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FORMATION OF Co_3O_4 CLUATERS IN TiO_2 SUPPORT OBSERBED BY EXAFS

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It was revealed by EXAFS that tiny clusters of Co_3O_4 are formed in TiO_2 support after the calcination step of Co/TiO_2 catalyst preparation procedure by alkoxide technique. The high dispersion of these small clusters is attributed to the reason why cobalt metal particles in the catalyst can be controlled in an even size level after the reduction by hydrogen.

As was previously mentioned[1)] the size of cobalt particles in Co/TiO_2 catalyst was controlled in an even level when the catalyst was prepared by the alkoxide technique using titanium tetra-isopropoxide and cobalt nitrate dissolved in ethylene glycol. The details of the alkoxide technique were described elsewhere [1,2)] and the preparation procedure is summarized in Table 1.

In the present work EXAFS spectroscopy was employed to reveal the reason why the alkoxide technique can control the size of Co particles in an even level. X-Ray were generated by a rotating anode of Ag operated at 17 kV and 150 mA and were focussed to a sample disc through a Johansson cut LiF crystal. The numbers of X-Ray photons in and out of the sample were counted by a semitransmitting ion chamber and a solid state detector, respectively. The details of the EXAFS equipment were described elsewhere.[3)]

An EXAFS spectrum of the catalyst after calcined at 450 °C in air is shown in Fig. 1 along with that of Co_3O_4 powder. An EXAFS spectrum of a calcined catalyst prepared by a conventional impregnation method (called catalyst(I)) is also given in Fig. 1 for comparison. Apparently the spectrum of the catalyst(I) is judged to be the same as that of the bulk-like Co_3O_4, while the spectrum of the catalyst prepared by the alkoxide technique (called catalyst(A)) is somewhat different from those of the other two samples.

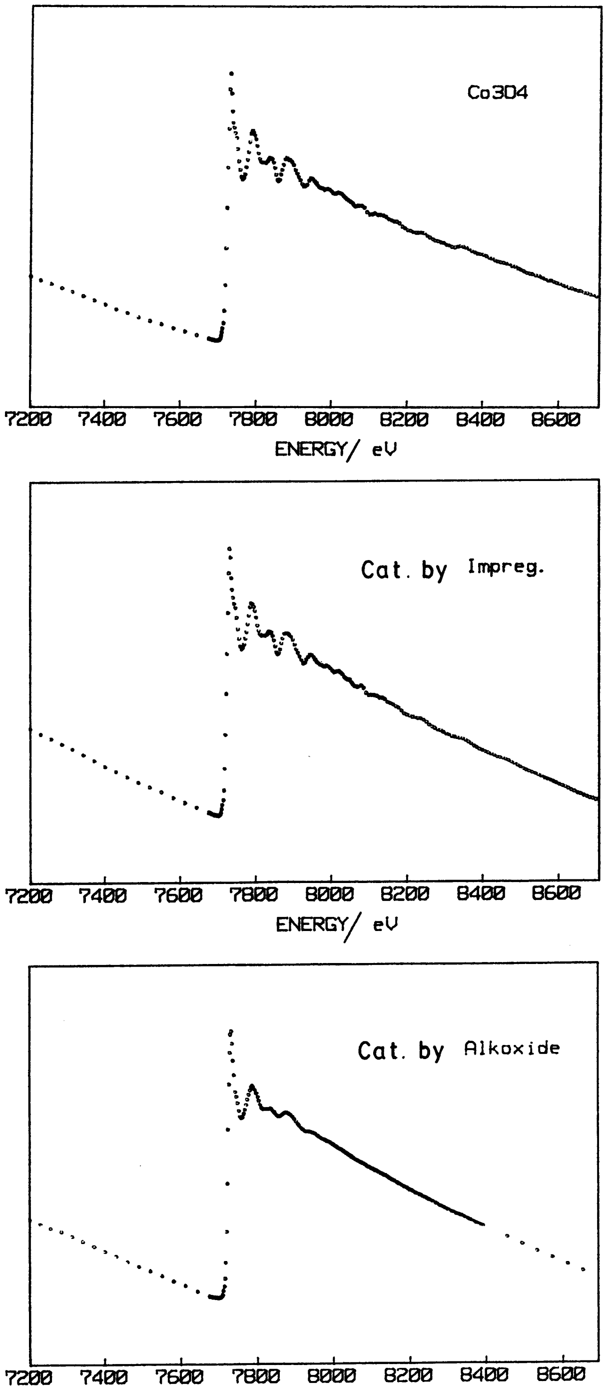
Fourier transforms of these three spectra are shown in Fig. 2. The transforms of the catalyst(I) and Co_3O_4 powder are naturally the same. Apparently the transform of the catalyst(A) does not resemble to that of Co_3O_4, however the positions of peaks coincide with those of Co_3O_4. This indicates that the local structure around Co ions in the calcined catalyst(A) is very similar to that in Co_3O_4. The size of the Co_3O_4 structures in the catalyst(A) must be very fine, since the peak intensity decreased with the distance from the central cobalt atom as shown in Fig. 2. This phenomenon is called the surface effect on EXAFS and was recently reported by Greegor and Lytle.[4)] They reported that the particle size can be estimated by measuring the $\bar{N}_j/N_j$, where $\bar{N}_j$ and N_j represent the peak intensities of the j-th shell of the small clusters and of the corresponding bulk-like sample, respectively.

Table 1. Preparation procedure of Co/TiO_2 catalyst by alkoxide method

step 1	dissolution of $Co(NO_3)_2$ in EG at 80 °C for 4 h
step 2	addition of $(i\text{-}C_3H_7O)_4Ti$ at 80 °C for 4 h
step 3	hydrolysis at 80 °C for 4 h
step 4	drying gels obtained at 110 °C for 24 h
step 5	calcination at 450 °C for 4 h in air
step 6	reduction at 500 °C for 4 h by hydrogen

(EG represents ethylene glycol.)

The resultant value of $\bar{N}_1/N_1$ from Fig. 2 is estimated around 0.45, suggesting, according to Greegor and Lytle,[4)] that the size of Co_3O_4 structures in the calcined catalyst(A) is less than 20 Å. Co_3O_4 has a spinel structure and the size of the unit cell is 8.08 Å. Accordingly, the Co_3O_4 formed in the calcined catalyst(A) is concluded to be a small cluster which consists of several unit cells of the spinel Co_3O_4. on the other hand, Co_3O_4 formed in the catalyst(I) is as large as a few hundreds angstrom because the $\bar{N}_1/N_1$ value was almost unit. The concentrations of cobalt in the catalyst(A) and (I) are both 10 wt%.



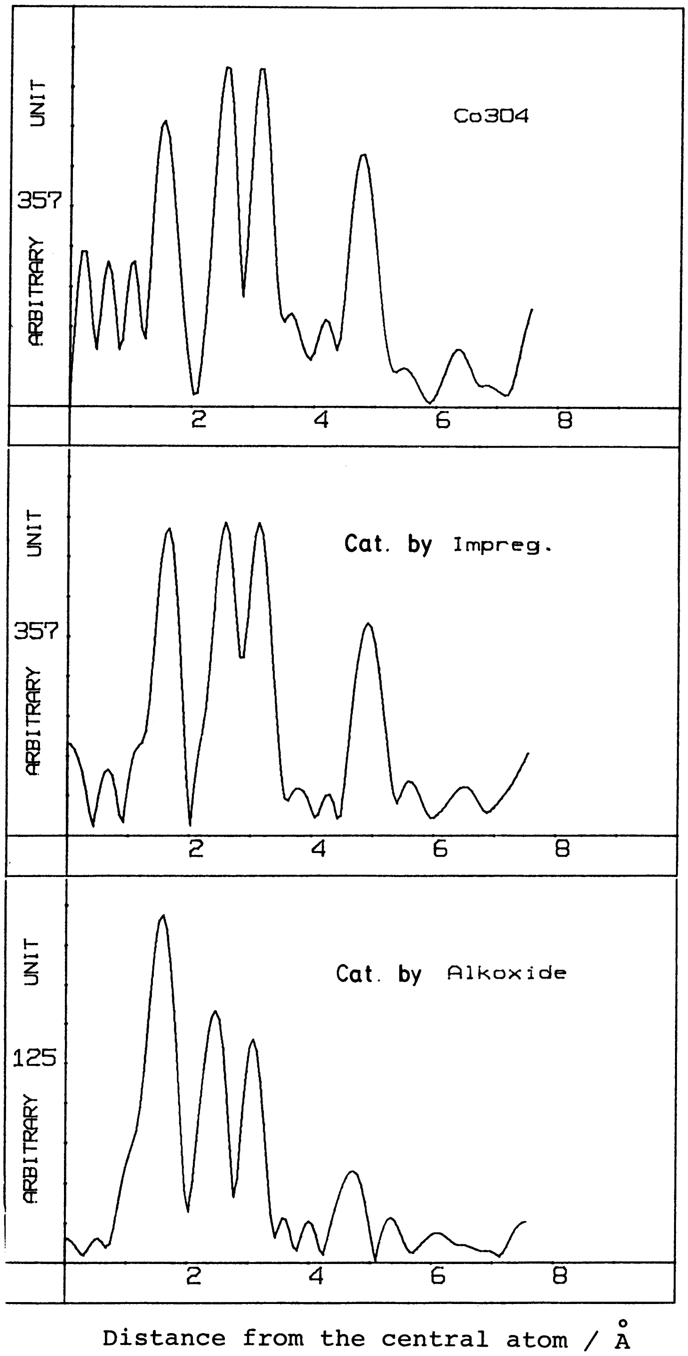


Fig. 1. EXAFS spectra of Co$_3$O$_4$ (a), catalyst(I) (b), and catalyst(A) (c).

Fig. 2. Fourier transforms of EXAFS spectra shown in Fig. 1.

In Fig. 3 is shown a typical photograph observed by transmission electron microscope, the catalyst(A) being reduced by hydrogen at 500 °C for 4 h. As can be seen in Fig. 3, the size of cobalt particles in the catalyst(A) was almost evenly controlled and this must be attributed to the formation of small Co_3O_4 clusters in the calcined catalyst(A). The size of cobalt particles in the catalyst(A) could be varied evenly depending upon the concentration of cobalt in the catalyst and upon the rediction temperature employed, the details being described elsewhere.$^{1)}$

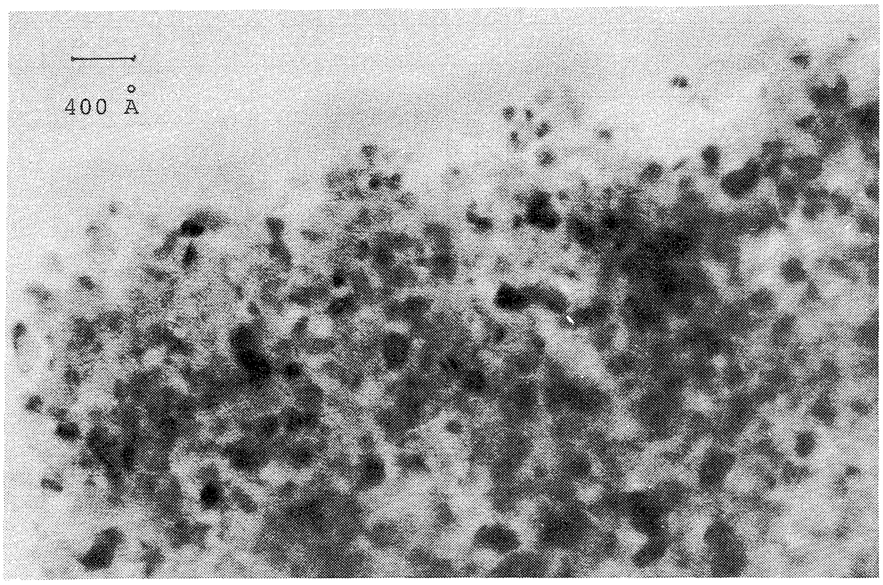


Fig. 3. TEM photograph of 3 wt% Co/TiO_2 catalyst(A) after reduction.

References

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