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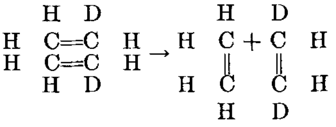
Adsorption of Ethylene on Supported Rhenium Oxide Catalysts

We are investigating the kinetics and mechanism of the disproportionation (*1*) of monodeuterated ethylene over supported rhenium oxide catalysts:



$$2\,H_2C{=}CHD \rightarrow H_2C{=}CH_2 + HDC{=}CHD$$

Products are analyzed by use of the mass spectrograph. The kinetics are relatively simple with this olefin, because the reaction proceeds essentially at adsorption equilibrium.

In the course of the study we have determined volumetrically the adsorption of nondeuterated ethylene on supported catalysts at room temperature. The results for alumina-based and silica-based catalysts are shown in Figs. 1 and 2, respectively, for catalysts containing 10 wt% of rhenium heptoxide. Adsorption of ethylene on the supports alone is rapid and completely reversible, as indicated by the superposition of the adsorption and desorption curves. Catalysts prepared by impregnation with rhenium oxide and pretreated in flowing air at 500°C behave similarly for rhenium content up to 20 wt%, the highest value investigated. But, in addition to a small amount of reversibly adsorbed ethylene, reduction of alumina-supported catalysts with hydrogen at 500°C gives rise to a considerable amount of slow, irreversible adsorption, which increases with reduction time, reaching a constant value after about 15 hr. Points on the ascending branch were taken at 1 hr intervals and those on the descending branch every 10–15 min.

Reduced silica-supported catalysts behave differently. Slow irreversible adsorption appears for intermediate reduction times, but disappears with continued reduction as adsorption becomes rapid and completely reversible again.

We have no firm explanations for the results yet. But it appears that an intermediate state of oxidation of rhenium oxide may exist on the surface, which adsorbs ethylene irreversibly and is far more resistant to reduction on alumina than on silica. Experimental evidence that transition metal oxides are more difficult to reduce on alumina than on silica is found in the work of Biloen and Pott (*2*). Oxidation states of rhenium oxide on oxidized, par-

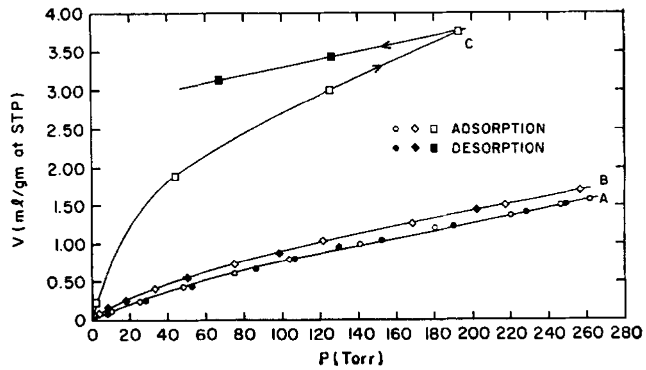


FIG. 1. Adsorption of ethylene at room temperature on: (A) alumina (reversible); (B) air oxidized (500°C) 10% Re_2O_7 on alumina (reversible); (C) hydrogen reduced 10% Re_2O_7 on alumina, 15 hr or more reduction at 500°C (irreversible).

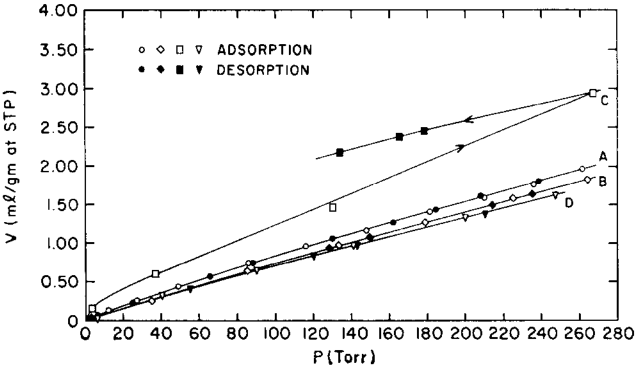


FIG. 2. Adsorption of ethylene at room temperature on: (A) silica (reversible); (B) air oxidized (500°C) 10% Re_2O_7 on silica (reversible); (C) hydrogen reduced 10% Re_2O_7 on silica, 2.5 hr reduction at 500°C (irreversible); (D) hydrogen reduced 10% Re_2O_7 on silica, 15 hr reduction at 500°C (reversible).

tially reduced and drastically reduced catalysts may be Re_2O_7, ReO_3 and ReO_2, with ReO_3 the state which adsorbs ethylene irreversibly. The effect of oxidation state on the kinetics of the disproportionation reaction will be studied.

ACKNOWLEDGMENTS

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