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The Isomerization of 1-Butene over the ReO_3 Catalyst

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Synopsis. The catalytic activity of the single crystals of ReO_3 was examined by using the isomerization of 1-butene as a test reaction. The results indicate that there are two types of surfaces: one is sensitive to the introduction of hydrogen, and the other is not.

The isomerization of butenes has been investigated extensively over various metal oxides, including both acidic and basic oxides, such as silica-alumina[1] and alkaline earth metal oxides.[2] In contrast with work with such oxides, little work has been done on single crystals of oxides. This report will deal with the catalytic properties of the single crystals of ReO_3, which have been prepared by different methods.

Experimental

Materials. Rhenium(VI) oxide (ReO_3) was prepared by the following methods. Rhenium(VII) oxide (Re_2O_7) was obtained by oxidizing Re metal (Hermann C. Starck, Berlin, 99.9%) in an oxygen stream.

Sample ♯1: Rhenium(VII) oxide was dissolved in methanol and heated in a CO atmosphere at 90 °C to yield ReO_3. The resulting oxide was washed with water, acetone, and methanol, and then dried under a vacuum at room temperature. An X-ray analysis revealed the oxide to be ReO_3, and an electron-micrographic analysis showed that the particles were in the form of a rectangle. An electron-diffraction pattern and a lattice image of a ReO_3 particle showed that the sample was a single crystal with {100} surfaces.

Sample ♯2: Rhenium(VII) oxide was reduced to yield ReO_3 as in the case of ♯1. The resulting oxide was annealed in air for 1 d at 230 °C, and then washed by acetone, water, and methanol and dried in air at 120 °C. An X-ray analysis revealed the oxide to be ReO_3.

Sample ♯3: Rhenium(VII) oxide was dissolved in water and reduced with H_2 at 300—320 °C. The resulting oxide was ennealed in air at 230 °C for 138 h, washed with water, and dried in air at 120 °C.

Sample ♯4: Rhenium(VII) oxide was dissolved in methanol and reduced with CO and H_2 at 280 °C. The resulting oxide was annealed in air at 230 °C for 1 d.

Sample ♯5: The impregnation of a Re_2O_7–methanol–water solution with silica gel and subsequent CO treatment at 280 °C yielded the oxide, which was washed with methanol and water, heated in air at 230 °C to remove the Re_2O_7, and annealed in air at 180 °C for one night. The atomic ratio of Re/Si was estimated to be 1/3.

Reaction. The isomerization of 1-butene was carried out in a closed recirculation system at 200 °C. The sample oxide was evacuated *in situ* at 300 °C for 3 h prior to use.

Results and Discussion

The results are summarized in Table 1. Samples ♯1 and ♯2 are characterized by intermediate activity, a large hydrogen effect, and no metathesis activity. Samples ♯3 and ♯4 have very low activity. Sample ♯5 shows high activity in the isomerization and the metathesis reaction.

Table 1. Reaction of 1-butene over ReO_3 catalysts

Catalyst	$\frac{\text{Rate}^{a)}}{10^{-5}\,\text{mol min}^{-1}\,\text{g}^{-1}}$	*cis*/*trans*	H_2 effect	$\frac{\text{Surface area}}{\text{m}^2\,\text{g}^{-1}}$
♯1	1.6	1.1	large	12
♯2	3.9	1.2	large	—
♯3	<0.3	—	—	1.7
♯4	<0.3	—	no	—
♯5	23[b)]	1.1	—	136

a) Initial rate; estimated on the basis of the disappearance of 1-butene. b) *Ca.* 20% of the metathesis reaction is included.

A distinct Re line with 4±1G of a full width at half the maximum was obtained by NMR at 300 K for the samples prepared similarly as in Samples ♯3 and ♯4; this indicates that the structure of both samples is pure ReO_3, since this line was not observed in a defective structure of ReO_3, even when the oxide has been identified as ReO_3 by X-ray spectrometry.

A higher activity was obtained when Samples ♯1 and ♯2 were evacuated at a higher temperature (about 500 °C) for a short period during the standard pretreatment. A drastic change in the isomerization rate upon the addition of 100 Torr of hydrogen during the reaction was observed only when the catalyst was evacuated

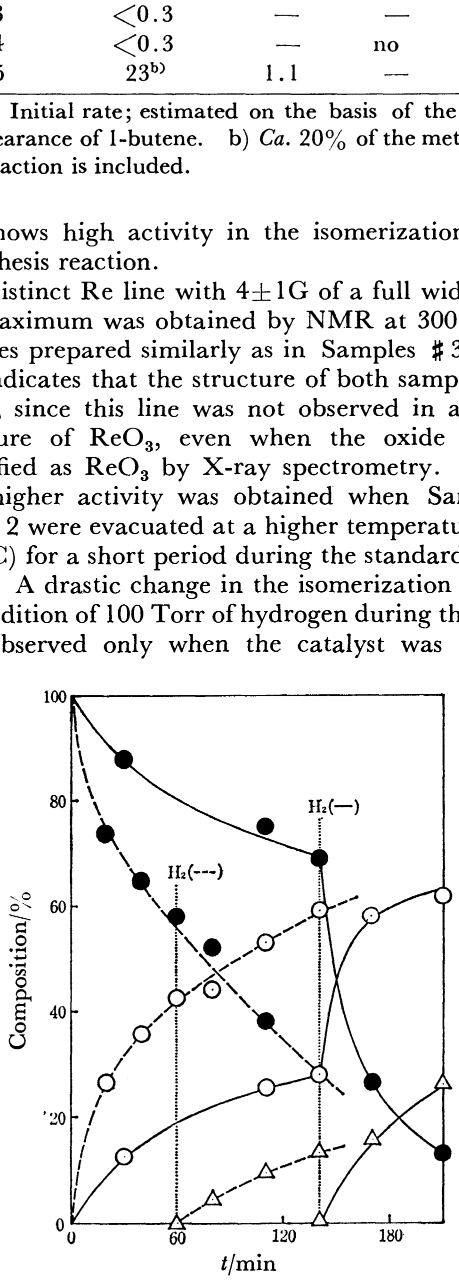

Fig. 1. Reaction of 1-butene over ReO_3 (♯2) catalyst. ——: Evacuated at 300 °C for 3 h, ----: evacuated at 300 °C for 2.5 h and 500 °C for 0.5 h. ●: 1-Butene, ○: 2-butene. △: butane. H_2 (—), H_2 (----): addition of 100 Torr of H_2, corresponding to the lines — and ----, respectively.

under the standard pretreatment conditions (Fig. 1).

Those observations indicate that the isomerization takes place on two types of surfaces; one (Surface I) is sensitive to the nitroduction of hydrogen, while the other (Surface II) is not. The former surface is dominant when the catalyst is prepared by methanol reduction and treated by successive evacuation at 300 °C. The introduction of hydrogen onto Surface I during the reaction caused a large enhancement of the reaction rate, with the formation of butane. This suggests that the isomerization proceeds *via* an alkyl intermediate (probably secondary-alkyl). The addition of one hydrogen atom to the C–C double bond gives the alkyl intermediate, and the following removal of one hydrogen from the intermediate yields 2-butene, or the addition of another hydrogen results in the production of butane.

Surface II is not sensitive to the introduction of hydrogen, and so its proportion may increase upon evacuation at an elevated temperature. This type of surface can be obtained by removal of the oxygen atoms from the surface lattice or by the partial decomposition of ReO_3 to ReO_2; the resulting surface will be highly defective. The exposed Re atom may act as a Lewis acid center. An increase in the region of the Surface II may be accompanied by the destruction of the Surface I.

Catalysts ♯3 and ♯4 showed low activity. This could be attributed to their lower surface area. However, if we consider the observation that even the addition of hydrogen during the reaction did not bring about any increase in the reaction rate, it seems more likely to conclude that the pure single crystals of ReO_3 do not have the Surface I and are tolerant of such a reduction upon evacuation that will bring about catalytically active sites.

The highest activity was obtained in Catalyst ♯5. This catalyst was the only one that gave the metathesis products. The acidic centers, which were produced by the combination of two oxides, may be responsible for the isomerization reaction, since it is known that the combination of two oxides can produce a new acidic center,[3] which will then act as an active center for the isomerization.

References

1) J. W. Hightower and W. K. Hall, *Chem. Eng. Prog. Symposium Series*, **63**, 122 (1959).

2) K. Tanabe, N. Yoshii, and H. Hattori, *J. Chem. Soc., Chem. Commun.*, **1971**, 464; H. Hattori, N. Yoshii, and K. Tanabe, *Proc. 5th Intern. Congr. Catal.*, **10**, 233 (1972).

3) K. Tanabe, T. Sumiyoshi, K. Shibata, T. Kiyoura, and J. Kitagawa, *Bull. Chem. Soc. Jpn.*, **47**, 1064 (1974).