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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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CATALYTIC DEHYDRATION OF ALCOHOLS OVER ANHYDROUS MAGNESIUM SULFATE

The dehydration of alcohols over metal sulfates in the vapor phase has been little studied. The work of Senderens (1) on the dehydration of ethanol over anhydrous calcium sulfate is known, as is Zakharova' s work (2) on the dehydration of methylethylethynylcarbinol over magnesium sulfate (3).

We set ourselves the task of finding the conditions for using magnesium sulfate as a catalyst in the dehydration of alcohols. In the present work the dehydration of the following secondary alcohols has been studied: propan-2-ol, pentan-2-ol, cyclopentanol, and cyclohexanol—and it is shown that these alcohols, at 400–410° and with their being fed at a volumetric rate of 0.4, are dehydrated over anhydrous magnesium sulfate almost completely. The catalytic properties of magnesium sulfate were studied in greatest detail using the dehydration of cyclohexanol as an example. It was established that the only reaction product is cyclohexene. Products of dehydrogenation and isomerization are absent from the catalyzate. Under these conditions the catalyst does not decrease in activity over 500 hr of operation and does not require regeneration. During prolonged dehydration of cyclohexanol at lower temperatures, of the order of 270–330°, however, the activity of the catalyst gradually decreases, and at the 80th–105th hour of operation (Fig. 1) a sharp drop in the yield of cyclohexene is observed.

Fig. 1

We explain this observation by a change in the composition of the catalyst associated with its hydration by the water released in the course of the reaction. In our experiments, hydration of magnesium sulfate occurs over time and gradually encompasses its entire surface.

Siso Hirano (4) indicates in his work the temperatures of transformation of some hydrates of magnesium sulfate into others—from $MgSO_4 \cdot 7H_2O$ to $MgSO_4 \cdot H_2O$.

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According to the authors' data, the transformation of $MgSO_4 \cdot H_2O$ into $MgSO_4$ occurs at 200–300°.

Berg and Nikolaev (^{5}) found that magnesium sulfate loses its last molecule of water in an atmosphere of water vapor in the temperature interval 340–360–370°, whereas when dehydration is carried out in air, loss of the last molecule of water begins at about 280°.

On this basis it may be assumed that, in carrying out our experiments at temperatures below 360–370°, magnesium sulfate evidently has a mixed composition, $MgSO_4 \cdot H_2O$—$MgSO_4$, which should possess lower catalytic activity than anhydrous magnesium sulfate, which can form only at temperatures above 370°.

The correctness of this assumption was confirmed in the work by the fact that our catalyst reached maximum and constant activity at 380–400°.

The influence of other factors, in particular changes in the magnitude and form of the surface, apparently proves to be less significant. In the work it was established that the surface area, determined by the adsorption method using benzene, remains practically unchanged even during prolonged operation of the catalyst.

The kinetics of the dehydration of cyclohexanol, cyclopentanol, propanol-2, and pentanol-2 over magnesium sulfate were also studied in the work. The values of the apparent activation energies were calculated and proved to be rather close to one another. This indicates that the dehydration mechanism is the same for all the alcohols studied, and that the alcohol molecule is oriented toward the catalyst surface by the hydroxyl groups.

Experimental Part

The work was carried out in a flow-type apparatus in a horizontal tubular furnace equipped with automatic feed.

The catalyst used in the work was prepared as follows: magnesium sulfate was placed in the catalytic tube and slowly heated in a stream of dry air. At 100° a noticeable evolution of water began. The largest amount of water was evolved at 150–160°. This temperature was maintained until the evolution of water ceased, after which it was gradually raised to 300°; in this process, a small additional amount of water was still evolved. When the temperature was raised to 400°, no evolution of water was observed.

All experiments were carried out over 30 ml of previously dehydrated magnesium sulfate.

The following were used in the work: cyclohexanol with b.p. 160.5/750 mm, n_D^{20} 1.4640, d_4^{20} 0.9460; cyclopentanol (obtained by hydrogenation of cyclopentanone at 50°, 200 atm hydrogen pressure over skeletal nickel) with b.p. 141°/758 mm, n_D^{20} 1.4520, d_4^{20} 0.9469; propanol-2 with b.p. 82°/755 mm, n_D^{20} 1.3778, d_4^{20}

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0.7888; and pentanol-2 (obtained from *n*-propyl bromide and acetaldehyde by the Grignard reaction) with b.p. 116–117°/744 mm, n_D^{20} 1.4000 and d_4^{20} 0.8087.

The yield of propylene was determined by gas analysis on a VTI apparatus. The yields of cyclohexene, cyclopentene, and pentene were determined by fractionation of the catalyzates or by titration according to Kaufmann' s bromine number method. Both methods gave coincident results. All yields were calculated on the alcohols taken into the reaction.

To determine the dependence of catalyst activity on the duration of its operation, a series of experiments was carried out at 270, 300, 330, and 360°. Cyclohexanol was fed at a space velocity of 0.4. At each temperature, the experiments were carried out for 190 hours over the same portion of catalyst; the activity of the catalyst gradually decreased (Fig. 1).

To explain the reasons for the decrease in catalyst activity, two catalyst samples were investigated—a freshly prepared sample and one that had operated for 80 hours—on an adsorption apparatus with quartz spring balances. Isotherms of benzene vapor adsorption at 0° were obtained.

From these, the specific surface area was calculated, and it was shown that in both samples it is practically identical and amounts to a value not exceeding 20 m^2/g.

The small number of narrow pores present in the freshly prepared sample disappears during prolonged operation of the catalyst.

On the basis of the data obtained, it may be concluded that the decrease in catalyst activity during prolonged operation is not due to a change in the structure of the catalyst. The optimum conditions for dehydration of cyclohexanol, cyclopentanol, and propanol-2 were established by varying the temperature of the experiments and the space velocity of alcohol feed. Each experiment was carried out over a fresh portion of catalyst. The results are given in Table 1.

Table 1

Dependence of the yields (in %) of unsaturated hydrocarbons on the temperature of the experiment and the alcohol feed rate

Experiment temperature, °C	Cyclohexene	Cyclohexene	Cyclopentene	Cyclopentene	Cyclopentene	Propylene	Propylene
Experiment temperature, °C	space velocity of alcohol feed 0.2	space velocity of alcohol feed 0.4*	space velocity of alcohol feed 0.6	space velocity of alcohol feed 0.2	space velocity of alcohol feed 0.4	space velocity of alcohol feed 0.2	space velocity of alcohol feed 0.4

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Experiment temperature, °C	Cyclohexene	Cyclohexene	Cyclopentene	Cyclopentene	Cyclopentene	Propylene	Propylene
350	86.0	88.0	78.0	65.0	75.0	73.0	70.0
360	90.0	90.0	83.0	72.5	80.5	76.0	74.0
370	92.5	92.0	86.0	77.0	81.0	82.0	75.0
380	95.0	95.0	86.0	80.0	83.0	88.0	76.0
390	98.0	98.0	86.0	87.0	86.0	94.0	82.5
400	100.0	100.0	86.0	92.0	93.0	100.0	88.4
410	–	–	86.0	96.0	98.0	98.0	88.0
420	–	–	–	100.0	100.0	95.6	84.5

* At 205° the yield is 44%; at 250°, 79%.

The isolated cyclohexene had constants coinciding with those in the literature (b.p. 81-82°/758 mm, n_D^{20} 1.4470, d_4^{20} 0.8111), and contained no impurity of the isomerization product—methylcyclopentene, as can be judged from the data of spectral analysis.

Spectrum of the dehydration product of cyclohexanol: 276 (2.5); 395(7); 455(1.5); 495(2); 641(1.5); 823(80); 875(2.5); 904(3); 963(2.5); 1020(0); 1038(3); 1068(4.5); 1117(0); 1144(2, b, d); 1223(12); 1243(3); 1267(6); 1296(0); 1342(2); 1352(1.5); 1377(0); 1432(10); 1443(4); 1545(0); 1593(0.5); 1652(25).

Cyclopentene isolated in the dehydration of cyclopentanol had b.p. 43°, n_D^{20} 1.4228, d_4^{20} 0.7791.

The apparent activation energy of the dehydration reaction was determined for cyclohexanol, cyclopentanol, pentanol-2, and propanol-2. This series of experiments was carried out at temperatures of 360–400° with a constant space velocity of alcohol feed equal to 0.4. The kinetic experiments with cyclohexanol and propanol-2 were carried out over 1 ml of catalyst; with cyclopentanol and pentanol-2, over 3 ml. In this case the degree of conversion of the alcohols did not exceed 25-30%. In the present case, the percentage conversion may, without substantial error, be equated to the reaction rate constant, and from the dependence of the percentage conversion on temperature the value of the activation energy can be determined by the Arrhenius equation. The results of this series of experiments are given in Table 2. It is seen from Table 2 that the values found for the apparent activation energy of the alcohols investigated are close to one another. This can be explained by identical orientation of the alcohol molecules toward the catalyst surface. Small differences in the magnitude of the activation energy are then due to the influence of shielding substituents. Another possible explanation is that the slowest limiting

stage in the dehydration of the alcohols studied is one and the same process: desorption of the water formed in the reaction. The question of which of these

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two possibilities occurs in dehydration over magnesium sulfate is of independent importance and will be studied further.

Table 2

Yield of olefins and apparent activation energies in alcohol dehydration reactions

Alcohol	Olefin yield, %, at 360°	Olefin yield, %, at 370°	Olefin yield, %, at 380°	Olefin yield, %, at 390°	Olefin yield, %, at 400°	Apparent activation energy, cal/mol
Cyclohexanol	16.6	17.7	22.1	29.4	32.4	14,980
Cyclopentanol	15.12	17.8	21.12	23.15	25.4	14,370
Pentanol-2*	16.8	18.0	25.5	26.1	28.9	15,190
Propanol-2	13.5	18.8	21.3	28.0	31.68	14,760

* The pentene isolated had b.p. 35–37°, n_D^{20} 1.3807 and d_4^{20} 0.6512.

An additional series of experiments was carried out with cyclohexanol at lower temperatures in the range 260–350° in order to determine the effect of the presence of $MgSO_4 \cdot H_2O$ on the activation energy. The activation energy was found to be 18,200 cal/mol. Evidently, the intermediate hydrates of magnesium sulfate formed as a result of the reaction with water are stable at low temperatures and hinder the dehydration of cyclohexanol.

Thus, in the present work the possibility has been established of using anhydrous magnesium sulfate as a catalyst in the dehydration of secondary alcohols: cyclohexanol, cyclopentanol, pentanol-2, and propanol-2. Dehydration of the indicated alcohols proceeds practically completely at a temperature of about 400° and with their feed at a space velocity of 0.2–0.4.

Anhydrous magnesium sulfate retains its catalytic activity for more than 500 hours of operation at a temperature of 400° and does not require regeneration. Magnesium sulfate does not promote isomerization of the ring in the dehydration of cyclohexanol.

The calculated values of the apparent activation energy for the dehydration of cyclohexanol, cyclopentanol, pentanol-2, and propanol-2 are close to one another. This gives grounds for supposing that the alcohol molecules are oriented identically by their hydroxyl groups with respect to the surface of the catalyst.

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