Co-Silicalite-1 using cobalt ion-exchanged magadiite precursor as a metallosilicate source. The overall results from X-ray powder diffraction, IR spectroscopy and  $\text{NH}_3$  TPD show that cobalt ions are substituted in the tetrahedral framework sites. The substitution of cobalt in the tetrahedral framework results in the change of lattice symmetry of Silicalite-1 and generation of relatively strong acid sites. Unlike the calcined Silicalite-1 that has monoclinic symmetry, the calcined Co-Silicalite-1 has orthorhombic symmetry. The synthetic procedure using metal exchanged layered silicates as precursors will lead to the syntheses of new metallosilicate framework materials.

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