CONCLUSIONS

1. On the alumina–rhodium catalyst obtained by decomposition of [(CH₃)₂S]₃RhBr₃, hetero-
genized on Al₂O₃, reactions that are typical for platinum-group metals take place: C₂-dehydro-
cyclization, skeletal isomerization, dehydroisomerization, and others.

2. The catalytic, structural, and adsorption properties of the alumina–rhodium catalysts
that we have investigated are determined by their genesis.

LITERATURE CITED

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CONVERSIONS OF ETHERS ON DEHYDRATING CATALYSTS.

4. KINETICS OF DISPROPORTIONATION REACTION

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In the present work, for an elucidation of the possible mechanism of disproportionation
of ethers, we carried out a study of the kinetic relationships of this reaction in the presence
of Al₂O₃ alone and Al₂O₃ treated with HCl (9.3%). We investigated the conversion of a mixture
of diethyl and dipropyl ethers to ethyl propyl ether,

\[
\text{Et}_2\text{O} + \text{Pr}_2\text{O} \rightleftharpoons 2\text{EtOPr}
\]

The kinetic experiments were performed at 200°C on Al₂O₃, and at 175°C, 185°C, and 200°C
on Al₂O₃–HCl.

EXPERIMENTAL

The reaction was carried out in a completely sealed flow-circulating unit at atmospheric
pressure; the original mixture was diluted with nitrogen. Cylinder nitrogen was purified by
passing successively through a column with nickel–chromium catalyst and a trap with zeolite,
chilled by a mixture of dry ice and acetone. The catalyst was regenerated in a stream of air
at 450°C. In all experiments, the catalyst charge was 4 cm³ (2.4 g), and the catalyst particle
size was 1-2 mm. The original mixture of ethers, from thermostated saturators, was passed
through the reactor, and the products were analyzed chromatographically every 10-15 min.
After establishing steady-state operation, the experiment was continued for 45-120 min, with
the activity remaining unchanged. The constancy of catalyst activity was checked in control

†For communication 3, see [1].
TABLE I. Kinetic Data on Disproportionation of Ethers on 
Al₂O₃, with Various Initial Conditions, at 200°C

| U₁ | c₁ | c₂ | c₃ | c₄ | c₅ | rₜ, mmol/ | Degree |
|----|----|----|----|----|----| (h⋅g cat) | dehydration, % |
| liters/h | mmoles/liter | experiment | calculation | | |
| 3,16 | 1,07 | 1,10 | 0,94 | 0,25 | 0,74 | 0,36 | 0,43 | 21,4 |
| 5,26 | 0,97 | 0,20 | 0,87 | 0,25 | 0,74 | 0,36 | 0,43 | 11,8 |
| 10,52 | 1,01 | 0,12 | 0,94 | 0,25 | 0,74 | 0,36 | 0,43 | 9,1 |
| 15,79 | 1,03 | 0,08 | 1,00 | 0,25 | 0,74 | 0,36 | 0,43 | 5,4 |
| 21,05 | 1,06 | 0,06 | 1,05 | 0,25 | 0,74 | 0,36 | 0,43 | 1,8 |
| 5,13 | 0,55 | 0,54 | 0,47 | 0,15 | 0,34 | 0,38 | 0,40 | 22,2 |
| 10,26 | 0,50 | 0,10 | 0,36 | 0,15 | 0,34 | 0,38 | 0,40 | 24,1 |
| 15,39 | 0,51 | 0,08 | 0,41 | 0,15 | 0,34 | 0,38 | 0,40 | 16,7 |
| 20,53 | 0,51 | 0,08 | 0,41 | 0,15 | 0,34 | 0,38 | 0,40 | 13,0 |
| 10,40 | 0,51 | 0,08 | 0,41 | 0,15 | 0,34 | 0,38 | 0,40 | 1,0 |
| 20,79 | 0,53 | 0,04 | 0,39 | 0,15 | 0,34 | 0,38 | 0,40 | 0,0 |
| 10,40 | 0,04 | 1,10 | 0,40 | 0,15 | 0,34 | 0,38 | 0,40 | 16,4 |
| 20,79 | 1,09 | 0,55 | 1,06 | 0,07 | 0,46 | 0,58 | 0,54 | 9,1 |
| 5,10 | 0,23 | 0,54 | 0,22 | 0,11 | 0,35 | 0,28 | 0,34 | 18,5 |
| 10,40 | 1,20 | 0,25 | 1,35 | 0,07 | 0,49 | 0,33 | 0,35 | 8,0 |
| 10,40 | 0,29 | 1,36 | 0,26 | 0,05 | 1,17 | 0,24 | 0,21 | 12,5 |

DISCUSSION OF RESULTS

A test for possible influence of internal diffusion was performed by calculating the Weiss number [3] from the formula

\[ W = \frac{r^* R^2}{3D^* C} \]  \hspace{1cm} (I)

where \( r^* \) is the reaction rate, moles/cm³ catalyst·sec; \( R \) is the mean radius of a catalyst particle, cm; \( D^* \) is the effective diffusion coefficient, cm²/sec; \( C \) is the concentration of the original substance, moles/cm³. The value of \( D^* \) for Et₂O·Pr was taken as \( 10^{-2} \) cm²/sec, corresponding to the extremal value of the effective diffusion coefficient for the system under consideration [4]. The value of the Weiss number calculated by the use of Eq. (I) was 0.08, i.e., \( W < 1 \), indicating that there is no internal-diffusion retardation under the conditions we have selected and that the reaction proceeds in the kinetic region.

The rate of accumulation of the mixed ether was calculated from the formula

\[ r = UC_2/G \]  \hspace{1cm} (II)

where \( U \) is the flow rate, liters/h; \( C_2 \) is the concentration of the mixed ether, mmoles/liter; \( G \) is the quantity of catalyst, g.

In order to account for the reverse reaction, we introduced a correction factor \( \gamma \) [5]. The value of the equilibrium constant, which is needed to calculate \( \gamma \), was assumed as unity [6]. In calculating the disproportionation rate, we took into account the occurrence of the ether dehydration reaction. According to [7], the rate of Pr₂O dehydration at 360°C is five times the rate of dehydration of Et₂O or EtOPr. On the basis of these data, it was considered that it is mainly the Pr₂O that is subject to dehydration. And in fact, as can be seen from Tables 1 and 2, the original concentration ratio Pr₂O/Et₂O in all cases was greater than the ratio of instantaneous concentrations of these substances. In order to determine the influence of the H₂O (formed by dehydration of the ethers) on the disproportionation reaction rate, we performed experiments in which water vapor was present (\( C = 0.27-1.10 \) mmoles/liter). It was established that the addition of water to the reaction mixture in an amount more than 10 times the maximum concentration of H₂O formed in the course of the experiments did not change the disproportionation rate.

A preliminary analysis of the experimental data showed that the dependence of the experiments under selected standard conditions. The original concentrations of Et₂O (\( C_1 \)) and Pr₂O (\( C_3 \)) were varied from 0.25 to 1.4 mmoles/liter. The feedstock space velocity was varied from 800 to 5260 h⁻¹. The highest rate of reactant feed was 20 liters/h, and the circulation rate was 500 liters/h, giving gradientless conditions [2].