Changes in Co_3O_4 Catalyst Composition during Catalytic Oxidation of CO

Two mechanisms of catalytic oxidation of CO over transition metal oxides are usually considered as possible, namely, a reaction between adsorbed carbon monoxide and adsorbed oxygen, and a reaction between adsorbed carbon monoxide and surface lattice oxygen. In the latter case, when CO_2 is desorbed, the catalyst is left in a reduced state; oxygen from the gas phase is then adsorbed and reoxidizes the surface. It has been established that, depending on temperature, either mechanism is possible in the presence of a Co_3O_4 catalyst (*1*).

In order to determine the mechanism of catalytic reactions and the kinetic equations describing them it is necessary to take into account the possibility of changes occurring in the catalyst under the effect of the reacting gases. In the present work, we have studied the magnetic properties of Co_3O_4 during catalytic CO oxidation on its surface. Simultaneous determination of the magnetic and catalytic properties enables one to establish whether the composition of Co_3O_4 changes during the catalytic reaction and how a change in mechanism of the catalytic reaction affects the catalyst composition.

Co_3O_4 was obtained by thermal decomposition of $Co(NO_3)_2 \cdot 6H_2O$ (A.R., BDH Chemicals, Limited) in air at 550°C for 5 h. According to previous work (*2*), stoichiometric Co_3O_4 is obtained under these conditions, and X-ray analysis showed the presence of Co_3O_4 alone. The specific surface area of the sample as determined by low-temperature adsorption of krypton was 4.9 m²/g.

The investigations were carried out with an apparatus allowing simultaneous mea-surement of magnetic and catalytic properties (*3*). The catalytic measurements were performed by a static method in isothermal conditions. A stiochiometric mixture of CO $+ \frac{1}{2}O_2$ was used. The reaction was followed by the change in pressure of the gas mixture, the reaction product being frozen out at liquid nitrogen temperature. The experiments were carried out at an initial pressure of the stoichiometric mixture of 1.2×10^{-1} Torr and a final pressure of 5×10^{-3} Torr within the temperature range 80–350°C. The reaction volume was 1500 cm³ and fresh samples (6 mg) were used for each experiment. The catalyst was subjected to a preliminary high-vacuum treatment for 1 hr at 350°C and a residual gas pressure of 10^{-6} Torr. The magnetic measurements were performed by the Faraday method at 130–650 K *in vacuo* before and after the catalytic reaction whereas during the catalytic reaction they were made in the reaction mixture. The accuracy of the magnetic measurements was 1% (*4*).

Figure 1 (Curve 1) shows the magnetic susceptibility χ (after the proceeding of the catalytic reaction) of Co_3O_4 at 25°C versus the reaction temperature. Evidently, when the reaction takes place at temperatures of 80–180°C, $\chi_{25} = (29.5 \pm 0.2) \times 10^{-6}$ emu and coincides with the magnetic suscepti-bility of the initial sample. χ does not change during a catalytic reaction proceed-ing in this temperature range. When the catalytic reaction proceeds at temperatures above 250°C, χ increases [$\chi_{25} = (30.4 \pm 0.2) \times 10^{-6}$ emu]. This was also established with direct measurements of χ during the cata-lytic reaction. However, the differences in this case are considerably smaller due to
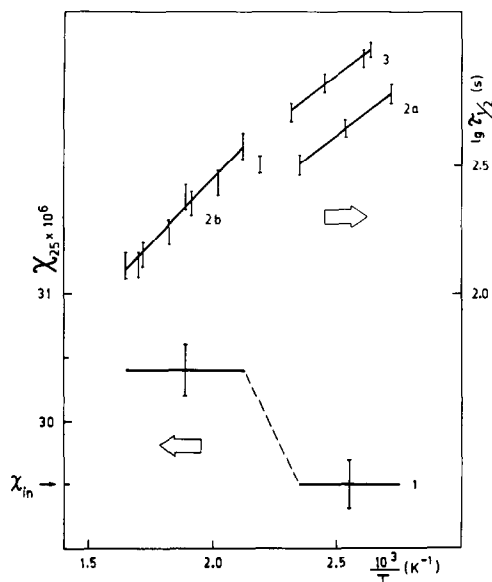
FIG. 1. (1) Magnetic susceptibility, χ_{25}, of Co_3O_4 at 25°C (after the catalytic reaction) versus the reaction temperature. (2a), (2b) Arrhenius plots for the oxidation of CO on Co_3O_4. All experiments are carried out with fresh samples. (3) Arrhenius plot for the oxidation of CO on Co_3O_4 after the proceeding of the reaction in the high temperature range.

the high temperature. Figure 1 (curves 2a and 2b) shows the Arrhenius dependences for the CO oxidation on Co_3O_4. The reaction proceeds in the different temperature ranges according to different mechanisms. At 80–180°C the reaction takes place with an activation energy of 3.3 ± 0.1 kcal/mol whereas at 250–350°C the activation energy is 4.6 ± 0.5 kcal/mol. An activation energy

of 3 kcal/mol has also been established in other work (5, 6) at 20–100°C. A comparison of dependences 1 and 2 in Fig. 1 shows that in the low-temperature region where an interaction between the adsorbed carbon monoxide and the adsorbed oxygen is assumed, no changes occur in the catalyst composition. At high temperatures, the catalyst changes under the effect of the stoichiometric mixture. Figure 1 (curve 3) shows the Arrhenius plot for Co_3O_4 at 80–180°C after using the catalyst in the high-temperature region. The straight line is shifted with respect to curve 2a, which indicates that some change has occurred in the catalyst composition and that this has affected the process in the low-temperature range.

The mean effective magnetic moment of the cobalt ion (μ_{eff}) was determined from the temperature dependence of χ for a Co_3O_4 sample before and after the catalytic reaction. The values obtained are given in Table 1. The values of μ_{eff}, θ and α were calculated by means of a computer search for the best fit with the equation

$$\chi_M = \frac{C}{T - \theta} + \alpha.$$

Here C is the Curie constant, θ the Weiss constant, and α the temperature-independent parmagnetism.

Co_3O_4 is a normal spinel in which the

TABLE I

Values of the Effective Magnetic Moment, μ_{eff}, and the Weiss Constant, θ, for Co_3O_4

Sample[a]	μ_{eff} (BM)	θ (K)	α (emu)
1	2.42 ± 0.05	-52 ± 10	0.8×10^{-3}
2	2.42 ± 0.05	-52 ± 10	0.8×10^{-3}
3	2.53 ± 0.05	-71 ± 10	1.0×10^{-3}
4	2.39	-53	0.74×10^{-3}

[a] 1, initial sample; 2, Co_3O_4 after catalytic reaction in the low-temperature region; 3, Co_3O_4 after catalytic reaction in the high-temperature region; 4, stoichiometric Co_3O_4 sample (ref. (8)).

Co^{3+} ions are in an octahedral field with a ground term $^1A_{1g}$ and an effective magnetic moment $\mu_{eff}(Co^{3+}_{octa|S|}) = 0$. The Co^{2+} ions have a tetrahedral position with the ground term $^4A_2$, and the mean effective magnetic moment of the Co ion in Co_3O_4, μ_{eff}, is due only to Co^{2+}_{tetra}. Therefore

$$C = \frac{NA\mu_B^2}{3k} \mu_{eff}^2(Co^{2+}_{tetra}),$$

$$\mu_{eff} = (1/3^{1/2}) \mu_{eff}(Co^{2+}_{tetra}).$$

The change in the effective magnetic moment of the Co ion in Co_3O_4 during the catalytic reaction proceeding at temperatures higher than 250°C means that reduction of Co_3O_4 takes place. The increase of μ_{eff} is due to the change $Co^{3+}_{octa} \rightarrow Co^{2+}_{octa}$. However, this reduction can lead to a change in the strength of the crystal field and distortion in the octahedral symmetry for part of the Co^{3+} ions and hence to the appearance of Co^{3+} ions with a ground term $^5T_{2g}$ and a magnetic moment, $\mu_{eff}(Co^{3+}_{octa|m|})$, which is not equal to zero (Co^{3+} being in the high-spin state). The change in the mean magnetic moment of the cobalt ion in Co_3O_4 due to symmetry distortions of Co^{2+}_{tetra} and Co^{2+}_{octa} are negligibly small. Thus, the mean magnetic moment of the cobalt ion in Co_3O_4 after a reaction in the high-temperature range will be

$$\mu_{eff}^2 = \tfrac{1}{3}[\mu^2(Co^{2+}_{tetra}) + \alpha_m\mu^2(Co^{3+}_{octa|m|})$$
$$+ \alpha_S\mu^2(Co^{3+}_{octa|S|}) + \beta\mu^2(Co^{2+}_{octa})],$$

where α_m and α_S are to Co^{3+} ions in the high- and low-spin states, respectively, and β is the part of Co^{2+} ions formed as a result of the catalytic reaction. In this case,

$$\alpha_m + \alpha_S + \beta = 2,$$

$$\mu_{eff}(Co^{3+}_{octa|S|}) = 0,$$

$$\mu_{eff}(Co^{2+}_{tetra}) = 2.42(3)^{1/2} = 4.19 \text{ BM}.$$

In the temperature range investigated, μ_{eff} values are (7):

$$\mu_{eff}(Co^{3+}_{octa|m|}) = 5.3 \text{ BM},$$

$$\mu_{eff}(Co^{2+}_{octa}) = 5.3 \text{ BM}.$$

Then,

$$\alpha_m + \beta = 0.6,$$

i.e., about 3% of the Co^{3+} ions have changed as a result of reduction or transition into the high-spin state after a reaction in the high-temperature range. With an ideal spinel structure, 0.3% of the Co^{3+} ions are on the surface. Therefore, the changes resulting from a catalytic reaction in the high-temperature range affect about 10 atomic layers, i.e., the bulk of the catalyst.

The results obtained show that under the effect of the reaction mixture $(CO + \tfrac{1}{2}O_2)$ changes take place in the catalyst (Co_3O_4) stoichiometry at high temperatures and affect the bulk of the catalyst. These changes are associated with a change in mechanism of the catalytic oxidation of CO.

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