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

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A model Co/SiO₂ 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 Co₃O₄ and enhanced interaction of Co-phase with SiO₂ which led to spreading and the appearance of particles with torus-like shape. The redispersion of Co₃O₄ particles and their reduction to metallic Co after heating of the oxidized samples in H₂ 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 H₂ 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/Al₂O₃ 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 CO₂ 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/SiO₂ 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$_2$O$_5$ 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 $\bar{D} = \frac{\sum N_i D_i}{\sum N_i}$, where $N_i$ is the number of particles with diameter between $D_i$ and $D_i + \Delta D_i$, and $\bar{D}_i = D_i + \Delta D_i/2$.

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 $\sim 16$ 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$_3$O$_4$ 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$_3$O$_4$. Contours of the particles became more irregular (tearing-like). The particle size