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Abstract

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On the Catalytic Properties of Radioactive Tungsten Disulfide in the Dehydration Reaction of *n*-Decyl Alcohol

It is known (1,2) that radioactive radiation from solids affects their physicochemical properties, including catalytic ones. Thus, using the dehydration reaction of alcohols as an example, it was shown that the introduction of a radioactive isotope into a catalyst affects the rate and activation energy of the catalytic reaction (3–6). Ionic salts of metals and oxides having the character of dielectrics were used as catalysts. In order to elucidate the changes that arise in radioactive catalysts and their influence on the yield of reaction products, it is necessary to investigate catalysts of various chemical structures, in particular semiconductors. Among the latter, tungsten disulfide plays a major role; it is used as a catalyst for hydrogenation, isomerization, dehydrogenation, and dehydration. We studied the effect of adding radioactive sulfur S^{35} ($T_{1/2} = 87.1$ days, $E(\beta)_{\max} = 0.167$ MeV) on the catalytic properties of WS_2.

Table 1

Characteristics of the obtained WS_2 preparations

No. of preparations	Specific radioactivity of WS_2, mCi/g	Found content S, %	Found content W, %	W : S
1	Nonradioact.	25.59	74.49	1 : 1.99
2	Nonradioact.	25.38	74.43	1 : 1.96
3	9.0	25.13	74.79	1 : 1.93
4	96.6			
Calculated for WS_2		25.89	74.11	1 : 2

The usual method for obtaining a tungsten sulfide catalyst is the process of decomposition of ammonium thiotungstate in a stream of hydrogen at a temperature of 400° (7). However, for the synthesis of radioactive WS_2, we chose, as simpler and safer, a method of heating a mixture of metallic tungsten and elemental sulfur (8). The starting materials were high-purity tungsten (99.99%

W) and extra-pure sulfur (99.999% S). The sulfur containing S^{35} used in the present work was approximately 98.9% pure and amounted to about 1% of the quantity of catalyst being prepared.

The introduction of radioactive sulfur into a nonradioactive preparation in order to obtain samples of elemental sulfur with different specific activity was achieved by joint dissolution in carbon disulfide. The latter was then evaporated at room temperature, and the sulfur crystals were dried to constant weight at 100°. Nonradioactive and radioactive preparations of tungsten disulfide were prepared under identical conditions.

A preliminary study of the interaction of tungsten and sulfur showed that, upon heating stoichiometric quantities of the substances for different times (from 1 to 12 h), samples of WS_2 of identical composition are obtained. In the X-ray diffraction patterns of all samples, taken with Cu radiation, there is no strong reflection (123) of tungsten, which does not coincide with the reflections of WS_2. In a mixture of crystalline W and WS_2, an impurity of tungsten can be detected starting from a content corresponding to the formula $WS_{1.90}$ (9).

Therefore, in the synthesis of tungsten disulfide, mixtures of W and S were kept in a sealed quartz ampoule for 1 hour at a temperature of 800–850°. In this way 3 samples of $\mathrm{WS_2}$ were obtained (Nos. 2, 3, 4, Table 1). Preparation No. 1 differed from the others in that, in its preparation, the stage of dissolving sulfur in $\mathrm{CS_2}$ was omitted.

The specific radioactivity of tungsten disulfide was determined on a gas-flow 4π-counter. A mixture of hydrofluoric and nitric acids was used to convert $\mathrm{WS_2}$ into a soluble state.

Fig. 1. Dependence of the degree of conversion of *n*-decyl alcohol on the $\mathrm{WS_2}$ catalyst (No. 2) on temperature.
1 —heating; 2 —cooling

Fig. 2. Temperature dependence of the yield of unidentified hydrocarbons from *n*-decyl alcohol on a $\mathrm{WS_2}$ catalyst.
1 —nonradioactive $\mathrm{WS_2}$; radioactive $\mathrm{WS_2}$; 2 —9.0 mCi/g; 3 —96.6 mCi/g

In the chemical analysis of the synthesized preparations, the method of reducing $\mathrm{WS_2}$ in a stream of hydrogen was used (^{10}). In this case sulfur is quantitatively converted into hydrogen sulfide, while tungsten is weighed as the metal. Hydrogen sulfide is absorbed by zinc sulfate, and the sulfide formed is determined iodometrically. The results of the analysis of the $\mathrm{WS_2}$ samples obtained and their characteristics are presented in Table 1.

Tungsten sulfide preparations Nos. 1-4 were subjected to X-ray photography with Cu radiation. Table 2 presents the parameters of the crystal

Table 2

Parameters of the $\mathrm{WS_2}$ crystal lattice

Preparation	a, Å	c, Å	c/a	Source
WS_2	3.18	12.50	3.9	(^{11,8})
WS_2, subl.	3.146	12.34	3.924	(^{9})
WS_2.00	3.148	12.33	3.916	(^{9})
WS_1.95	3.150	12.29	3.902	(^{9})
WS_2.05	3.145	12.25		(^{12})
(No. 1,2) WS_1.99	3.15	12.35	3.921	Our preparations
(No. 3,4) WS_1.93	3.18	12.48	3.925	Our preparations

lattice of WS_2. The nonradioactive and radioactive WS_2 samples practically do not differ from one another in their structure. At the same time, the calculated parameters agree with the data available in the literature.

Measurement of the specific surface area of the tungsten disulfide preparations obtained was carried out by low-temperature adsorption of air and gave the following results:

Activity (mCi/g):	–	9.0	96.6
Surface area (m^2/g)	2.8	2.4	3.8
Change in surface area (%)	–	−17	+36

With a measurement accuracy of ±20%, for these comparatively small surface areas it cannot be concluded that, even at a specific radioactivity of about 100 mCi/g, a significant change in the surface area of WS_2 is observed.

The catalytic properties of radioactive WS_2 were investigated using the dehydration reaction of *n*-decyl alcohol as an example. For a tungsten sulfide catalyst, the process of dehydration of alcohols is not characteristic. However, it was studied in works (^{13,14}). It was shown that this reaction proceeds at atmospheric pressure; moreover, in the case of some alcohols, dehydrogenation is observed simultaneously.

The study of the dehydration of *n*-decyl alcohol over WS_2 was carried out by us in a flow-type apparatus (^{15}) in the vapor phase at atmospheric pressure. A catalyst with grain size 1-2 mm was used in the reaction. *n*-Decyl alcohol had the following characteristics: d_4^{30} 0.8231, n_D^{30} 1.4329, and MR found 49.91, calculated 49.95. The alcohol feed rate was 0.17 ml/min. The volume of catalyst taken for the reaction was 0.25 cm^3. The duration of the experiment at each temperature was 15 min.

Fig. 1 shows curves of the dependence of the degree of alcohol conversion on temperature, obtained during heating (curve 1) and cooling (curve 2). Each curve corresponds to a fresh portion of catalyst. At a temperature of 360°, the degree of alcohol conversion proved to be the same in both cases. Subsequently we carried out experiments starting from low temperatures.

Fig. 3. Dependence of the content of α-decene in the olefin mixture on temperature. 1 –nonradioactive catalyst (No. 1); 2 –radioactive $W\overset{x}{S}_2$, 9.0 mCi/g

Figure 1: Fig. 3. Dependence of the content of α-decene in the olefin mixture on temperature. 1 –nonradioactive catalyst (No. 1); 2 –radioactive $W\overset{x}{S}_2$, 9.0 mCi/g

Time of preservation of the catalytic properties of WS_2 decreases with increasing temperature. Thus, at 315° the reaction rate does not change for 50 min, at 335° for 32 min, and at 360° for only 15 min. In addition, separate experiments established that equilibrium at each of the indicated temperatures is reached in 7–8 min. Therefore, the portion of catalyst collected during the first 8 min was discarded.

Fig. 3. Dependence of the content of α-decene in the olefin mixture on temperature. 1 –nonradioactive catalyst (No. 1); 2 –radioactive $W\overset{x}{S}_2$, 9.0 mCi/g

Our study showed that gaseous products are not formed in the course of the reaction under investigation. This indicates the absence of a dehydrogenation reaction of *n*-decyl alcohol. The total amount of olefins was determined by bromometric titration, and the content of the α-isomer in the mixture by infrared spectrophotometry.

After preliminary observations, three series of experiments were carried out: on a nonradioactive catalyst and on radioactive samples of $W\overset{x}{S}_2$ with specific activities of 9.0 and 96.6 mCi/g.

The results are presented in Fig. 2.

In the temperature range 290–360°, the degree of alcohol conversion increases with increasing concentration of the radioactive isotope in the catalyst. For a temperature of 360°, an increase in the degree of alcohol conversion by 50% is observed at a catalyst radioactivity of 9.0 mCi/g and by 80% if the specific radioactivity of $W\overset{x}{S}_2$ is 96.6 mCi/g.

Fig. 3 shows the dependence of the yield of the α-isomer in the olefin mixture on temperature.

As can be seen, on the radioactive catalyst the isomerization of α-decene proceeds to a greater extent than on the nonradioactive one.

Thus, the introduction of the radioactive isotope S^{35} into tungsten disulfide increases its catalytic activity in the dehydration reactions of *n*-decyl alcohol and in the isomerization of the resulting α-decene. It may be noted that, similarly to the dehydration reactions of isopropyl alcohol ([6]) and *n*-dodecanol ([16]) over radioactive catalysts, at low specific radioactivity in the low-temperature region there is observed some decrease in the rate of dehydration of n-decyl alcohol over $W\overset{x}{S}_2$. With increasing

As the specific radioactivity of W^xS_2 increases, the rate of alcohol dehydration increases substantially, but not to the same extent as was observed for various alcohols$^{(6,16)}$ when ionic compounds—$MgSO_4$ or $Ca_3(PO_4)_2 \cdot H_2O$—were used as catalysts.

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References

1. Vikt. I. Spitsyn, *Izv. AN SSSR, OKhN*, 1958, No. 11, 1296; 1960, No. 7, 1325.
2. V. G. Baru, *Usp. khim.*, **32**, issue 11, 1340 (1963).
3. A. A. Balandin, Vikt. I. Spitsyn et al., *DAN*, **121**, 495 (1958).
4. A. A. Balandin, Vikt. I. Spitsyn et al., *DAN*, **137**, 628 (1961).
5. Vikt. I. Spitsyn, G. N. Pirogova, I. E. Mikhailenko, *Izv. AN SSSR, OKhN*, 1962, No. 9, 1515.
6. Vikt. I. Spitsyn, A. A. Balandin et al., *DAN*, **146**, 1128 (1962).
7. S. V. Tatarskii, K. K. Papok, E. G. Semendo, *Neftyanoe khozyaistvo*, **24**, No. 2, 52 (1946).
8. O. Glemser, H. Sauer, P. König, *Zs. anorg. Chem.*, **257**, 241 (1948).
9. P. Ehrlich, *Zs. anorg. Chem.*, **257**, 247 (1948).
10. E. Corleis, *Lieb. Ann.*, **272**, 244 (1886).
11. A. Evan Arkel, *Rec. trav. chim., Pays-Bas*, **45**, 437 (1926).
12. S. M. Samoilov, A. M. Rubinshtein, *Izv. AN SSSR, OKhN*, 1959, No. 11, 1905.
13. A. A. Tolstopyatova, A. A. Balandin et al., *Izv. AN SSSR, OKhN*, 1961, No. 4, 583.

14. S. Landa, O. Weisser, J. Mostecký, *Chem. listy*, **57** (82), 60 (1958).

15. A. A. Balandin, V. I. Spitsyn et al., *Kinetika i kataliz*, **2**, No. 2, 626 (1961).

16. Vikt. I. Spitsyn, I. E. Mikhailenko, G. N. Pirogova, *DAN*, **140**, 1090 (1961).

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