August, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 60, 2881—2885 (1987)* 2881

Control of the Impregnation Profile of Co in an Al_2O_3 Sphere

Masashi Otsuka, Takeshi Fujiyama, Yoshikazu Tsukamoto,
Hideyasu Tsuiki, and Akifumi Ueno*
Department of Materials Science, Toyohashi University of Technology, Tempakucho, Toyohashi, Aichi 440

(Received February 16, 1987)

A radial distribution of cobalt metal particles in an alumina sphere was controlled by impregnation of the spheres with a solution composed of cobalt nitrate dissolved in ethylene glycol, ethyl silicate, and a small amount of nitric acid. The radial position of cobalt narrow band in the sphere was varied with the impregnation time and the cobalt loading was controlled by the concentration of cobalt nitrate in the impregnation solution. It was also found that porous SiO_2 film resulted from the gelling of ethyl silicate covered whole external surface of the sphere.

From the viewpoints of catalyst durability and poison, a control of the impregnation profile of an active component in a support sphere has been desired for catalysts of practical use; especially for steam reforming and automotive catalysts.[1,2] Four kinds of profiles are well-known, designated as uniform, egg shell, egg white, and egg yolk,[3] respectively. The uniform and egg shell types of catalysts are considered to be applied for reactions whose rate determining steps are in the reactions between surface species or in the diffusions of reactant molecules.[4] These profiles are easily achieved by control of the impregnation time[5] or by alteration of the starting materials of the catalyst constituents.[6] While the egg white and egg yolk types of catalysts are often employed to minimize the catalysts poison or the loss of active components during operations.[4] The preparation of catalysts with these profiles requires proper additions to the impregnating solutions. As additives to control the impregnation profiles, citric acid,[7] oxalic acid,[8] urea,[9] and nitric acid[10] have often been employed. These additives are volatile and decomposed when the catalysts are calcined at high temperature.

Besides the technical developments, theoretical approaches to the control of impregnation profiles have been studied by Vincent and Merril[11] with an assumption of one dimensional diffusion of metal ions in micropores of a catalyst support. Komiyama et al.[12] developed the assumption to three-dimensional diffusion of metal ions and showed that this model was consistent with an actual impregnation profile of Ni in an alumina sphere. Despite these advanced techniques and theories, impregnation profiles are not always reproducible, probably because of the heterogeneity of solid surfaces and the lack of knowledge about micropore structure.[13]

In conventional impregnation, free metal ions are formed in the impregnating solution and are ready to penetrate in micropores of support spheres when the spheres are immersed. The size of free metal ions is generally considered to be smaller than those of the micropores in the support spheres. What will happen in the impregnation profile and the metal loading, if macromolecules, larger than the micropores in size, containing metal ions are in the impregnating solution? The present work was done to answer this question using the impregnating solution composed of cobalt nitrate dissolved in ethylene glycol and ethyl silicate. In our earlier paper,[14] the solution consisting of a metal nitrate dissolved in ethylene glycol and ethyl silicate was proved to form macromolecules containing $(\text{-M-O-Si-})_n$ structures, where M represents the metal ion.

Experimental

Impregnation Procedure. $Co(NO_3)_2 \cdot 6H_2O$ (8.9 g) was dissolved in 153 ml of ethylene glycol (EG) at 80 °C and then pored into 30 ml of ethyl silicate at the same temperature with 3 ml of nitric acid. The solution (pH=1) was transparent and colored pale violet. Alumina spheres (5 g) with 3 mm of diameter and 298 m^2g^{-1} of BET surface area were immersed with the solution at room temperature. The impregnation time was varied from 1 min to 30 h. After the impregnation, the spheres were dried at 110 °C in an oven for

Table 1. Procedure for the Preparation of Catalyst with the Controlled Impregnation Profile of Cobalt

$Co(NO_3)_2 \cdot 6H_2O$
EG →
$Si(OC_2H_5)_4$ →
HNO_3 →
↓
Stirring at R.T. for 2 h
↓
Immersing Al_2O_3 beads (3 mmϕ)
↓
Gelling in steam
↓
Dry at 110 °C for 24 h
↓
Calcination in air at 300 °C for 4 h
↓
Reduction in H_2 at 900 °C for 4 h
↓
$Co/SiO_2/Al_2O_3$

24 h and then calcined at 300 °C for 4 h in air, followed by reduction at 900 °C in flowing hydrogen. The impregnation conditions were settled above unless specified. The amount of $Co(NO_3)_2 \cdot 6H_2O$ in EG could be varied, if necessary.

The impregnation procedure employed in this work is summarized in Table 1.

EPMA Measurement. The shperes thus impregnated were mounted in a polyester support and the support was polished with fine alumina powder until the cross section of a sphere appeared. The alumina powder adhered to the support was removed by ultrasonication. In order to avoid charge-up phenomenon, Pt was evaporated over the support surface. The radial distributions of Co and Si in the sphere was measured by electron probed X-ray microanalyser (EPMA, Hitachi model X-650), operated at an accelerating voltage of 20 kV with an energy dispersion detector.

Measurement of Co Loading. The impregnated spheres calcined at 300 °C were ground and then mixed with the appropriate amount of $Na_2B_4O_7$ to be fired at 1000 °C in platinum crucible. In a B_2O_3 disk thus prepared, the catalyst constituents were well dispersed and the disk was subjected to X-ray fluorescence spectrometer (Rigaku Denki, Model 3080), operated at 50 kV with a filament current of 50 mA to generate Rh *Kα* radiation.

Pore Size Measurements. The micropore size distributions of bare alumina spheres and the impregnated spheres reduced at 900 °C were measured with a porosimeter (Carlo Erva, Sorptmatic 1800) using nitrogen as a sorption gas at the liquid nitrogen temperature.

Results

Radial Distribution of Cobalt. Typical photographs of the cross sections of reduced catalysts and the associated EPMA profiles are given in Fig. 1. The position of the narrow cobalt band in the catalyst sphere was proved to shift into the center of sphere with increasing the impregnation time, as shown in Fig. 2. The bars given in Fig. 2 represent the width of the Co metal bands in the impregnated catalysts. The loading of cobalt in the reduced catalyst was found not

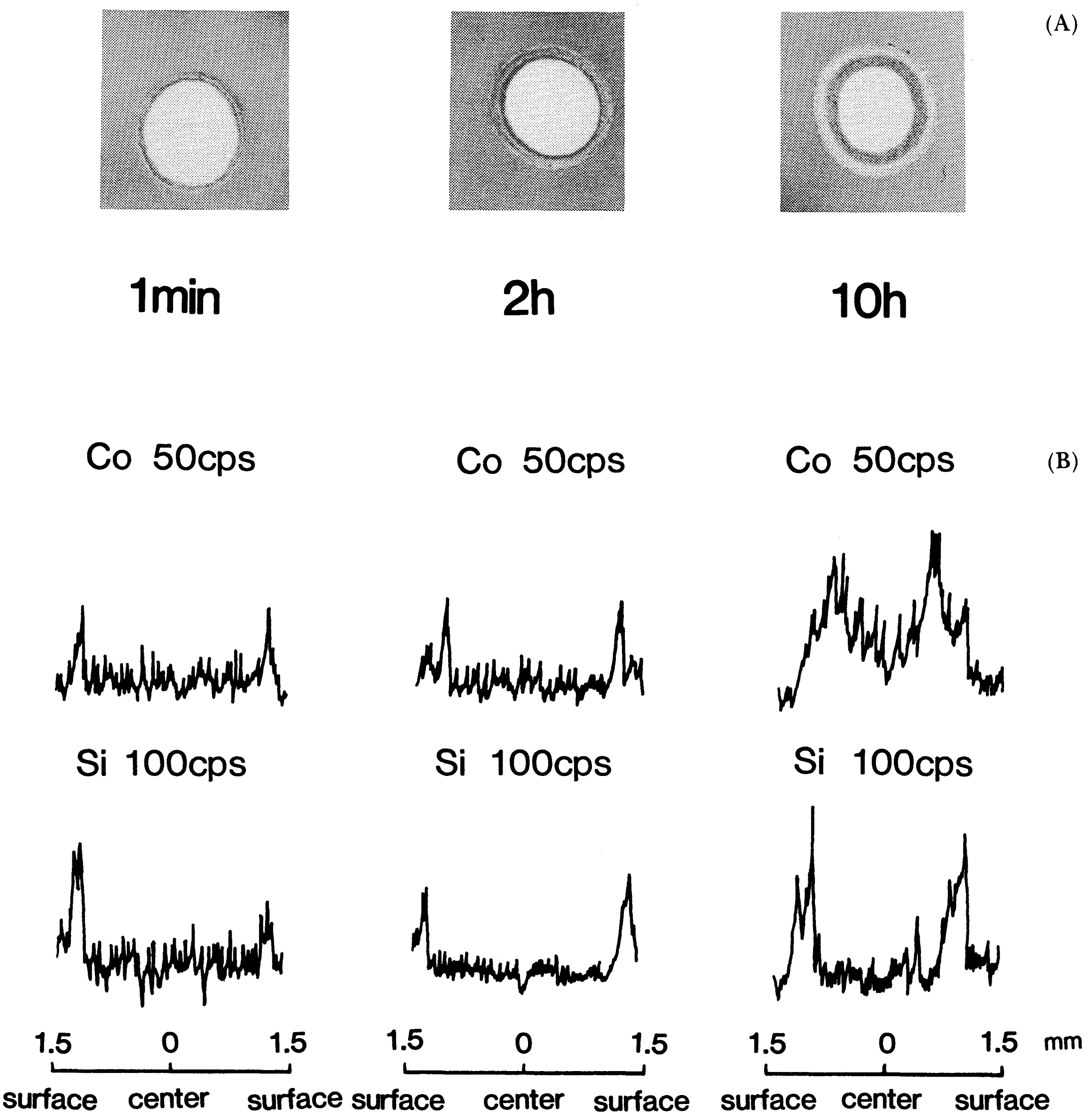


Fig. 1. Typical photographs of the cross sections of impregnated catalysts (A) and the associated EPMA profiles (B) with various impregnation times.

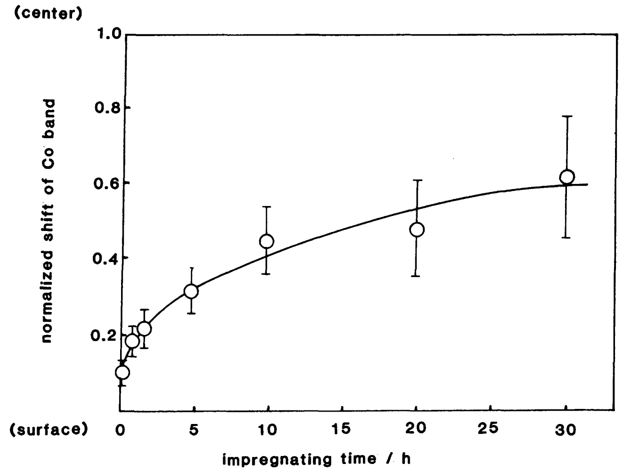


Fig. 2. Shift of the narrow cobalt band in the alumina sphere with the impregnation time; the distance from the center of the sphere was normalized in this Figure.

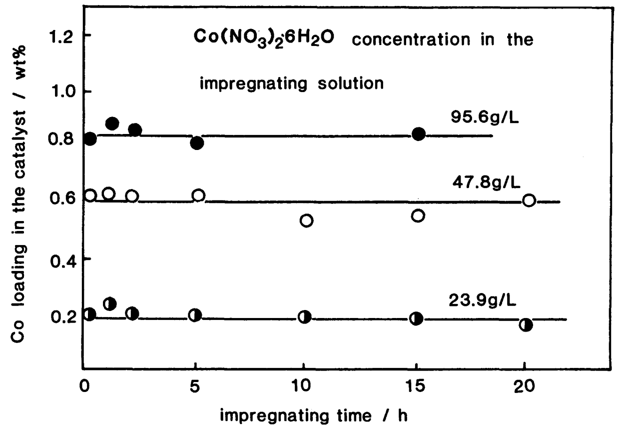


Fig. 3. Change in Co loading with the impregnation time; the concentrations of cobalt nitrate in the impregnation solutions were 23.9, 47.8, and 95.6 g L^{-1}, respectively.

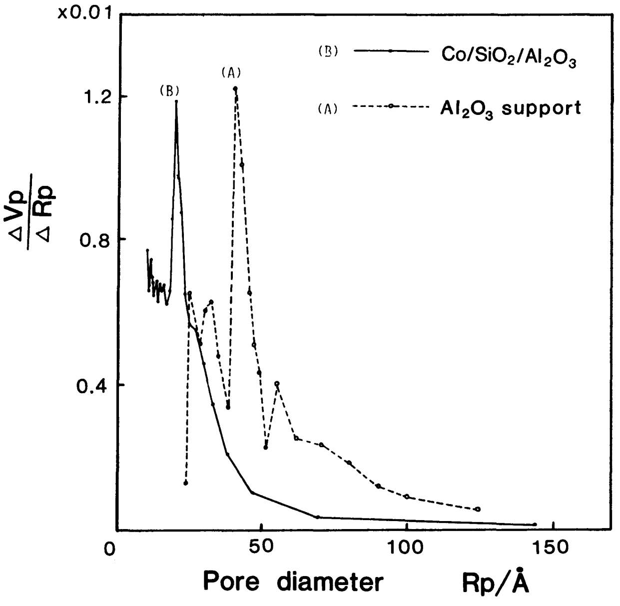


Fig. 4. Pore size distributions of the alumina sphere (A) and the impregnated catalyst (B).

to depend upon the impregnation time but to depend upon the concentration of cobalt nitrate in the impregnating solution (see Fig. 3).

Distribution of Si. On the contrary, Si was observed on the external surface of spheres, forming thin SiO_2 film, revealed by EPMA profiles shown in Fig. 1. The apparent thickness of this SiO_2 film was estimated less than 50 μm from an EPMA result shown in Fig. 4.

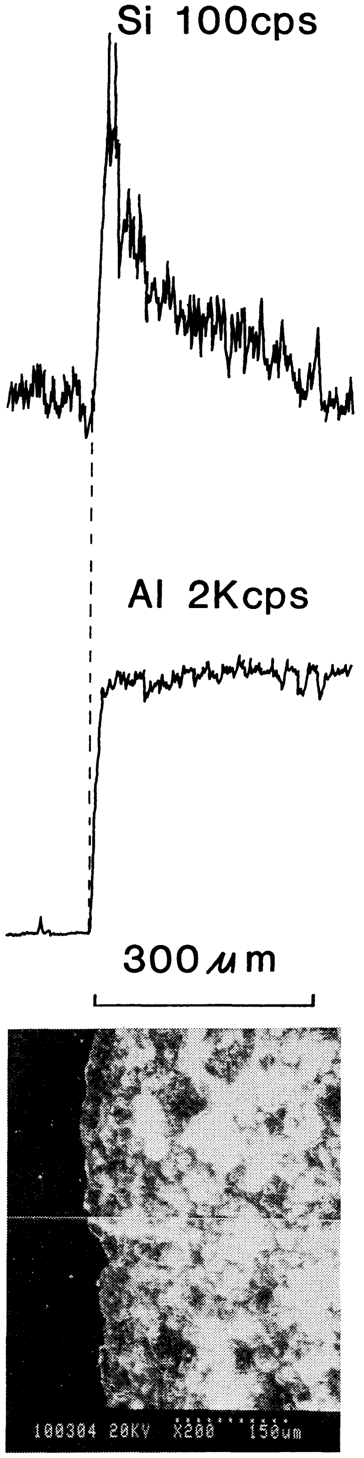
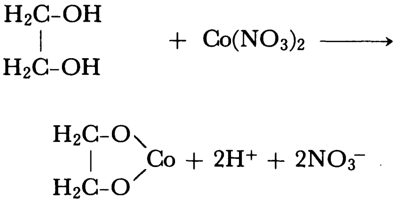


Fig. 5. EPMA profile of the impregnated catalyst at its fringe.

Pore Size Distribution. Pore size distributions of bare alumina spheres and the reduced catalyst are depicted in Fig. 5. The pore size of the bare alumina was sharply distributed at about 45 Å, while that of the reduced catalyst was observed at 20 Å. Thus, the mean pore size of alumina spheres was found to shift to the smaller one when they were immersed with the impregnation solution employed. The pore volume of the reduced catalyst was 0.36 ml g^{-1}, almost the same as that of the bare alumina spheres, 0.33 ml g^{-1}, nevertheless the specific surface area of the reduced catalyst decreased to 256 m^{2}g^{-1}.

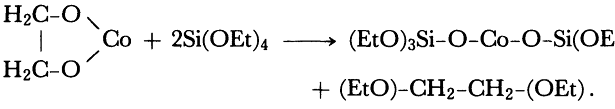
Discussion

As was mentioned previously,[14] metal nitrate dissolved in ethylene glycol forms the metal glycolate as follows;



$$\begin{array}{l}H_2C\text{-}OH\\ \quad|\\ H_2C\text{-}OH\end{array} + Co(NO_3)_2 \longrightarrow \begin{array}{l}H_2C\text{-}O\diagdown\\ \quad|\qquad Co\\ H_2C\text{-}O\diagup\end{array} + 2H^+ + 2NO_3^- \qquad (1)$$

The metal glycolate thus produced reacts with tetraethyl silicate to form the species containing -M-O-Si-structure according to the following reaction;



$$\begin{array}{l}H_2C\text{-}O\diagdown\\ \quad|\qquad Co\\ H_2C\text{-}O\diagup\end{array} + 2Si(OEt)_4 \longrightarrow (EtO)_3Si\text{-}O\text{-}Co\text{-}O\text{-}Si(OEt)_3 + (EtO)\text{-}CH_2\text{-}CH_2\text{-}(OEt). \qquad (2)$$

The reaction between the species containing -M-O-Si- structure results in the three-dimensional expansion of -M-O-Si- structure producing Et-O-Et, diethyl ether. Thus, macromolecules possessing cobalt ions are produced in the impregnating solution employed in this work. If the size of these macromolecules is smaller than that of the micropores on the alumina spheres, the macromolecules may penetrate into the spheres. The EPMA profiles given in Fig. 1 showed that Si ions in the macromolecules are deposited over the external surface of the sphere forming SiO$_2$ thin film but not inside the sphere. This indicates that the size of the macromolecule is larger than 50 Å, since the micropore size of the alumina spheres is sharply distributed at 50 Å (see Fig. 5). When alumina spheres with micropores sized around 100 Å were immersed with the solution, Si ions were clearly observed inside the spheres by EPMA, suggesting that the macromolecules are sized smaller than 100 Å. Once an appropriate amount of macromolecules adhered over the surface of sphere, no more molecules seem to adsorb on the sphere. This resulted in the constant loading of cobalt ions in the catalyst even when the impregnation time was prolonged (see Fig. 3). By changing the concentration of cobalt nitrate in the impregnating solution, the cobalt concentration in the macromolecules may change, hence the cobalt loading in the catalyst can be controlled by the concentration of cobalt ions in the solution, as also could be seen in Fig. 3.

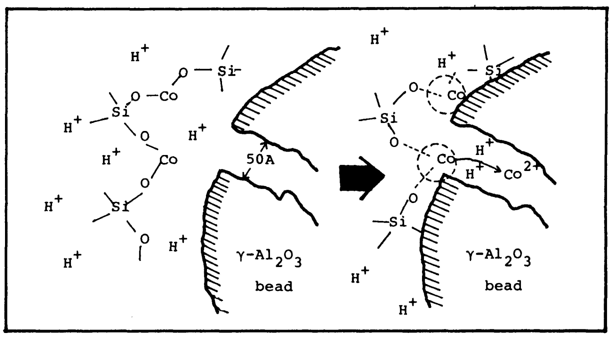


Fig. 6. Model of the mechanism for controlled impregnation profile and formation of SiO$_2$ thin film.

The impregnation mechanism was imagined as shown in Fig. 6. The (-M-O-Si-)$_n$ structures in adsorbed macromolecules may decompose somehow on the alumina surface and the cobalt ions eliminated diffuse into the spheres,competing with H$^+$ ions[15] produced by the Reaction 1 and originating from nitric acid added. H$^+$ ions may adsorb more strongly on alumina than cobalt ions, resulting that the position of cobalt ions adsorbed moved to the center of the sphere with increasing the impregnation time. Thus, the cobalt narrow band is achieved as shown in Fig. 1. The SiO$_2$ film was not deposited inside the micropores of the reduced catalyst but just over their external surface, since the pore volumes of the bare alumina spheres and the reduced catalyst are almost the same with each other.

It must be mentioned that when the alumina spheres with the pore size of 50 Å were immersed with mere tetraethyl silicate, i.e., monomeric tetraethyl silicate, Si ions were observed not only on the surface but inside the spheres of the reduced catalyst.

Conclusion

The impregnation profile of cobalt in alumina spheres was controlled by the impregnation time of alumina shperes with the micropore sized around 50 Å, the impregnating solution consisting of cobalt nitrate dissolved in ethylene glycol, tetraethyl silicate, and a small amount of nitric acid. The cobalt loading in the catalyst was adjusted by the concentration of cobalt nitrate in the impregnating solution. Thus, by employing an appropriate solution both the impregnation profile and the loading of cobalt in the alumina sphere can be simultaneously controlled. On the external surface of the reduced catalyst thus produced was found to be covered with thin and porous SiO$_2$ film, the pore size on this SiO$_2$ film being sharply distributed at 20 Å.

The mechanism and the driving force of the decomposition of macromolecules containing (-M-O-Si-)$_n$ structures over the alumina surface are still unrevealed in the present work.

The authors express their thanks to Dr. Goro Satoh at Shokubai Kasei Company for supplying alumina spheres and to Dr. Akio Furuta at Nikki (JGC) company for measurements of micropore sizes of various catalysts and alumina spheres.

References

1) L. L. Hegedus, T. S. Chou, J. C. Summers, and N. M. Potter, "Preparation of Catalysts II," ed by B. Delmon, P. A. Jacobs, and G. Poncelet, Elsevier Sci. Pub. Co., Amsterdam (1978), p. 171.

2) J. C. Summers and L. L. Hegedus, *J. Catal.*, **51**, 185 (1978).

3) I. Kobiya, "Preparation of Catalysts (Shokubai Chosei)," ed by A. Ozaki, Kodansha Pub. Co., Tokyo (1980), p. 56.

4) E. R. Becker and J. Wei, *J. Catal.*, **48**, 365 (1977).

5) A. W. Adamson, "Physical Chemistry of Surfaces," Interscience Pub. Co., New York (1960), p. 264; Y. Ogino, *Shokubai*, **19**, 334 (1977).

6) M. Kotter and L. Riekert, "Preparation of Catalyst II," ed by B. Delmon, Elsevier Pub. Co., Amsterdam (1979), p. 51.

7) E. R. Becker and T. A. Nuttall, "Preparation of Catalyst II," ed by B. Delmon, Elsevier Pub. Co., Amsterdam (1979), p. 159.

8) E. Michelko, U. S. Patent, 3259454, 3259589 (1966).

9) T. Hori, Jpn. Patent, 54-136589, 149391 (1979).

10) R. W. Maatmann, *Ind. Eng. Chem.*, **51**, 913 (1959).

11) R. C. Vincent and R. P. Merrill, *J. Catal.*, **35**, 209 (1974).

12) M. Komiyama, R. P. Merrill, and H. F. Harnsberger, *J. Catal.*, **63**, 35 (1980).

13) P. M. Tewari and W. J. Lee, *J. Colloid Interface Sci.*, **52**, 77 (1975).

14) A. Ueno, H. Suzuki, and Y. Kotera, *J. Chem. Soc., Faraday Trans. 1*, **79**, 127 (1983); K. Tohji, Y. Udagawa, S. Tanabe, and A. Ueno, *J. Am. Chem. Soc.*, **106**, 612 (1984).

15) I. Kobiya, "Preparation of Catalysts (Shokubai Chosei)," ed by A. Ozaki, Kodansha Pub. Co., Tokyo (1980), p. 59.