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Note

Application of gas chromatography for investigating slow sorption processes

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Pulsed gas chromatography is used for investigating fast and irreversible sorption processes. Slow sorption processes are difficult to measure¹ or cannot be measured directly by these means.

The degree of slow oxygen sorption on some metallic catalysts² can be relatively easily determined indirectly by reduction of the oxidized sample with hydrogen at higher temperatures. Difficulties arise when hydrogen reacts with oxygen slowly, which often occurs on oxide catalysts¹. However, even then, the pulsed gas chromatography method may prove useful for investigating slow oxygen sorption. The possibility of such investigations on the Fe-Fe₂O₃-SiO₂ has been studied.

EXPERIMENTAL

Catalysts

Catalysts were obtained by impregnation. Iron nitrate Fe(NO₃)₃·9 H₂O (Reachim, U.S.S.R.) was used. The support for chromatography was silica D-08 60-80 mesh (Coast Engineering Laboratory) with a specific surface area of 349 m²/g determined by BET method. After supporting, water from the catalysts was evaporated in a water bath at temperature 330-340°K for *ca.* 2 h. Samples prepared in this way were reduced *in situ*, the temperature being gradually increased to 723°K. At that temperature the reduction was continued for *ca.* 24 h. A carrier gas was then passed through the catalysts for *ca.* 1 h at 723°K.

Methods

The apparatus used for chromatographic measurements, the methods of obtaining hydrogen and oxygen, and gas purification were described previously^{3,4}. The flow-rate of the carrier gas was 50 cm³/min.

The volumes of the adsorbate pulses introduced into the carrier gas were 0.4 cm³. Within the temperature range 193-723°K, no sorption effects of oxygen and hydrogen on the support surface were observed.

RESULTS AND DISCUSSION

Supported iron catalysts show a multi-layer character of oxygen sorption, even at low temperatures. Long ago⁵ it was found that for these catalysts fast oxygen sorp-

tion (measurable in chromatographic way) is followed by slow sorption. It has also been observed that reduction of such supported catalysts is not complete at temperatures which do not cause considerable sintering of the surface of the catalyst⁶. Slow reduction⁷ does not allow direct observation of the process under the dynamic conditions of the chromatographic method.

Figs. 1 and 2 show oxygen sorption on 1% and 3% Fe-SiO₂ catalysts as a function of temperature. Before each measurement the samples were reduced at 723°K for several hours, although even a 2 h reduction leads, practically, to reproducible results of sorption⁸. The continuous lines show fast oxygen sorption. It appears that analogous plots can be obtained by measuring oxygen sorption starting from the lowest temperature (193°K), then raising the temperature and estimating additional oxygen sorption at successively higher temperatures. The values of sorption for individual temperatures were obtained by summing all the results of oxygen sorption at lower temperatures and at the investigated one.



Fig. 1. Oxygen sorption on a reduced 1% iron catalyst as a function of temperature (continuous curve). Oxygen sorption after prolonged contact with oxygen for various temperatures (dashed curve). The points for the dashed line were obtained in an indirect way, based on additional oxygen sorption at 723°K after prolonged contact of a sample with oxygen at various temperatures. The amount of oxygen sorbed during this contact (dashed line) was determined as the difference between oxygen sorption at 723°K (no earlier contact of a sample with oxygen) and additional oxygen sorption at that temperature (after contact with oxygen at the investigated temperatures). The horizontal dashed line corresponds to the value of oxygen sorption at 723°K, which was assumed for estimating individual points on the dashed curve.

Fig. 2. Oxygen sorption on 3% catalyst (continuous curve) and after 48-h oxidation in a stream of oxygen (dashed curve) obtained by indirect method; see Fig. 3.

The results obtained are analogous to the results of oxygen sorption obtained by the pulse method on a sample reduced before each measurement. It was also found that at 723°K even prolonged rinsing of adsorbed oxygen with carrier gas does not result in additional oxygen sorption, indicating the absence of desorptive effects of oxygen.

The facts presented above show that oxygen sorption on the investigated catalysts, within the temperature range 196–723°K, shows additive character.

At 723°K no oxidation-inhibiting effect of the thickness of oxide layer on the surface of supported metal was observed —there was no slow sorption. All the previously reduced metal is transformed into Fe_2O_3 . This result confirms investigations carried out by Roberts⁸, who predicted for iron films the decay of slow oxygen sorption starting at 700°K.

Since this sorption does not occur for the investigated catalysts, it is easy to determine their complete sorptive capacity for oxygen, using pulsed gas chromatography (horizontal dashed line in Figs. 1 and 2). The sorptive capacity at 723°K was, for the investigated catalysts, a reproducible value (Figs. 1 and 2) within experimental error.

Contact between a catalyst and oxygen at any temperature results in a decrease of oxygen sorption at 723°K. Owing to the additive character of sorption the decrease corresponds to the amount of earlier adsorbed oxygen. The result of oxygen sorption obtained directly by the pulse method at room temperature and that obtained from the decrease in oxygen sorption at 723°K are in good agreement.

It can thus be assumed that based on the decrease in oxygen sorption at 723°K, it is possible to determine the degree of oxidation of a sample which has been in prolonged contact with oxygen at any lower temperature. Similar measurements can not be carried out either directly by pulsed gas chromatography or indirectly by

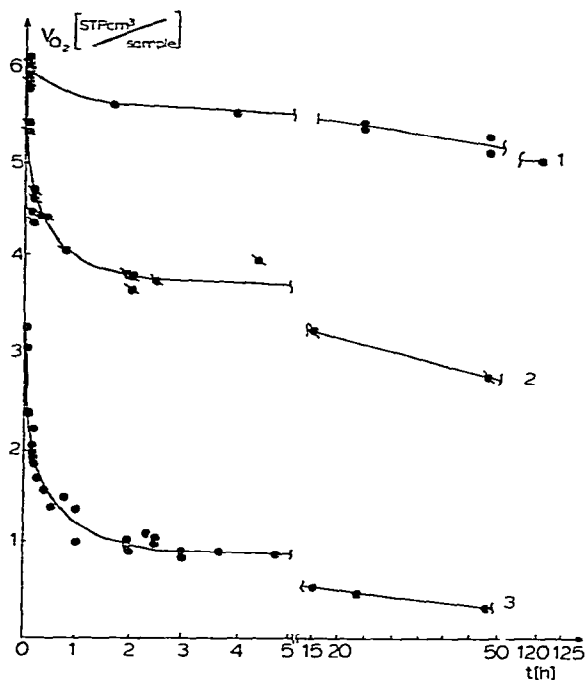


Fig. 3. Oxygen sorption at 723°K for 3% iron catalyst, depending on the time of previous contact of a sample with a stream of oxygen at a lower temperature: curve 1, 193°K; curve 2, 298°K; curve 3, 433°K.

titration of adsorbed oxygen with hydrogen (when, as in the case of supported iron, hydrogen sorption is slow even at relatively high temperatures⁶⁻⁸).

Based on the above statements, the value of complete oxygen sorption under given conditions can be determined by raising the temperature to 723°K (after sorption), and additional oxidation of the sample. The difference between this value and earlier measured complete sorptive capacity gives the value of complete oxygen sorption under the given conditions. It is shown by the dashed curves in Figs. 1 and 2 in the investigated temperature range after prolonged contact of oxygen with the catalysts.

The difference between the dashed and continuous lines is the measure of slow sorption. It is at a maximum for the investigated catalysts at *ca.* 430°K.

This method also proved useful for determination of the time course of oxygen sorption (Fig. 3) at different temperatures. A similar procedure would seem useful for investigating slow oxygen sorption for other oxide systems or supported metals.

The method of measurement described here widens the range of application of gas chromatography, and the knowledge of slow oxygen sorption processes on iron surfaces may contribute to a better understanding of corrosion processes.

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