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Abstract

Full Text

Chemistry

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Effect of Oxygen and Water on the Hydrogenating and Isomerizing Activity of a Tungsten Sulfide Catalyst

(Presented by Academician B. A. Kazanskii, November 11, 1960)

Hydrogen used in various hydrogenation processes usually contains impurities and, in particular, oxygen. For example, according to Makarov's data ⁽¹⁾, the circulating gas of industrial units for liquid-phase hydrogenation of heavy oils contains 80-83% H₂, 0.1-0.2% O₂, 0.2-0.4% CO, 0.2-0.3% CO₂, 9-11% hydrocarbons C H₂, and 7-8% N₂. Technical electrolytic hydrogen may contain up to 0.5% oxygen*.

The purpose of the present work was to determine the effect of traces of oxygen and water on the activity of an industrial WS₂ catalyst. To this end, in a flow apparatus ⁽²⁾ we investigated the hydrogenation of benzene and the isomerization of cyclohexane under hydrogen pressure. The technical electrolytic hydrogen we used contained up to 0.1% oxygen. To remove oxygen, hydrogen compressed to the required pressure was passed at 300-320° through a tube with granulated copper (250 g; the copper had been obtained by preliminary reduction of copper oxide). The water formed from oxygen was retained in a drier filled with caustic potash (280 g) and silica gel (110 g). Experiments were carried out both with untreated hydrogen and with hydrogen purified of oxygen and water. The entire study was conducted with a single sample of catalyst (28 g, 12 ml) with a grain size of 3-5 mm. The catalyst was mixed with pieces of porcelain (60 ml) of the same size. The temperature was measured with an XA thermocouple introduced 25 mm into the beginning of the catalyst bed (bed length 190 mm). Before the experiment, the catalyst was held in a weak stream of hydrogen (~2 l/min) for 4 hours at 400° and 250 atm.; the method of hydrogen purification was the same as in the experiment. The hydrogenation of benzene was investigated at 310°*, 250 atm., and feed rates of benzene 0.60 mole/hour and hydrogen 15 mole/hour. Benzene hydrogenates were analyzed by the methods of relative dispersion ⁽³⁾ and, in some cases, by gas-liquid chromatography. The isomerization of cyclohexane was investigated at 370°, 150 atm., and feed rates of cyclohexane 0.11 mole/hour and hydrogen 2.0 mole/hour. The degree of conversion of cyclohexane to methylcyclopentane and hexanes was determined by fractionation of the catalyzates ⁽²⁾ and sometimes by gas-liquid chromatography. Both methods gave similar results (the difference in determining the

extent of isomerization usually did not exceed 2%). Experiments on benzene hydrogenation were alternated with experiments on cyclohexane isomerization. The data obtained are presented in Tables 1 and 2.

The experiments performed showed that the presence of oxygen and water in hydrogen causes a very substantial decrease in hydrogenating activ-

* In experiments with high benzene conversion, overheating was observed in the catalyst bed (see Table 1).

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Table 1

Hydrogenation of benzene at 250 atm.

Experiment no.	Hydrogen used	temp., °C	Depth of benzene hydro- gena- tion, %	Experiment no.	Hydrogen used	temp., °C	Depth of benzene hydro- gena- tion, %
1	With purifi- cation	310— 318	84,8	16	Without purifi- cation	310	13,9
2	» »	301— 309	87,5	18	» »	310	8,0
3	Without purifi- cation	310— 314	56,9	19	» »	310	9,0
4	» »	308— 310	19,6	20	With purifi- cation	309	43,3
7	» »	310	13,3	21	» »	308— 309	65,2
8	With purifi- cation	310— 314	87,1	22	» »	310— 311	69,7
11	» »	305— 310	92,8	23	» »	310	83,2
13	Without purifi- cation	310	15,2	24	» »	309— 312	86,6
15	» »	310	9,5				

of the catalyst activity and an increase (although not as sharp) in its isomerizing

activity. As can be seen from the data in Tables 1 and 2, experiments were carried out alternately on the same catalyst sample with hydrogen purified from oxygen and water (nos. 1–2, 8–12, and 20–24), and with unpurified hydrogen (nos. 3–7 and 13–19). In all three series of experiments with purified hydrogen, activation of the catalyst occurred in the benzene hydrogenation reaction

Table 2

Isomerization of cyclohexane at 370° and 150 atm.

Experiment no.	Hydrogen used	Depth of cyclohexane isomerization, %
5	Without purification	31,0
6	» »	33,8
9	With purification	14,1
10	» »	14,1
12	Without purification	34,0
14	» »	32,9
17	» »	34,2

(the depth of hydrogenation increased to 87–93%); in series of experiments with unpurified hydrogen, the conversion decreased to 8–13%. Thus, the observed effect is reversible. The same applies to the isomerization of cyclohexane: as a result of hydrogen purification, the extent of this reaction decreased from 34 to 14%; however, after the purification system was switched off, the depth of isomerization again reached its former value.

On passing from experiments with purified hydrogen to experiments without gas purification (and back), the hydrogenating activity of the catalyst either rapidly stabilized (after a sharp change), or changed gradually (see experiments nos. 20–24). Apparently, the gradual nature of the change in activity in the indicated series of experiments was due to the relatively long duration of the preceding series, carried out without gas purification (experiments nos. 13–19), and, consequently, to the larger amount of oxygen introduced into the catalyst.

The sharp change in the hydrogenating and isomerizing activity of the catalyst observed by us upon purification of hydrogen could have been due both to oxygen adsorbed or dissolved in the catalyst (for example, in the form of atomic oxygen), and to water formed from oxygen and adsorbed on the surface. To clarify this question, we carried out a number of additional experiments on the hydrogenation of benzene and the isomerization of cyclohexane, in which the hydrogen drier was switched off, and the moist gas from the furnace with copper entered the reactor through a steel capillary, the temperature of which was maintained at 300–320°. Thus, the hydrogen was purified only from oxygen,

while the water formed entered the catalyst. The depth of hydrogenation in these experiments increased somewhat in comparison with experiments carried out without purification of hydrogen from oxygen, and amounted to 15–22%. The results obtained make it possible to assume that the hydrogenating activity of the catalyst is suppressed not only by the water formed, but also by oxygen itself. At the same time, when the drier was switched off from the hydrogen purification system, no change was observed in the depth of

isomerization of cyclohexane compared with experiments carried out without gas purification at all.

Let us first try to analyze the results obtained in the experiments on benzene hydrogenation. The sharp decrease in the hydrogenating activity of the WS_2 catalyst on going over to unpurified electrolytic hydrogen, as we have already seen, is to a considerable extent due to the water formed. It is possible that water, despite its negligible concentration in hydrogen, is capable, upon being adsorbed, of blocking the catalytic surface; in this case its adsorption must be considerably greater than the adsorption of benzene. We note that the amount of water formed from the oxygen introduced with the hydrogen during the experiment amounted to only about 5 mol.% of the amount of benzene introduced.

Another reason for the observed effect of water on the hydrogenating activity of the WS_2 catalyst could have been a change in its semiconductor properties. It is known that water has both acceptor and donor properties, depending on the adsorbent (see, for example, ^(4,5)). It may be assumed that, upon adsorption of water, the concentration of free electrons on the surface of the catalyst decreases, which in turn leads to a decrease in the rate of benzene hydrogenation.

As for the inhibiting effect exerted on the hydrogenation process by the presence of oxygen itself, and not by the water formed from it (see above), it should be thought that the assumption of surface blocking in this case can hardly be accepted: it is highly improbable that, under the conditions studied, a layer of adsorbed molecules or atoms of oxygen would be retained on the surface of the hydrogenating catalyst. More plausible here is the concept of the influence of oxygen on the semiconductor properties of the catalyst. Indeed, oxygen is an acceptor of free electrons on various semiconductors, and its dissolution in WS_2 crystals could have led to the observed effect.

As is known, the cracking activity of aluminosilicate catalysts increases in the presence of water. According to Hansford ⁽⁷⁾, adsorbed water promotes the formation of carbonium ions and, consequently, increases the rate of reactions proceeding by an ionic mechanism. From this point of view one can also explain the increase in the isomerizing activity of the WS_2 catalyst that we observed when hydrogen containing traces of water (or traces of oxygen, which is converted into water on the surface of the catalyst) was introduced into the reaction zone.

The data obtained indicate that purification of hydrogen from traces of oxygen

and water is of great importance in the hydrogenation of benzene and the isomerization of cyclohexane on a WS_2 catalyst. It makes it possible to “control” the selectivity of the catalyst and to sharply increase its hydrogenating activity. In this connection, we note that when hydrogen purified from traces of oxygen and water was used, cyclohexane containing no more than 0.3% impurities was obtained from benzene over the catalyst investigated in the present work. It may be expected that purification of hydrogen from oxygen and oxygen-containing compounds will prove effective not only for the hydrogenation of aromatic compounds over a WS_2 catalyst, but also for hydrogenation reactions of other compounds over other sulfide catalysts.

E. A. Udaltsova and Yu. I. Ryzhov took part in the work.

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