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GAS CHROMATOGRAPHIC INVESTIGATIONS OF THE SYSTEM TRICOBALT TETROXIDE-HYDROGEN

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SUMMARY

The system Co_3O_4–H_2 has been investigated by a gas chromatographic method in the temperature range 325–623 °K. Three intervals, in which the Co_3O_4–H_2 interaction differed, were found, namely, 323–448 °K, in which irreversible adsorption of H_2 on the Co_3O_4 surface predominated, 448–503 (553) °K, in which the reduction of Co_3O_4 began, and 503 (553)–623 °K, in which the reduction of Co_3O_4 continued.

INTRODUCTION

Cobalt oxides are used as catalysts for many contact reactions, and Co_3O_4 is known to be the most active catalyst in reactions involving the deep oxygenation of hydrocarbons[1–3] and of such inorganic compounds as ammonia[4,5] or carbon monoxide[6]. Other important catalytic reactions, carried out with this catalyst are dehydrogenation[7] and isomerisation[8] reactions and the decomposition of hydrogen peroxide[9].

Interactions in the system Co_3O_4–H_2, which are important in studies of the properties of oxygen adsorbed on the catalyst surface as well as oxygen bound in the crystal lattice, have hitherto been investigated mainly by static[10,11] or thermogravimetric[12] methods. A gas chromatograph method has been used only for determination of the irreversible adsorption of H_2 at temperatures from 78 to 293 °K[13].

Here we report gas chromatographic investigations of the system Co_3O_4–H_2 in temperature range 323 to 623 °K.

EXPERIMENTAL

Preparation of catalysts

Cobalt hydroxide, precipitated by aqueous ammonia from a solution of cobalt nitrate, was used as the starting material for all the oxides investigated. The series of catalysts was obtained by heating this cobalt hydroxide at 573, 673, 773, 873 or 973 °K in the presence of air; at these temperatures, decomposition of cobalt hydroxide was complete.

The specific surface areas of each oxide obtained was determined by the BET

method for the adsorption of krypton at 78 °K; for sintering temperatures of 573, 673, 773, 873 and 973 °K, the respective specific surface areas were 22.6, 15.5, 8.1, 5.7 and 2.0 m²/g.

Studies showed that all the oxides had the structure of spinel, and derivatograms indicated that, in the temperature range under study, the oxides did not undergo any structural changes.

Methods

In this work, a gas chromatograph (ISCO 571 A) equipped with a thermal-conductivity detector was used, and the carrier gas was argon containing less than 20 ppm of oxygen. Oxygen was removed from the carrier gas by copper–alumina and manganese oxide–alumina catalysts[14,15], and moisture was removed by molecular sieve 5A. Electrolytic hydrogen was purified from traces of oxygen by means of a palladium–silica catalyst and dried on molecular sieve 5A.

Tablets prepared from powders of the oxides under test were crushed, and the size fraction 0.14–0.4 mm was used; 6–10 g of the sample were placed in a stainless-steel tube. Before the experiment, the oxide was standarised by heating at 573 °K for 2 h in a stream of the carrier gas.

Hydrogen was introduced into the column by means of a valve of volume 1 ml, and experiments were performed at temperatures in the range 323–623 °K. At higher temperatures in this range, additional chromatographic analysis of the reduction products was carried out with the use of a column of Porapak Q.

RESULTS AND DISCUSSION

Based on the difference in interaction between Co_3O_4 and H_2, the range of temperature investigated can be divided into three intervals, for which the chromatograms are shown in Fig. 1.

The interval 323–448 °K

In this interval, the first portions of H_2 are irreversibly adsorbed, as shown by the lack of peaks on the chromatogram. After a certain amount of H_2 has been adsorbed, further portions are practically not adsorbed (Fig. 1a). Thus, in this temperature range, the predominant process is irreversible adsorption of H_2. The amount of H_2 adsorbed increases with the temperature (Figs. 2 and 3).

A similar phenomenon, but in the temperature range 72–293 °K, was observed by Shigehara and Ozaki[13], who, by static and chromatographic methods, calculated that the amount of H_2 irreversibly adsorbed at 293 °K was 3 ml/100 m². In our work, the value measured for Co_3O_4 (sintered at 573 °K; surface area 22.6 m²/g) changed from 6.4 to 10.8 ml/100 m² with increase in temperature from 323 to 448 °K. The amount of H_2 sorbed on oxides sintered at various temperatures (different as far as their specific surface area is concerned) decreases per mass unit of the oxide with increase in the sintering temperature; however, it remained constant per unit of surface area (Fig. 4).

From this, it follows that the process being studied occurs mainly on the surface. It can be used, therefore, for determination of the specific surface area of Co_3O_4
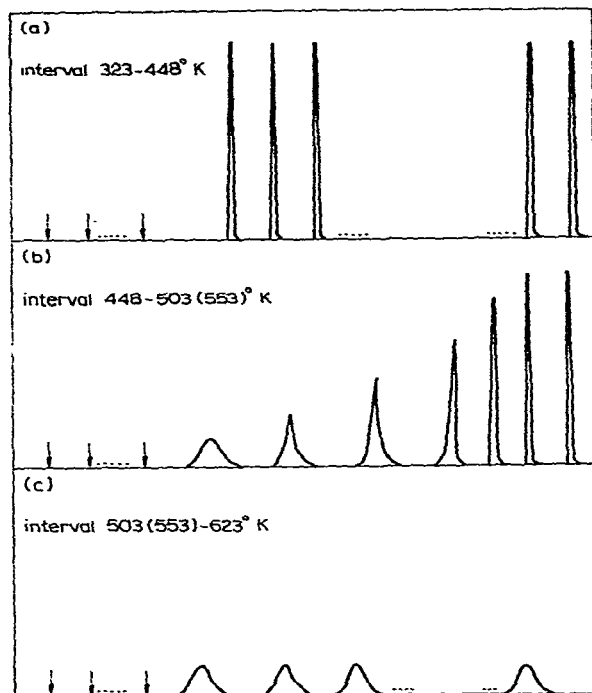
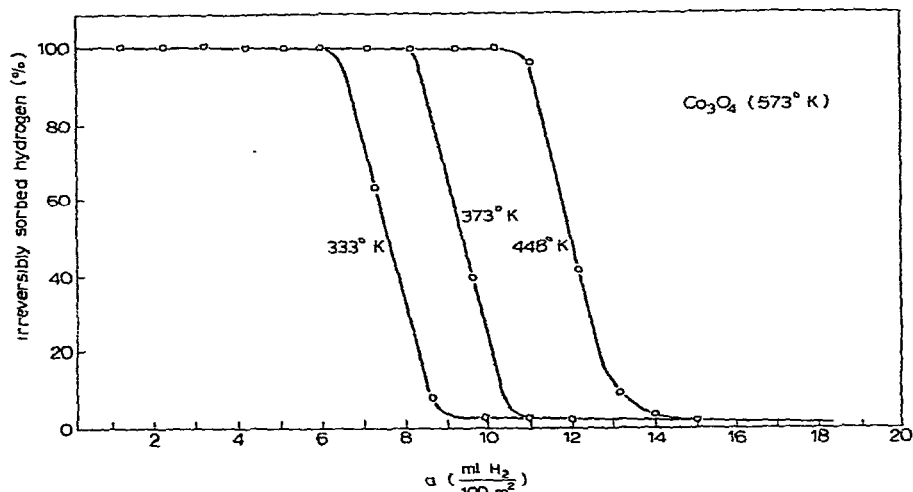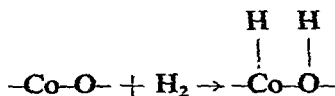Fig. 1. Chromatograms for the system Co₃O₄-H₂.

Fig. 2. Amounts (a) of H_2 irreversibly sorbed during introduction of successive volumes of H_2.

by the pulsed-chromatographic method, with H_2 as adsorbate. The probable mechanism of irreversible sorption of H_2 on the surface of the oxide is as follows:
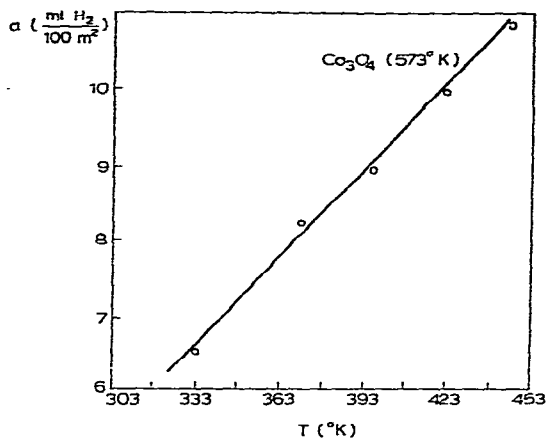
$$\begin{array}{cc} H & H \\ | & | \\ -Co-O- + H_2 \rightarrow -Co-O- \end{array}$$

Fig. 3. Dependence of amount (*a*) of irreversibly sorbed H_2 on temperature.
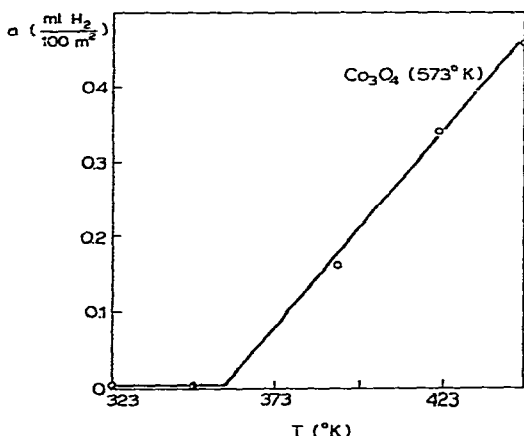

Fig. 4. Dependence of amount (*a*) of irreversibly sorbed H_2 on temperature after heating of the Co_3O_4 for 1 h at a given temperature.

In order to establish the irreversible character of the sorption in the temperature range under discussion, the test oxide was heated for 1 h at the measurement temperature in the stream of the carrier gas (after the maximum of the H_2 peak had been reached); after this period, H_2 was once more introduced. There was no reproduction of the active adsorption centers at temperatures of 323 and 358 °K, and for temperatures from 373 to 448 °K there was only slight reproduction (2–4% of the H_2 was sorbed, relative to the amount originally adsorbed); this is shown in Figs. 5 and 6.

It is probable that this is due to slight desorption of H_2 or migration of oxygen to the surface of the Co_3O_4 with simultaneous migration of H_2 into the catalyst.

The interval 448–503 (553) °K

In this interval, as in the preceding one, the first portions of H_2 are irreversibly sorbed; after a certain amount of H_2 has been sorbed, a diffuse peak for water appears on the chromatogram (Fig. 1b).
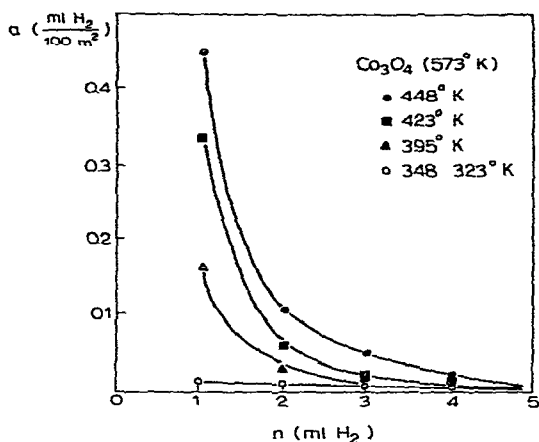
Fig. 5. Dependence of amount (a) of irreversibly sorbed H_2 on succesive volumes (n) of H_2 introduced hydrogen after heating of Co_3O_4 for 1 h at a given temperature.
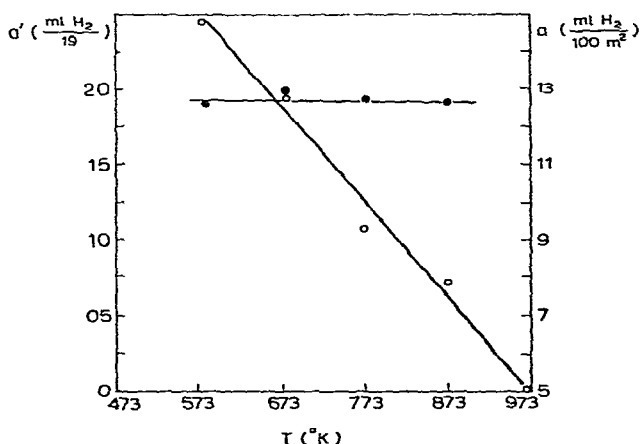

Fig. 6. Dependence of amount of irreversibly sorbed H_2 on sintering temperature (T) of Co_3O_4 per unit of surface ($a-●$) and mass ($a'-○$) of Co_3O_4.

With further portions of H_2, the peaks become more and more symmetrical, until eventually each portion gives a H_2 peak of constant height.

Thus, in this temperature range, reduction of oxide begins. The characteristic feature of this interval is the small amount of H_2 used in the reduction of the oxide. It is difficult precisely to assign the temperature at which reduction begins, but it increases with increase in the sintering temperature of the oxide (and thus with the decrease in specific surface area).

It can be assumed that reduction begins at the expense of the most mobile oxygen atoms on the surface of the oxide. This assumption is supported by the fact that for the oxide with a small specific surface area (sintered at 973 °K), reduction begins at a considerably higher temperature (about 553 °K).

The interval 503 (553)–623 °K

In this interval, after a definite amount of H_2 has been sorbed, further portions of H_2 appear on the chromatogram as diffuse peaks for water. Thus, all the H_2 introduced is used for reduction of the Co_3O_4 (Fig. 1c), which is the predominant reaction. The characteristic feature of this interval is the rapid reproduction of the active centres on the surface of the oxide. This can be explained by the diffusion of oxygen from the crystal lattice to the surface of the oxide, where it is liberated because the equilibrium of the reaction

$$2Co^{3+} + O^{2-} \rightleftharpoons 2Co^{2+} + O$$
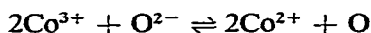
is displaced to the right.

In this reaction, electron exchange is followed by a change in valency of the ions, which, in turn, is connected with the change in volume. This increase in temperature is followed by the formation of Co^{2+} ions, which have a radius greater than that for Co^{3+} ions, and the formation of oxygen atoms, with a radius significantly smaller than that of O^{2-} ions. The liberated oxygen atoms diffuse towards the surface of the oxide.

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