

NOTE

## SYNTHESIS AND STRUCTURE OF COBALT LAYER SILICATE

Jong Rack SOHN and Jin Ick JEON

Department of Industrial Chemistry, College of Engineering,

Kyungpook National University, 702-701 Taegu, Korea

(Received 19 May 1988 • accepted 19 July 1988)

**Abstract**—Two cobalt layer silicates were synthesized by hydrothermal treatment at 275°C and 54 atm from corresponding stoichiometric coprecipitate of cobalt hydroxide and silica. From IR absorption spectra and X-ray diffraction patterns, one sample was proved to be cobalt montmorillonite [ $\text{Co}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2$ ], while the structure of the other was cobalt antigorite [ $\text{Co}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ] of one silica layer combined with an octahedral layer of the type  $\text{Co}_3^{2+}(\text{OH})_6$ .

### INTRODUCTION

Silica in various forms is often used as carrier for catalysts containing a metal as active component. A widely used industrial hydrogenation catalyst is, for instance, nickel on silica. The dependence of the activity of supported metal catalysts on the nature of the carrier has initiated a large number of studies devoted to a better understanding of the way the carrier may modify the properties of the active phase [1-4]. Most often, the influence of the carrier has been attributed to its interaction with the active phase. The occurrence of a chemical interaction between silica supports and nickel compounds was first postulated by de Lange and Visser [5]. Subsequent investigations have supported arguments for the formation of basic hydrosilicates [6-9]. The ease of reduction of the oxide to nickel metal is greatly influenced by the support and, in all cases, supported nickel oxide is more difficult to reduce than the pure oxide.

On the other hand, it was also reported that supported cobalt catalysts are more difficult to reduce than unsupported cobalt oxide powder [10]. However, little is known about the formation of cobalt hydrosilicates between cobalt oxide and silica. In this paper, we deal with the syntheses of cobalt hydrosilicates and their structures are studied by means of X-ray diffraction and infrared absorption.

### EXPERIMENTAL

The coprecipitate of cobalt hydroxide-silica was prepared by adding aqueous ammonia slowly into a

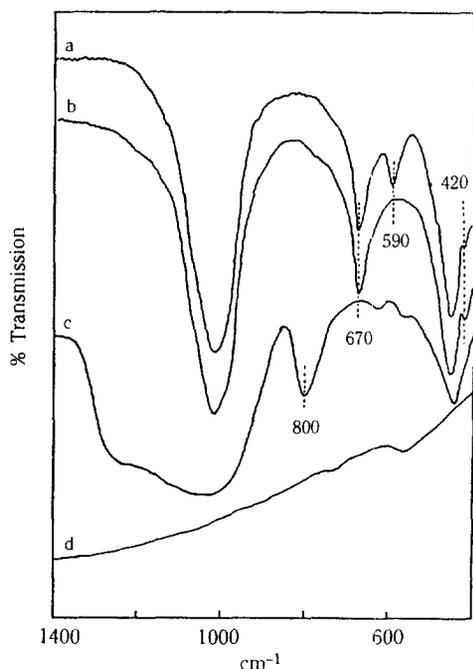
mixed aqueous solution of sodium silicate, cobalt nitrate, and sulfuric acid at 60°C with stirring until the pH of mother liquid reached about 7.5, and then allowing the precipitate to stand for 3 hr at room temperature. Two kinds of precipitates, of which Co/Si ratios are 3/4 and 3/2, respectively, were prepared. The precipitate thus obtained was washed thoroughly with distilled water and was dried at 120°C. The dried precipitate was again washed with successive portions of a 5% hot ammonium nitrate solution and then with hot distilled water to remove the strongly adsorbed Na. Thus, it was subjected to hydrothermal treatment at 275°C and 54 atm for 100 hr.

The infrared spectra were recorded at room temperature on a JASCO IR-2 spectrometer. Usually 2 mg of sample was mixed with 150 mg of KBr and pressed into a disk (600 kg/cm<sup>2</sup>). X-ray diffractograms were taken by a Jeol Model JDX-88 X-ray diffractometer using copper target and nickel filter at 30 kV and 800 cps.

### RESULTS AND DISCUSSION

The structure of cobalt layer silicate prepared by hydrothermal treatment was examined by infrared absorption. The IR spectra of two samples are given in Fig. 1. When they are compared with IR spectra of cobalt oxide and silica, it is clear that new bands are formed at 670, 590, and 420 cm<sup>-1</sup>, indicating the formation of new phase between cobalt oxide and silica. As shown in Fig. 1, however, the spectrum of sample I (Co/Si ratio = 3/4) is different from that of sample II (Co/Si ratio = 3/2). Namely, sample I shows two absorption bands at 670 and 590 cm<sup>-1</sup> while sample II shows only one band at 670 cm<sup>-1</sup>, suggesting the pre-

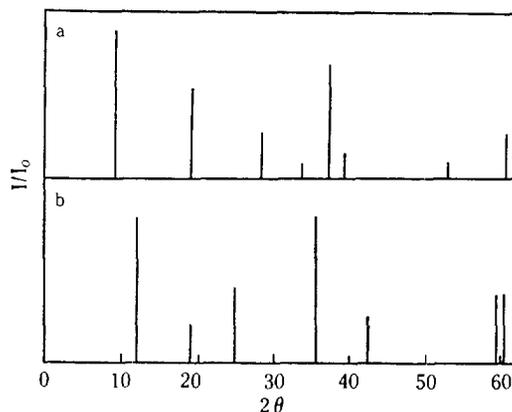
\* To whom all correspondence should be addressed.



**Fig. 1. Infrared spectra of sample I(a), sample II(b), silica gel(c), and cobalt oxide(d).**

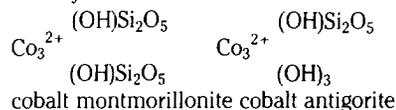
sence of two types of cobalt layer silicates. Both 670 and 590  $\text{cm}^{-1}$  bands are assigned to Si-O stretching affected by  $\text{Co}^{2+}$  [11]. Really, for nickel layer silicate, two types of nickel montmorillonite  $[\text{Ni}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2]$  and nickel antigorite  $[\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4]$  are known [11-12]. Both 710 and 665  $\text{cm}^{-1}$  bands were observed with the former, while only the 665  $\text{cm}^{-1}$  band was observed with the latter. The IR spectra of hydrothermally synthesized cobalt layer silicates are similar to those of nickel layer silicate reported previously [11]. For the presence, it seems likely that two types of cobalt layer silicates are cobalt montmorillonite and cobalt antigorite as observed in nickel layer silicate. In the following section, X-ray analyses will support this fact more clearly.

The structure of cobalt silicate was checked by X-ray diffraction. Fig. 2 represents X-ray diffraction patterns of two types of cobalt layer silicates synthesized in this work. As shown in this figure, X-ray diffraction patterns of two samples are different from each other as the case of IR spectra. The pattern of sample I was very similar to that of nickel montmorillonite  $[\text{Ni}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2]$ , while the pattern of sample II was very similar to that of nickel antigorite  $[\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4]$  reported by Martin et al. [13]. In the structure of montmorillonite one octahedral layer of the type  $\text{Ni}_3^{2+}(\text{OH})_6$  is sandwiched between two silica layers of the type  $(\text{Si}_2\text{O}_5)^{2-}$ , while in antigorite, one silica layer is combin-



**Fig. 2. X-ray diffraction patterns of sample I(a) and sample II(b).**

ed with an octahedral layer. Therefore, in view of the above IR results and X-ray analyses, it is concluded that sample I has the structure of cobalt montmorillonite while sample II has that of cobalt antigorite, in conformity with the formulas:



## REFERENCES

- Houalla, M. and Delmon, B.: *J. Phys. Chem.*, **84**, 2194 (1980).
- Houalla, M., Delacnny, F., and Delmon, B.: *J.C.S. Faraday I*, **76**, 1766 (1980).
- Holm, V.C.F. and Clark, A.: *J. Catal.*, **11**, 305 (1986).
- Wu, M. and Hercules, D.M.: *J. Phys. Chem.*, **83**, 2003 (1979).
- de Lange, J.J. and Visser, G.H.: *Ingenieur*, **58**, 24 (1946).
- Longuet, J.: *Compt. Rend.*, **225**, 869 (1947).
- Schuit, G.C.A. and van Reijen, L.L.: *Adv. Catal.*, **10**, 242 (1958).
- Francois-Rosetti, J. and Imelik, B.: *Bull. Soc. Chim.*, 1115 (1957).
- Jacono, M.L., Schiavello, M., and Climino, A.: *J. Phys. Chem.*, **75**, 1044 (1971).
- Choi, J.G., Rhee, H.K., and Moon, S.H.: *Korean J. Chem. Eng.*, **1**, 159 (1984).
- Sohn, J.R. and Ozaki, A.: *J. Catal.*, **59**, 303 (1979).
- van Eijk van Voorthuijsen, J.J.B. and Franzen, P.: *Rec. Trav. Chim. Pays-Bas Belg.*, **70**, 793 (1951).
- Martin, G.A., Imelik, B., and Prettre, M.: *C.R. Acad. Sci. Paris Ser. C*, **264**, 1536 (1967).