A. M. RUBINSHTEIN and A. A. SLINKIN

Abstract

Full Text

PHYSICAL CHEMISTRY

A. M. RUBINSHTEIN and A. A. SLINKIN

MAGNETIC PROPERTIES OF Cr_2O_3–Al_2O_3 CATALYSTS

(Presented by Academician B. A. Kazanskii, January 5, 1959)

The magnetic properties of Cr_2O_3–Al_2O_3 catalysts prepared by impregnating γ-Al_2O_3 with chromic acid followed by reduction with H_2 at 360° and containing 0.1-40 wt. % Cr_2O_3 were studied by Selwood and co-workers ([1]). They found that the magnetic moment at low Cr_2O_3 concentrations is ~3.7 μB, while in the interval from ~5 wt. % to 40% Cr_2O_3 it is equal to 3.2 μB; the authors associate this with the presence of Cr^{6+} ions. At ~8% Cr_2O_3 a sharp break was observed in the course of the susceptibility curve (χ), and χ increased rapidly as the Cr_2O_3 concentration decreased. On the curve of the dependence of the Weiss constant (Δ) on composition, a break occurred at the same point, and Δ fell to zero as the Cr_2O_3 concentration decreased. The authors related these changes in the concentration dependence of χ and Δ to the character of the distribution of Cr_2O_3 over the surface of γ-Al_2O_3.

A study of the process of oxidation by oxygen of deposited Cr_2O_3–Al_2O_3 and Cr_2O_3–ZnO catalysts, by constructing curves of the dependence of magnetic susceptibility on the degree of oxidation, was carried out by Matsunaga ([2,3]). He was able to show that the oxidation processes of Cr^{3+} ions to Cr^{6+} ions proceed most intensively in the initial region of Cr_2O_3 concentrations (approximately up to 10 wt. %), and that oxidation becomes more difficult as the surface area of the support decreases. Similar results were obtained by him in a magnetochemical study of the process of thermal decomposition of CrO_3 deposited on γ-Al_2O_3 ([4]), and in work ([5]) on the study of CrO_3–SiO_2 catalysts.

It seemed of interest to us to investigate the processes of oxidation of Cr^{3+} ions to Cr^{6+} ions for coprecipitated catalysts over a wide range of Cr_2O_3 concentrations, and to determine how the content of Cr^{6+} ions in the catalysts changes under the conditions of the catalytic reaction carried out on them, as a function of the Cr_2O_3 concentration. In addition, on the basis of a detailed magnetic analysis of the system, we intended to give an approximate picture of the distribution of Cr_2O_3 within the bulk of Al_2O_3.

Cr_2O_3–Al_2O_3 catalysts with contents of 0; 1.48; 4.4; 7.28; 14.2; 20.8; 33.2; 60.0; 80.0; 93.2 and 100 wt. % Cr_2O_3 were prepared by coprecipitation of Al and Cr hydroxides from mixtures of 10% solutions of the nitrates of these metals with a 10% NH_4OH solution. By heat treatment in air of the washed precipitates,

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

dried at 110°, for 6 hours at 450° and 600°, two series of catalyst samples were obtained. The catalytic activity of the resulting samples was investigated in the decomposition reaction of iso-C_3H_7OH in the temperature range 275–320°. We carried out a magnetochemical study of the catalysts of both series before and after the catalytic experiments, as well as additional measurements of χ for fresh catalysts subjected to sintering by calcination in air at 1000° for 6 hours.

Figure 1 presents the change in magnetic susceptibility, calculated per 1 g Cr ($\chi_{\mathrm{Cr}} \cdot 10^6$), as a function of the concentration of Cr_2O_3 in the cata-

catalysts calcined at up to 450°, before and after operation. A sharp difference is evident in the values of χ_{Cr} for used and unused catalysts at Cr_2O_3 concentrations up to ~ 40 wt. %. It is characteristic that the concentration range of Cr_2O_3 in which a sharp decrease in χ_{Cr} is observed for unused catalysts, as compared with catalysts reduced in the course of the reaction—in our case jointly precipitated oxides—is much broader than in the case of impregnated catalysts. This is apparently connected with the greater dispersity of Cr_2O_3 in jointly precipitated catalysts than in impregnated catalysts. Further, as is seen from Fig. 1, χ_{Cr} of the catalysts before and after carrying out the alcohol-decomposition reaction, beginning at ~ 60 wt. % Cr_2O_3,

Fig. 1. Dependence of χ_{Cr} on composition for catalysts calcined at 450°.
a—before operation; *b*—after operation

Fig. 2. Dependence of μ $(1, 2)$ and Δ $(3, 4)$ on composition for catalysts calcined at 450°.
$1, 3$—before operation; $2, 4$—after operation

are practically identical. This, however, does not mean that in this range of Cr_2O_3 concentrations there are no Cr^{6+} ions. On the basis of the temperature dependence of χ_{Cr}, we calculated the magnetic moments (μ) of the catalysts before and after operation. The corresponding data are given in Fig. 2. Unused catalysts containing up to 40 wt. % Cr_2O_3 have a lower μ than after operation, which is due to the presence in the former of a considerable quantity of Cr^{6+} ions. The magnetic moments of catalysts with 60, 80, and 93.2 wt. % Cr_2O_3, both before and after operation, are the same ($3.3\,\mu_{\mathrm{B}}$) and lower than the theoretical value of μ for the Cr^{3+} ion. Consequently, these catalysts also contain Cr^{6+} ions (which it was possible to confirm by qualitative chemical analysis), which are not reduced in the course of the reaction. The amount of Cr^{6+} ions in the series of catalysts calcined at 450°, calculated from the values of μ, is presented in Fig. 3.

Analogous data were obtained for catalysts calcined at 600°, but in this case the limiting Cr_2O_3 content up to which a significant concentration of Cr^{6+} ions

Fig. 3

Figure 2: Fig. 3

is present in unused catalysts is reduced to 20 wt. %, and the concentration of Cr^{6+} ions in catalysts calcined at 600° is approximately 1.5 times smaller than in the corresponding preparations calcined at 450°. In this series as well, the value of χ_{Cr} at Cr_2O_3 contents of 60 wt. % and higher is the same for used and unused catalysts; i.e., Cr^{6+} ions are not reduced during catalyst operation under conditions of alcohol dehydrogenation–dehydration.

To elucidate the reasons that may cause such behavior of preparations with a Cr_2O_3 content ≥ 60 wt. %, we considered the possible pha-

phase composition of the Cr_2O_3—Al_2O_3 catalysts, based on magnetic data. Let us turn again to Fig. 1. We see that χ_{Cr} decreases with increasing concentration of Cr_2O_3 not smoothly, and at 60 wt. % Cr_2O_3, χ_{Cr} is equal to χ_{Cr} at 33 wt. % Cr_2O_3 (this corresponds to the maximum susceptibility calculated per 1 g of catalyst). The same is observed for catalysts calcined at 600°. On going from 33 wt. % Cr_2O_3 to 60 wt. %, a sharp increase in Δ from 125 to 250° is also observed (Fig. 2). An increase in Δ on going from 33 to 60% Cr_2O_3 also occurs in the case of catalysts calcined at 600 and 1000°: Δ increases, respectively, from 125 to 300° and from 130 to 460°; however, in catalysts calcined at 1000°, no increase in χ_{Cr} is observed on going from 33 to 60 wt. % Cr_2O_3.

Fig. 3. Dependence of the ion content on composition for catalysts calcined at 450°.
1 —before operation; 2 —after operation

A characteristic change in Δ is observed for all three series of catalysts in the interval 1.5-33 wt. % Cr_2O_3. For catalysts calcined at 450°, Δ in the interval 1.5-14% Cr_2O_3 changes from 75 to 100°, and in the interval 14-33% Cr_2O_3 from 100 to 130° (Fig. 2). Catalysts calcined at 600° in the interval 1.5-14 wt. % Cr_2O_3 are characterized by Δ varying from 30 to 70°, and in the interval 14-33% Cr_2O_3 from 70 to 130°. In catalysts calcined at 1000°, Δ in the interval 1.5-14% Cr_2O_3 is close to zero, and in the interval 14-33% Cr_2O_3 its value changes from 100 to 130°.

Thus, we have three regions of Cr_2O_3 concentrations in which Δ, depending on the calcination temperature, changes in completely different ways: 1) the region 1.5-14% Cr_2O_3, where Δ decreases approximately to 0 with increasing catalyst calcination temperature; 2) the region 14-33% Cr_2O_3, where Δ practically does not change with increasing calcination temperature, remaining at the level of 100-130°; 3) the concentration region $\geq 60\%$ Cr_2O_3, where Δ increases sharply with increasing calcination temperature. This last region of Cr_2O_3 concentrations is also of interest because the catalyst with 93% Cr_2O_3 calcined at 600° is antiferromagnetic, whereas pure Cr_2O_3 under these preparation conditions is paramagnetic. When the calcination temperature is increased to 1000°, catalysts with 93 and 100% Cr_2O_3 become antiferromagnetic. On the basis of the foregoing, the following approximate picture can be given of the distribution of Cr_2O_3 in Al_2O_3 for the catalysts studied.

In the interval 0-14 wt. % Cr_2O_3 there is a solid solution of Cr_2O_3 in Al_2O_3, which becomes ordered as the calcination temperature is increased, leading to a decrease in Δ. In the interval 14-33% Cr_2O_3 there is a mixture of different phases. Along with the solid solution of Cr_2O_3 in Al_2O_3, substitutional solid solutions of Al_2O_3 in Cr_2O_3 apparently also form here, i.e., there are phases rich and poor in Cr_2O_3. In some of them Δ may decrease with increasing calcination temperature, and in others it may increase. On average, these two processes may lead to an unchanged value of Δ. In the concentration interval 60-93% Cr_2O_3, a phase of free Cr_2O_3 appears for the first time; moreover, in catalysts calcined at 450 and 600°, this phase is in a sufficiently dispersed state, and its appearance (at 60% Cr_2O_3) is accompanied by an increase in χ. In addition, in this region of Cr_2O_3 concentrations, an interstitial solution of Al_2O_3 in Cr_2O_3 apparently appears, with which the appearance of antiferromagnetism in catalysts with a high Cr_2O_3 content, calcined at 600 and 1000°, is connected.

It is probable that, in forming an interstitial solid solution, the Al^{3+} ions produce local displacements of O^{2-} ions in the lattice and thereby create favorable conditions for the occurrence of indirect exchange between Cr^{3+} ions as a result of the valence angle Cr^{3+}—O^{2-}—Cr^{3+} approaching 180°.

In light of the above, the absence of noticeable differences in the magnetic properties of fresh and used catalysts with $Cr_2O_3 \geq 60$ wt. % can be explained by the fact that the number of surface Cr^{6+} ions is very small in comparison with their number contained in the bulk of the catalyst crystals. Surface Cr^{6+} ions are readily reduced. The ions located in the bulk of the crystal, however, are not reduced under the given conditions (T, time) because of the absence of direct contact with the gas phase and the slow diffusion of vapors and gases into the crystals.

In addition to the Cr_2O_3—Al_2O_3 catalysts described above, we carried out a series of measurements for Cr_2O_3—SiO_2 catalysts obtained* by depositing CrO_3 on SiO_2 followed by thermal treatment. Treatment of CrO_3—SiO_2 was carried out in two ways: 1) with ethyl alcohol at room temperature, and then with H_2 at 515° for 1 hour; 2) treatment with H_2 or air, also at 515° for 1 hour. These two groups of catalysts differed sharply in their magnetic and crystallographic properties. The former proved to be paramagnetic with $\mu = 3.2\mu_B$ and X-ray amorphous. The latter were antiferromagnetic, and their X-ray patterns contained distinct lines of crystalline Cr_2O_3. We consider it possible that this difference in the magnetic behavior of the two groups of catalysts is explained by the formation of chromium silicates in the case of treatment of CrO_3—SiO_2 with alcohol, owing to the large heat evolution in the oxidation-reduction process. More detailed data on these catalysts will be published, together with a characterization of their catalytic activity, in one of the forthcoming communications.

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
2 I 1959

REFERENCES CITED

1. R. P. Eischens, P. W. Selwood, J. Am. Chem. Soc., **69**, 2698 (1947).

2. Y. Matsunaga, Bull. Chem. Soc. Japan, **30**, 868, 984 (1957).

3. Y. Matsunaga, Bull. Chem. Soc. Japan, **31**, 58 (1958).

4. Y. Matsunaga, Bull. Chem. Soc. Japan, **31**, 745 (1958).

5. R. Mihail, P. Corlateanu, A. G. Ionesco, J. Chim. Phys., **56**, 568 (1959).

* Together with M. I. Rozengart.

Note: Figure translations are in progress. See original paper for figures.