EFFECT OF OXIDATION-REDUCTION TREATMENT ON THE BEHAVIOR OF MODEL SILICA SUPPORTED COBALT CATALYST

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A model Co/SiO_2 catalyst has been investigated by transmission electron microscopy and electron diffraction. It has been shown that the calcination at 673 and 773 K causes formation of Co_3O_4 and enhanced interaction of Co-phase with SiO_2 which led to spreading and the appearance of particles with torus-like shape. The redispersion of Co_3O_4 particles and their reduction to metallic Co after heating of the oxidized samples in H_2 at 673 K was established. Attach at grain boundaries is seen to be very important.

Keywords: Dispersion and redispersion, spreading phenomena, diffraction, electron microscopy

1. Introduction

It is well known that appropriate thermal treatment of certain transition metals results in strong enhancement of their activity in methanation reactions [1–6]. For example, nickel and cobalt foils oxidized and subsequently reduced [1] with H_2 at mild temperature are ten and one hundred times more active in methanation reaction than samples reduced at higher temperature. Lee et al. [2] observed an increase of the activity of Co/Al_2O_3 catalysts with decreasing extent of their reduction; and enhanced methanation activity over Co single crystals can be related [3] to the presence of a surface cobalt oxide. Jnioni et al. [4] observed that the oxidizing preatreatment is a means of activating Co in CO_2 methanation. These facts suggest that surface oxygen may be responsible for the enhanced activity of the systems preheated in oxidizing conditions, but that this effect is not explicable by surface cleaning of the metals or by simple increase of their surface area during the pretreatment procedures.

The present study was undertaken to establish the influence of oxidation-reduction treatments on the structure and phase composition of the Co/SiO_2 model catalysts using the direct methods of transmission electron microscopy (TEM) and electron diffraction (ED).

2. Experimental

Thin Co films of about 2 nm thickness were obtained in vacuum 10^{-6} Pa by thermal evaporation of spec-pure Co directly on Pt microscope grids coated with the amorphous SiO_2 films. The thickness of Co films was determined gravimetrically. After aging in vacuum at 653 K for 4 h the films were heated in air at 673 and 773 K for 4 h. Next, they were reduced with flowing H_2 at atmospheric pressure. (The hydrogen was purified by passing it over Pd/asbestos catalyst kept at 573 K and then over KOH, P_2O_5 and active carbon.) After each stage of the heat-treatment, Co/SiO_2 samples were investigated by TEM and ED. The information obtained pertains to the bulk phase composition of the samples and morphology of the metal phase (particle size distribution and particle shape) following their oxidation-reduction thermal treatments. About 1000 particles have been measured for each specimen. The mean particles size was calculated using the formula $\overline{D} = \Sigma_i N_i \overline{D}_i / \Sigma_i N_i$, where N_i is the number of particles with diameter between D_i and $D_i + \Delta D_i$, and $\overline{D}_i = D_i + \Delta D_i/2$.

3. Results

Figs. 1 and 2 show the transmission electron micrographs and electron diffractograms of discontinuous Co films supported on SiO_2 and subjected to thermal treatment in vacuum, air and hydrogen, while fig. 3 shows the size distributions of Co particles. It is evident that the interaction of Co particles with the gas phase and with the support alters the shape of Co particles, their size distribution and chemical state of the system.

Cobalt film aged at 653 K for 4 h in vacuum, used as initial state (fig. 1a), was composed of separate particles with approximately rounded shapes, with average particle sizes of ~ 16 nm. In the electron diffraction pattern only rings from hcp and fcc Co were observed (fig. 1b).

HEATING IN AIR

In the samples heated in air at 673 K for 4 h (fig. 1c) the formation of pits on the particles was visible. Most of the particles, except for the smallest ones, exhibited torus-like shape and some of them seemed to be composed of interlinked units showing various contrast in the micrographs. There is a broadening of particle size distribution (fig. 3b), and the mean diameter of the crystallites increases to 22.9 nm. In the diffraction pattern (fig. 1d) only continuous lines from Co_3O_4 were observed. Additional heating at 773 K for 4 h (fig. 1e) resulted in disappearance of pits, flattening of crystallites and spreading of the oxidized particles over the silica surface due to wetting of the substrate by Co_3O_4. Contours of the particles became more irregular (tearing-like). The particle size

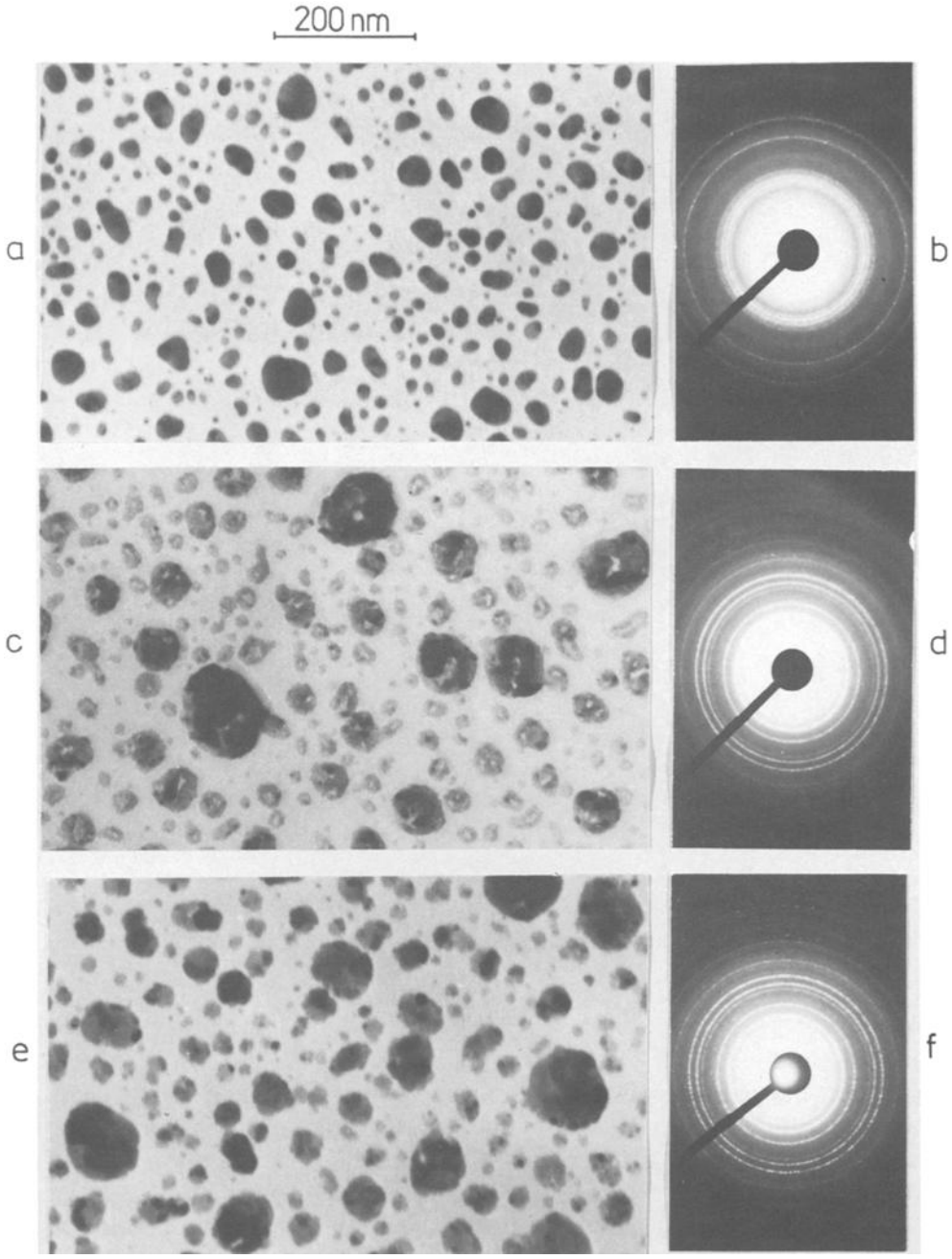

Fig. 1. Electron micrographs and corresponding electron diffraction patterns of Co/SiO_2 films ($d \sim 2$ nm). (a and b) After heating at 653 K for 4 h in vacuum; (c and d) after further heating in air at 673 K for 4 h; (f and g) after further heating in air at 773 K for 4 h.

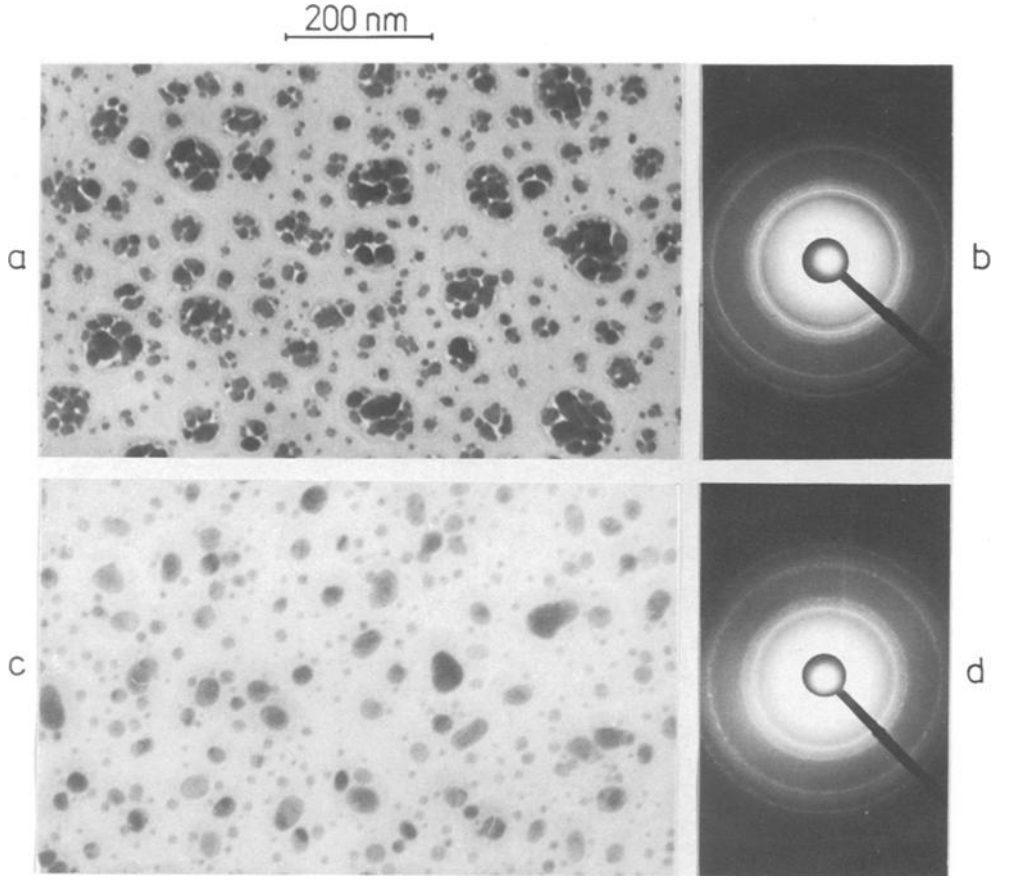

Fig. 2. Electron micrographs and corresponding electron diffraction patterns of the calcinated Co/SiO_2 films after heating in H_2 (a and b) at 673 K for 4 h; (c and d) after further heating at 973 K for 4 h.

distribution was as bimodol (fig. 3c) and the mean particle size increased to 25.2 nm. Only spotted diffraction rings of Co_3O_4 were obtained in this state (fig. 1f).

REDUCTION IN H_2

Thermal treatment of previously oxidized Co/SiO_2 sample in a reducing atmosphere changed dramatically the morphology of the system. After heating in H_2 at 673 K for 4 h the splitting of the larger particles into smaller units took place and the mean size decreased to 13.4 nm (figs. 2a, 3d). As it is shown in electron micrograph (fig. 2a) many particles appeared as ensembles of small units, while some were present as individual crystallites. In the diffraction pattern only lines corresponding to hcp and fcc Co were visible (fig. 2b). Further heating of these films in H_2 at 973 K for 4 h led to sintering of the particles and increase of their average diameter to 14.3 nm. The shape of the particles approached the

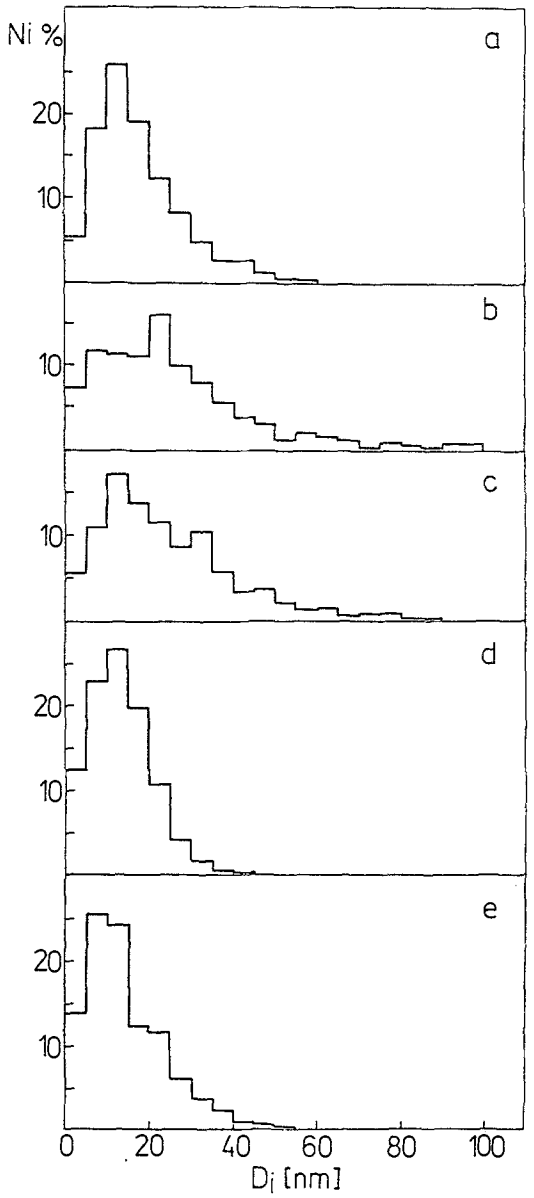

Fig. 3. Particle size distribution for Co/SiO_2 films after subsequent stages of thermal treatment. (a) after heating in vacuum at 653 K for 4 h; (b) after further heating in air at 673 K for 4 h; (c) after further heating in air at 773 K for 4 h; (d) after further heating in H_2 at 673 K for 4 h; (e) after further heating at 973 K in H_2 for 4 h.

equilibrium form (fig. 2c) exposing mostly low index planes on the surface. Electron diffraction study revealed the existence of only Co phase in this state. As it appears from micrographs (cf. figs. 1c and 2c) the particles in the reduced state are more compact than in the oxidized one. The phase composition of Co/SiO_2

Table 1
Composition and mean particle size of Co films (~ 2 nm thick) supported on SiO_2 after thermal treatment in various conditions

Specimen	Treatment conditions *		Co observed phases	Mean particle size, D (nm)
	Atmosphere	Temperature (K)		
1	vacuum	653	hcp, fcc Co	16.0
2	air	673	Co_3O_4	22.9
3	air	773	Co_3O_4	25.2
4	H_2	673	hcp, fcc Co	13.4
5	H_2	973	hcp, fcc Co	14.3

* heated for 4 hours.

system resulting from thermal treatment in various conditions is presented in table 1.

4. Discussion

HEATING IN AIR

Formation of the torus shape particles and their spreading over support observed in this study have been already reported for other systems: Fe/Al_2O_3 [7,8], Ni/Al_2O_3 [9–11], Ni/SiO_2 [9,10] and Ni/TiO_2-SiO_2 [12]. In certain systems heating of metal with the support led to the formation of a new chemical compound. For example aluminates were found after interaction of Ni [11] and Co [13] supported on Al_2O_3 in oxidizing atmosphere and formation of silicate has been suggested for Co supported on silica [14]. In our study, however, only Co_3O_4 was established after calcination of Co/SiO_2 at 673 and 773 K. This finding is in agreement with the results of Van't Blik et al. [15], who found, by temperature-programmed oxidation (TPO), that the oxidation of Co in 4.4 wt% Co/SiO_2 catalyst was already complete at 573 K and the total oxygen uptake ($O_2/Co = 0.66$) attained the value expected for oxidation to Co_3O_4. Although no evidence for the formation of a chemical compound between the metal and the support has been found in this investigation, the observed morphological changes indicate the enhanced metal-support interaction and may be explained according to the model of Ruckenstein and Lee [11]. After oxidation the interfacial tension between the silica and the new Co phase decreases leading to the spreading of crystallites to a lower equilibrium wetting angle as well as to the formation of a torus. It is likely that the torus is a thermodynamically preferred shape after heating Co/SiO_2 in air at 673 K. Flattening of the particles and wetting of the SiO_2 by Co_3O_4 after calcination at 773 K, visible in micrographs (fig. 1e), may be interpreted as further strengthening of the metal-support interaction. The difference in the

diffraction patterns of Co_3O_4 phase (cf. figs. 1d and 1f) in samples calcinated at 673 K (continuous rings) and 773 K (spotted rings) indicated the formation of larger, better ordered crystallites during the heating at the higher temperature. The relatively small increase of the mean particle size (from 22.9 nm to 25.2 nm) after heating in air at 773 K can be explained by filling of the cavities existed in the particles heated at 673 K.

REDUCTION IN H_2

Previous results [13–16] indicated that completely oxidized Co particles are reduced in two following steps $Co_3O_4 \rightarrow CoO \rightarrow Co$ and the course of reduction of supported Co catalysts depends on the support on metal loading and on the preparation procedures [13–17]. Temperature-programed reduction data [15] show that a temperature of 973 K is needed for complete reduction of cobalt in the oxidized 4.1 wt% Co/SiO_2 catalyst. Paryjczak et al. [14] found that for 10 wt% Co/SiO_2 catalyst the reduction process was completed at 825–873 K, but for the catalyst containing 1 wt% of the active phase the reduction was still incomplete at this temperature. Our electron diffraction investigation revealed the presence of Co only in the preoxidized samples reduced in H_2 at 673 K and 973 K. This result indicated that during the oxidation-reduction thermal treatment no significant amount of a new compound detectable by ED was formed, though formation of a small amount of a new phase at the interface is still possible. As shown in fig. 2a, reduction at 673 K of the samples previously calcinated at 773 K causes the splitting of the particles leading to redispersion. The effect of redispersion has been reported already for other systems too [9–11,18,19]. Evidently, the shape of the particles has been affected by the reduction process of defected, oxidized Co crystallites. Initially the reduction proceeds along the grain boundaries, twinning planes, strains and other grain defects. During this process the interlinked units shrink to form individual particles having a greater wetting angle, thus resulting in splitting of the original particles. This process may create specific atomic arrangement on the Co surface which is responsible for the enhanced activity in the methanation reaction. The samples reduced at 973 K exposed probably mostly low index planes on the surface which are less active in dissociation of CO. This fact may account for the reported lower methanation activity for samples reduced at higher temperature [1].

4. Conclusions

(i) We showed that silica-supported Co particles can be redispersed by oxidation-reduction treatment.

(ii) The state of Co established just after reduction at mild temperature, i.e., connected with the splitting of the particles, has a unique structural arrangement responsible for the high methanation activity.

(iii) The strong interaction between Co and SiO_2 in oxidizing atmosphere leads to spreading phenomena and formation of crystallites with unusual shapes.

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