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Catalytic Dehydration of Ethers on Nickel Oxide–Silica–Alumina

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The dehydration of diethyl ether was studied on synthetic nickel oxide–silica–alumina catalysts in the temperature range of 340—400 °C and at pressures less than 50 Torr. It was found that ethylene, butenes, water, and small amounts of carbon monoxide and methane were formed on the catalysts of lower nickel content. The rate constant for the formation of butenes showd a maximum on the catalyst of 10 atom% nickel. The mechanism of the formation of the butenes was discussed by studying the catalytic dehydration of various ethers.

The dehydration of alcohols or ethers on solid acid catalysts has been studied for many years.[1,2] However, the dehydration of alcohols or ethers on supported nickel oxide has been reported only rarely. In a series of papers, Pines *et al.*[3] studied the dehydration of alcohols in the presence of hydrogen over supported and unsupported nickel oxide catalysts, and found the following facts: In most of these dehydration reactions, ether is the main product, while the other dehydration products are the paraffins formed by hydrogenation of the olefins produced from the alcohol. Paraffins with one carbon less than the original alcohols are also formed in competition with the dehydration reaction.

In the present research, the reaction of diethyl ether on nickel oxide–silica–alumina catalysts was investigated. It was found that in addition to ethylene, which was a normal dehydration product of the ether, butenes were formed on the catalysts of lower nickel content. The mechanism of the formation of the butenes is studied by investigating the reaction products of various ethers and alcohol.

Experimental

Materials. Nickel oxide–silica–alumina catalysts were prepared by a co-precipitation method with sodium silicate and nickel nitrate solutions in the same way as described elsewhere[4]. The catalysts were sized (1—2 mm) and stored for use after the treatment in a stream of dried air for 16 h at 350°C. Some properties of the catalysts are summarized in Table 1. The specific surface area was obtained by applying the standard B. E. T. method to the adsorption isotherm of nitrogen at −196 °C.

Ethers and ethanol were of guaranteed grade. All of these reagents were distilled in a vacuum and stored in glass reservoirs for use in the reactions.

Apparatus and Procedures. The activities of the catalysts were measured by an all-glass circulatory flow system, 713 ml in total volume. Prior to the reaction, the catalyst was treated *in situ* in a stream of dried air for 16h at 400°C, and then evacuated for 3 h ($\approx 10^{-5}$ Torr) at the same temperature. After admitting 50 Torr of ether vapor to the gas circulation system, a small portion (*ca.* 2 ml) of the circulating gas was withdrawn at intervals from the system for the analysis. The analysis was made by gas chromatographs (6 m benzyl cyanide–$AgNO_3$, 5 m Carbowax 1500 and 1.5 m activated carbon columns) and by a Hitachi RMU-6E mass spectrometer.

Table 1. Catalysts

Catalyst	Composition 100 Ni/(Ni+Si)	Surface area m^2/g
NS-0	0	150
5	5.0	205
10	10	259
20	20	337
40	40	425
50	50	442
80	80	265

Results and Discussion

Figure 1 is an example of the reactions of diethyl ether on the catalysts of lower nickel content. Ethylene, butenes, water, and small amounts of carbon monoxide and methane were formed on the NS-20 catalyst at 360 °C; the initial pressure of the ether was 50.0 Torr. The composition of the reacting mixture, expressed as atom% of the carbon in each molecule, changed linearly with an increase in the reaction time. This fact indicates that all these reactions are zero order with respect to ether pressure. The butenes were produced as an almost equilibrium mixture of 1-butene, *cis*-2-butene, and *trans*-2-butene (1-butene: *cis*-2-butene : *trans*-2-butene=1.0 : 1.6 : 2.2). While carbon monoxide and methane were produced at small rates on the catalysts of lower nickel content, they were produced at much higher rates on the catalyst of NS-80, as shown in Fig. 2. Ethylene was formed only at the beginning of the reaction on this catalyst. No butene was found, but small amounts of ethane and carbon dioxide were found in the products. The ratio of carbon monoxide to methane was found to be almost unity on all the catalysts studied. A material

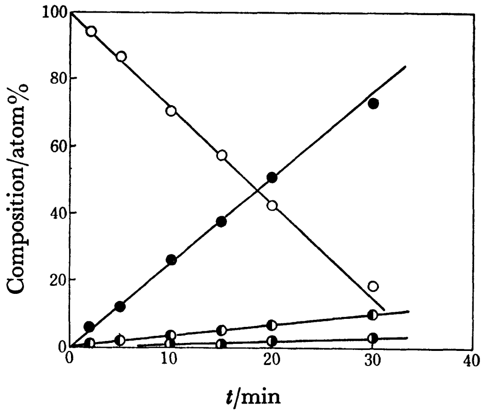

Fig. 1. Reaction of diethyl ether on NS-20 catalyst at 360 °C.
○: Ether, ●: ethylenes, ◑: butenes, ◐: CO+CH_4.

Table 2. Reactions of ethers and ethanol[a)]

Reactant	$[k_s/(\text{mol min}^{-1}\text{ m}^{-2})] \times 10^7$				
	Ethylene	Propene	Butenes	Pentenes	Hexenes
$C_2H_5OC_2H_5$	5.41	—	0.327	—	—
$C_2H_5OC_2H_5$ + Propene	5.32	—	0.301	—	—
$C_2H_5OC_3H_7$	3.20	5.26	0.231	0.107	0.025
$C_3H_7OC_3H_7$	—	28.9	—	—	0.027
C_2H_5OH	7.02	—	0.445	—	—

a) Catalyst: NS-20; temperature: 360 °C.

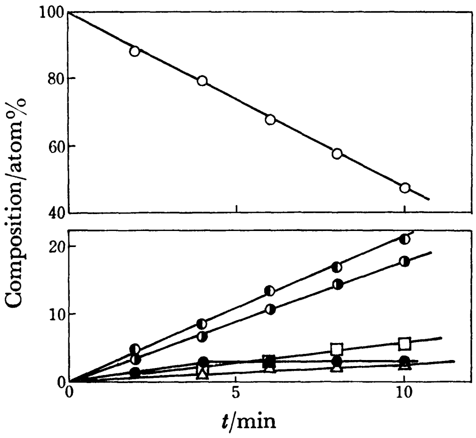

Fig. 2. Reaction of diethyl ether on NS-80 catalyst at 360 °C.
○: Ether, ◐: CO, ◑: CH_4, ●: ethylene, □: ethane, △: CO_2.

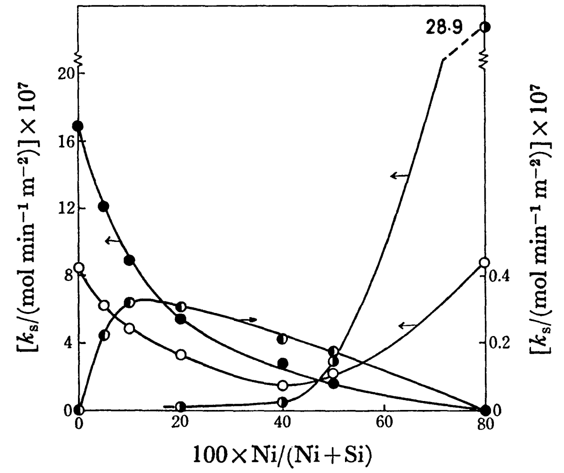

Fig. 3. k_s *vs.* catalyst composition.
○: Ether, ●: ethylene, ◐: butenes, ◑: CO+CH_4.

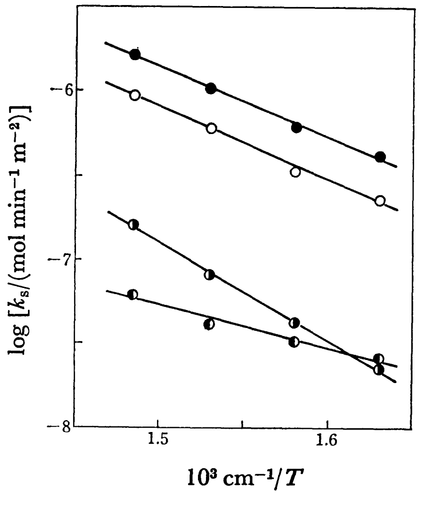

Fig. 4. Arrhenius plots.

		E/(kcal mol^{-1})
○:	Ether	20.6
●:	Ethylene	19.7
◐:	Butenes	12.2
◑:	CO+CH_4	27.7

balance of the products obtained at the reaction time of 10 min revealed that about 50% of the oxygen atoms in the products originated from the catalyst.

The effect of catalyst composition on the catalytic activity is shown in Fig. 3. In this figure, the zero order rate constant per unit surface area of the catalyst (k_s) is plotted against the catalyst composition (atom% of nickel). The rate constant for the consumption of the ether decreases with an increase in the nickel content and then increases with a further increase in the nickel content. This increase observed in the catalysts of higher nickel content (>50%) can be ascribed to the increase in the rates of formation of carbon monoxide and methane. The rate constant for the formation of ethylene decreases with increasing nickel content. On the other hand, the rate constant for the formation of butenes shows a maximum at a nickel content of about 10%.

The effect of temperature was studied by using the catalyst of NS-20, as shown in Fig. 4. The Arrhenius plots of the rate constants are linear and the apparent activation energies obtained are also shown in the figure. The fact that the activation energies of these reactions are different suggests that these reactions take place at different active sites or by different mechanisms. The value of the activation energy for the formation of ethylene falls within the range of the literature values (14—24 kcal/mol)[1)] obtained in the catalytic dehydration on silica and alumina surfaces. As shown in Fig. 3, the rate constant for the formation of ethylene decreases with increasing nickel content until its value becomes zero at the catalyst of NS-80. These facts may suggest that the formation of ethylene takes place on the surface of silica. The formation of carbon monoxide and methane, on the other hand, may take place on the surface of nickel oxide, because carbon monoxide and methane are produced as the main products on the catalyst of high nickel content (NS-80). As to the formation of butenes, it can be presumed that the reaction takes place on the active sites of the dimerization of olefins, because the nickel oxide–silica–alumina is known to be active for the dimerization of olefins.[5–8]

The following three mechanisms can be considered for the formation of the butenes: (1) Ethylene is produced from the ether and desorbed to the gas phase. The desorbed ethylene is again adsorbed on the active sites for the dimerization to form butenes. (2) Ethylene is produced from the ether. The chemisorbed ethylene reacts, before desorption to the gas phase, on the active sites to form butenes. (3) Butenes are formed by the intramolecular dehydration condensation of diethyl ether.

The reactions of various ethers were studied on NS-20 catalyst at 360 °C in order to get an insight into the mechanism of the reaction. The results are summarized in Table 2. In all cases, the rate of formation of olefins could be expressed by a zero-order rate equation, as in the case of diethyl ether. The reaction products of diethyl ether were ethylene and butenes, as described before. Carbon monoxide and methane are not listed in the table, although small amounts of these molecules were produced in every case. When a mixture of diethyl ether (50.1 Torr) and propene (26.1 Torr) was in contact with the catalyst, ethylene and butenes were formed, but neither pentenes nor hexenes were formed. Moreover, the rate constant for the formation of butenes was almost the same as that obtained when only diethyl ether was the reactant. If the reaction takes place according to the first mechanism, it is expected that pentenes and hexenes will also be produced when the reactant is the mixture of diethyl ether and propene. Thus, it is concluded that the first mechanism, *i.e.*, the desorbed ethylene is adsorbed again to form butenes, does not hold in the present case. If the reaction takes place according to the third mechanism, *i.e.*, the intramolecular dehydration condensation, it is expected that only pentenes will be produced in the reaction of ethyl propyl ether. The experimental result obtained with ethyl propyl ether showed that butenes, pentenes, and small amount of hexenes were produced in the molar ratio of 1.0 : 0.46 : 0.11, respectively, in addition to ethylene and propene. This fact indicates that the third mechanism also does not hold in the present case. The result of the reaction with dipropyl ether was almost the same as that obtained for diethyl ether, except that the ratio of the formation of olefin dimer was smaller in the former case. When ethanol was used as the reactant, ethylene and butenes were produced, and the rate constant for the formation of butenes was comparable to that obtained in the reaction of diethyl ether—the former was 1.36 times of the latter. These facts suggest that the second mechanism, *i.e.*, the chemisorbed ethylene which was produced by the dehydration of ether reacts, before desorption, to form butenes, may hold in the present case.

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