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Abstract

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STUDY OF THE CATALYTIC PROPERTIES OF PYROPHORIC MANGANESE

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The catalytic properties of metallic manganese have so far been studied comparatively little. O. Schmidt (1,2), comparing the activity of a series of metallic blacks, showed that manganese is very active in the reaction of low-temperature hydrogenation of ethylene; G. K. Boreskov and co-workers (3), who studied the catalytic activity of manganese in the form of small granules in the reaction of the interaction of oxygen with hydrogen, came to the conclusion that manganese is inferior in activity to the metals of the eighth group of the periodic system; Gudry (4) proposed using manganese, along with other metals, as a catalyst for the flameless oxidation of fuels; Anderson and Kemball (5) established that a manganese film is completely inactive in the exchange reaction $C_2H_6 + D_2$ and in the cracking of ethane.

The limited number of works devoted to the study of the catalytic properties of manganese is, to a considerable extent, due to the fact that this metal is difficult to obtain in the form of a pyrophoric black. In contrast to the metals of the eighth group, manganese can be obtained by reduction of oxides only at temperatures above 1300°; the metal formed in this process sinters and loses activity. Therefore, to obtain manganese we used the method proposed by Guntz (6), Prelinger (7), and Schmidt (1,2), based on the thermal decomposition in vacuum of manganese amalgam. The latter, in turn, was obtained by electrolysis of an aqueous solution of manganese chloride on a mercury cathode. To avoid contact with air, the black obtained directly in the apparatus for decomposing the amalgam, under vacuum conditions, was covered with absolute benzene, under which it was subsequently stored until being introduced into the catalytic reactor.

In order to establish the degree of purity of the black obtained, we carried out an additional experiment, obtaining a small amount of manganese according to the method described above, but using as the cathode in the electrolysis mercury containing the isotope Hg_{203}. Comparing the activity of dilute nitric-acid solutions of precisely weighed portions of the resulting black and of the initial mercury, we established that the sample treated in vacuum at 10^{-6}-10^{-7} mm Hg at a temperature of 340-380° for 7 hours contains about 0.03 at.% Hg.

In accordance with the literature data, the manganese obtained in this way possessed high chemical activity. When a mixture of hydrogen with air was rapidly drawn through a layer of a freshly prepared sample, an exothermic reaction occurred, accompanied by a flash.

We obtained an X-ray diffraction pattern of manganese black. It was shown that decomposition of the amalgam by the method described gives α-manganese, crystallizing in a complex cubic lattice of the A-12 type, the parameter of which a is equal to 8.923 ± 0.020 Å (literature data: $a =$

$= 8.894$ Å (8). It may be considered that in the present case a looser lattice is formed than in metallic manganese obtained by other methods. It should be noted that the X-ray diffraction pattern did not contain a single line corresponding to manganese oxides or to its other compounds. Since pyrophoric manganese is oxidized not only by oxygen but also by such oxygen-containing compounds as H_2O, CO_2, and even CO, we were forced to limit the scope of investigation of the catalytic properties of manganese to reactions of dehydrogenation and hydrogenation of hydrocarbons.

The experiments were carried out in a flow system with automatic feeding of the substance into the reactor. Manganese black in an amount of 23-23.5 ml was introduced into the tube in a manner excluding its direct contact with air; benzene and air were removed from the system in the cold for 2 hours by electrolytic hydrogen freed from traces of oxygen by passing the gas through a heated tube containing reduced copper. The space velocity of feed of the reacting substance was 0.4. After each experiment, lasting 30-40 min, the catalyst was regenerated with hydrogen at the experimental temperature for 1.5-2.0 hours.

Dehydrogenation of cyclohexene. The cyclohexene used in the work was obtained by dehydration of cyclohexanol over magnesium sulfate. In accordance with literature data (9), this catalyst does not cause isomerization of the resulting cyclohexene with formation of methylcyclopentene. The preparation had the constants: b.p. 80.0-80.5°/736 mm; n_D^{22} 1.4451; d_4^{20} 0.8105. (Literature data (10): b.p. 83°/760 mm, n_D^{22} 1.44507; d_4^{20} 0.8102.)

The reaction was studied in the temperature range 320-400°. The percentage conversion of cyclohexene was determined from the amount of hydrogen evolved, assuming that the reaction proceeds exclusively according to the equation

$$\text{cyclohexene} \longrightarrow \text{benzene} + 2\,\mathrm{H}_2,$$

as well as from the change in the amount of unsaturated hydrocarbons in the liquid catalyzate (titration with brominating mixture).

The gaseous reaction products were analyzed on a VTI apparatus, and it was shown that they consist to 98.5-99.5% of hydrogen with an admixture of 0.5-

1.5% saturated hydrocarbons. The absorption spectrum of the catalyzate, recorded in the ultraviolet region, showed the presence of benzene in addition to the initial cyclohexene. Frequencies characteristic of cyclohexadiene were not found.

During the first 4-5 experiments the activity of the catalyst was not stable, and only subsequently were reproducible results obtained. The data obtained are given in Table 1.

Table 1

	Freshly prepared catalyst, $t = 380°$	Catalyst with stabilized activity, $t = 322°$	Catalyst with stabilized activity, $t = 360°$	Catalyst with stabilized activity, $t = 397°$
Conversion by hydrogen, %	60.0	2.0	5.0	13.6
Conversion by unsaturated compounds, %	40.0	2.5	5.6	13.7

As can be seen, first, for the freshly prepared catalyst there is a discrepancy in the percentage conversion determined by the two indicated methods; hydrogen on this catalyst is formed not only

due to the dehydrogenation of cyclohexene; secondly, the stabilized catalyst is considerably inferior in activity to the freshly prepared one; thirdly, the percentage conversion calculated by both methods for the catalyst with stabilized activity is practically one and the same value. This last point may serve as evidence of the absence of irreversible catalysis occurring in parallel with dehydrogenation, since otherwise the percentage conversion calculated from the titration data would have been higher than that calculated from hydrogen.

We obtained an X-ray diffraction pattern of a catalyst that had operated for eight experiments. It was shown that during operation some compaction of the α-manganese lattice occurs (the lattice parameter a became 8.894 ± 0.020 Å) and, more importantly, that along with the α-manganese lines there appeared a large number of bright lines corresponding to manganese carbide of composition $Mn_{23}C_6$. The lattice parameter of this substance, calculated from the photograph ($a = 10.57 \pm 0.03$ Å), coincided exactly with that reported in the literature ([11]). In this photograph there was also not a single line characteristic of any manganese oxide.

Thus, freshly prepared manganese not only catalyzes the dehydrogenation reaction of cyclohexene, but also cracks it with formation of manganese carbide and an additional amount of hydrogen. We calculated the apparent activation energy of the dehydrogenation reaction of cyclohexene on carburized manganese: $E = 19.3$ kcal/mole.

Dehydrogenation of cyclohexane. Taking into account that α-manganese crystallizes neither in a hexagonal nor in a cubic face-centered system, we could count only on stepwise dehydrogenation of cyclohexane by the edge mechanism (12).

The initial cyclohexane had the constants: b.p. 79—79.3°/748 mm; $n_D^{20}1.4268$; d_4^{20} 0.7785. (Literature data (13): b.p. 80.75°/760 mm; $n_D^{20}1.4263$; d_4^{20} 0.7786.)

It was shown that in the temperature range 440—500°, dehydrogenation of cyclohexane with formation of cyclohexene proceeds to a very slight extent, as evidenced by the evolution of hydrogen and the appearance of olefins in the condensate; however, the yield did not exceed 2.5%, calculated on the cyclohexene formed. The absence of diene and benzene was demonstrated by the spectral method. In this case we also observed that the percentage conversion calculated from hydrogen was higher than that from titration data. This indicates that part of the cyclohexene formed undergoes cracking with liberation of hydrogen.

Dehydrogenation of ethylbenzene. It was of interest to ascertain whether manganese black is capable of dehydrogenating the side chain of aromatic compounds. We used ethylbenzene having the following constants: b.p. 133.2—133.8°/749 mm; $n_D^{20}1.4966$; d_4^{20} 0.8656. (Literature data (13): b.p. 136.19°/760 mm; $n_D^{20}1.4959$; d_4^{20} 0.8670.)

It was established that in the temperature range 300—450° manganese is capable of partially cracking the initial hydrocarbon with formation of carbon and hydrogen. This conclusion was made by us on the basis of gas analysis, the results of titration and distillation of the liquid condensate, and also investigation of it in the infrared region of the spectrum.

It was also shown in the work that pyrophoric manganese in the temperature range 150—215° practically does not catalyze the hydrogenation reactions of benzene and cyclohexene.

Thus, in the present work it was established that pyrophoric manganese catalyzes the dehydrogenation reaction of cyclohexene with formation of benzene, at the same time causing partial cracking of the initial product with formation of manganese carbide and hydrogen. The activation energy of the dehydrogenation reaction on carburized manganese is 19.3 kcal/mole.

It has been shown that manganese practically does not dehydrogenate cyclohexane and ethylbenzene, and also does not hydrogenate benzene and cyclohexene.

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

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