

The Effect of Preliminary Treatment on the Catalytic Activity of Cobalt–Silica Gel Catalysts in the Complete Oxidation of Methane

S. S. Goryashchenko, K. I. Slovetskaya, and A. A. Slinkin[†]

Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119992 Russia

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Abstract—The effect of temperature in multiple oxidative–reductive treatments on the activity of cobalt–silica gel catalysts in the complete oxidation of methane is studied. A decrease in the temperature of oxidative–reductive treatments from 500°C to 300°C results in an irreversible decrease in the activity of samples prepared by the impregnation of SiO₂ with cobalt nitrate. A sample prepared from cobalt acetate and calcined at 500°C shows a lower activity, which was close to the activity of samples prepared from nitrates and calcined at 300°C.

INTRODUCTION

It is known that both bulk Co₃O₄ and supported cobalt oxides are one of the most active catalysts for the complete oxidation of hydrocarbons [1]. Cobalt oxide supported on SiO₂ and reduced in H₂ can also be used as a material that readily chemisorbs oxygen [2]. However, it has been shown that cyclic oxidative–reductive treatments may substantially affect the phase composition of the cobalt–silica gel system [2]. Depending on the pretreatment temperature (500 or 300°C), either Co₃O₄ or CoO phases can be stabilized on the SiO₂ surface. This paper deals with the effect of the temperature of oxidative–reductive treatments on the catalytic activity of the cobalt–silica gel system in the complete oxidation of methane.

EXPERIMENTAL

Supported cobalt oxide catalysts prepared by two methods were used. According to one procedure, samples containing 1.1 to 7.7 wt % Co (based on metal) were prepared by the incipient-wetness impregnation of support with aqueous solutions of Co(NO₃)₂. In the second case, a 5.0 wt % Co/SiO₂ sample was prepared from cobalt acetate. KSK silica gel used in this work had a specific surface area of 250 m²/g. All samples were dried at room temperature for 10 h and then in a desiccator at 100°C for 6 h. Then, the catalysts were calcined in a flow of dry air for 1 h at 300 or 500°C.

The catalytic activity was determined in a flow-type reactor. The reactor cross-section was 1.8 cm². The catalyst loading weighed 2 to 3 g and had a bulk density of 0.7 g/cm³. The reaction mixture contained 2.9 × 10^{−2} vol % CH₄ + 17.0 vol % O₂ + balance He. Products were analyzed using an LKhM-8MD chromatograph with a flame-ionization detector and a col-

umn packed with NaX zeolite. The sensitivities to methane and oxygen-containing products were 2 × 10^{−7} and 3 × 10^{−5} vol %, respectively. The space velocity of the gaseous mixture (V_{sp} , h^{−1}) at 500°C at which 99% methane conversion was achieved was taken as an activity measure. In all runs, CO₂ and H₂O were the only products.

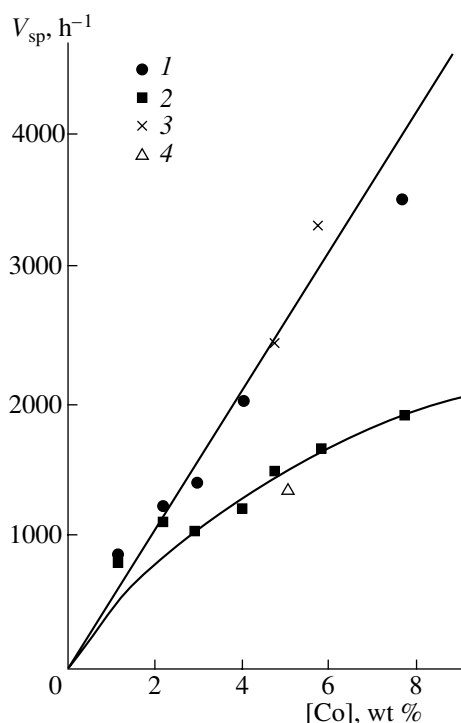
Catalysts were subjected to cyclic oxidative–reductive treatments in the same reactor at 300 or 500°C and a space velocity of 1000 h^{−1}. The samples were calcined beforehand for 30 min in a flow of hydrogen. Then, after cooling to room temperature in a flow of hydrogen, the latter was replaced by an oxygen flow, heated to the desired temperature, and treated for 30 min. Air was cleaned by passing through a NaX-packed column. Hydrogen was cleaned over a Ni–Cr catalyst and a chromium silicate sorbent. The residual amount of oxygen was at most 2 × 10^{−6} vol %.

RESULTS AND DISCUSSION

The figure shows the dependence of the catalytic activity on the concentration of cobalt in the samples calcined at 500°C that were not subjected to oxidative–reductive treatments. The activities of these catalysts are stable and do not change after calcination for 12 h at a given temperature. The linear dependence of the activity on the concentration of CO can be indicative of the same structure and close parameters of the active-phase crystals over the whole range of Co concentrations.

The activities of the samples after three cycles of oxidative–reductive treatment at 500°C coincide with the initial activity and are stable. Thus, cyclic treatments at this temperature do not change the states of samples. As it has been shown earlier [2], the Co₃O₄ phase is present on the SiO₂ surface in the catalysts of this sort. The size of crystals in this phase is ~160 Å.

[†] Deceased.



The activity (the space velocity at 99% conversion) in the complete oxidation of CH_4 at 500°C vs the concentration of cobalt in the catalysts prepared from cobalt nitrate: (1) a sample calcined in air at 500°C ; (2) a sample after oxidative–reductive treatments at 300°C (three cycles); (3) a sample after oxidative–reductive treatments at 500°C (three cycles); and (4) the catalyst prepared from cobalt acetate calcined at 500°C .

Therefore, an increase in the catalyst activity with an increase in the concentration of Co is associated with an increase in the number of Co_3O_4 crystals on the support surface.

The samples subjected to cyclic treatments at 300°C behave differently. Since, we chose 500°C to measure the activity of samples in methane oxidation, the activity of these samples after treatment at 300°C was measured as follows. After calcination in a flow of air at 300°C , the temperature was raised to 500°C for 10 min and then the activity was measured. The activity of catalysts containing less than 3 wt% Co does not change

after such treatment. The activity of samples containing more than 3 wt % Co was lower than that of the same samples treated at 500°C (see the figure). Subsequent calcination in a flow of air at 500°C for 12 h did not affect the catalytic activity. Thus, a decrease in the catalytic activity cannot be due to the incomplete decomposition of cobalt nitrate because it is completed at 300°C [3]. The most plausible explanation for a decrease in the activity of these catalysts can be the formation of the CoO phase along with Co_3O_4 as it was proposed earlier in [2]. It is known that, upon the reduction of samples obtained from acetate, cobalt is stabilized in the finely dispersed state in the form of Co(II) [4, 5]. The 5.0 wt % Co/SiO_2 samples prepared from cobalt acetate and calcined at 500°C were studied in methane oxidation. We found that the activity of these samples is similar to that for the samples prepared from nitrate and treated at 300°C . The amount of oxygen chemisorbed on the 5.0 wt % Co/SiO_2 sample corresponds to the formation of the Co_3O_4 phase, which accounts for ~40% of the overall amount of cobalt [2]. This fact agrees very well with the activity of the sample. Thus, the oxidative–reductive treatments at 300°C probably lead to the formation of the inactive CoO phase on the surface of SiO_2 . The amount of this phase increases with an increase in the overall amount of cobalt in the samples. The activity of the $\text{CoO}_x/\text{SiO}_2$ samples is apparently due to Co_3O_4 as agrees with the constant value of the apparent activation energy, which is 105 ± 10 kJ/mol for all the samples studied in this work.

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