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LETTERS TO THE EDITORS

The Hydrogenolysis of Alkanes on Metallic Molybdenum on Alumina

$Mo(CO)_6$ on dehydroxylated alumina heated in flowing helium to between 300 and 500°C and then in flowing hydrogen at 650°C ($(MoCO)_6$/DA;He,300–500°C;H_2, 650°C) consists of ca. 3- to 4-nm particles of metallic molybdenum on Al_2O_3 which still contains about 0.01 C per Mo (*1, 2*). Further heating in H_2 to 950°C removes the residual carbon but results in no detectable change in catalytic activities and selectivities. $MoO_3/\gamma\text{-}Al_2O_3$;$H_2$,950°, produces what is essentially the same material (*1, 2*). At 500°C, MoO_3/Al_2O_3 with less than one monolayer loading cannot be reduced below Mo(IV)/Al_2O_3, but at 600°C some Mo(III) appears to be formed (*3*). Neither reduction at temperatures greater than about 600°C nor studies of catalytic activity of MoO_3/Al_2O_3 reduced below Mo(IV) appear to have been reported before Ref. (*2*). Both the Mo(0)/Al_2O_3 catalyst prepared from $Mo(CO)_6/Al_2O_3$ and that from MoO_3/Al_2O_3 were essentially the same in the amount of oxygen consumed in titration at 500°C ($O_2/Mo = 3$), in susceptibility to poisons, in behavior on regeneration, in catalytic activity for the hydrogenolyses of propane and cyclopropane, and in that for the hydrogenation of propylene (*1, 2, 4*). In particular, both catalysts have the same high activity for the hydrogenolysis of propane at 250°C and the same selectivities for single and double hydrogenolysis (*1, 2*). A number of other alkanes were studied on Mo(0)/Al_2O_3 prepared by $Mo(CO)_6$/DA; He,300–500°C;H_2,650–950°C (*5*). After Ru, these Mo(0)/Al_2O_3 catalysts are among the most active hydrogenolysis catalysts so far reported. The rate of any skeletal isomerization must have been less than 0.02 that of hydrogenolysis (*5*). The results given above have been confirmed in more recent work (*6*). In Refs. (*1, 2, 4–6*), the O_2 contents of the mixtures flowing over the catalyst were measured at the reactor and maintained below 0.03 ppm. Metallic Mo itself is clearly active for hydrogenolysis although perhaps its surface becomes converted to carbide during reaction but with little loss of hydrogenolytic activity.

Holl *et al.* (*6–8*) have recently employed XPS to study the reduction of MoO_3/Al_2O_3 By H_2,950°C. They concluded that the Mo(VI) was reduced nearly to the state of metallic molybdenum (*7*). They studied the reaction of several alkanes in hydrogen at 350°C on a commercial molybdenum powder pretreated H_2,500°C,15 h (*8*), and on a MoO_3/Al_2O_3 pretreated H_2,950°C (*9*). At 350°C, both materials exhibited a weak activity for skeletal isomerization (about 0.001 that of Pt) and a much lower activity for hydrogenolysis. In one case in a flow reactor, a sample of 4 wt% Mo catalyst with ~80 μmol of Mo, 350°C, and a flow rate of 10 $cm^3\ min^{-1}$ gave 2.4% conversion of 2-methylpentane (mostly bond-shift isomerization), whereas, in Ref. (*1*), a 7.4 wt% Mo catalyst containing 2 μmol of Mo, 249°C, and 74 $cm^3\ min^{-1}$ gave 6% hydrogenolysis of propane. There was some difference in the ratio, alkane/H_2, which was 0.0067 in Ref. (*9*) and 0.038 in Ref. (*1*).

Unfortunately Holl *et al.* did not comment upon the drastic difference in hydrogenolytic activity noted above since they had not come upon Refs. (*1, 2, 4*) and stated that "Up to now, no one has studied the high-temperature reduction (between 550 and 950°C) of alumina-supported MoO_3 catalysts" (*7*).

Holl *et al.* found that evaporated Mo film

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was a hydrogenolysis catalyst unlike Mo powder, but they decided that it was Mo powder; H_2,550°C,15 h, that was characteristic of Mo metal, in part, because injection of pulses of O_2 and H_2O at 350°C into the reactant flow or further heating of the Mo powder to 950°C had little effect upon the catalytic character of the catalyst (*8*). They concluded that the O_2 adsorbed from injections was removed by H_2,350°C, and that the H_2,550°C treatment produced a clean surface of Mo. The contrary assumption that the Mo powder and the Mo/Al_2O_3 of Holl *et al.* were contaminated in all of the situations just described, probably by oxygen adsorbed from the reactant stream, is equally compatible with the data. Oxygen is extracted from H_2 by $Mo(0)/Al_2O_3$ at 300°C and not removed from Mo metal by H_2 until temperatures much above 550°C (see Fig. 2 of Ref. (*1*)). Since hydrogenolysis by $Mo(0)/Al_2O_3$ is extremely sensitive to poisoning by O_2, CO, H_2O, and even to some extent by N_2 (*1*), we suggest that surface contamination resulting from oxygen in the reactant streams of Holl *et al.* led to drastic poisoning of hydrogenolysis. The suggestion must be tentative since Holl *et al.* did not describe purification procedures for hydrocarbons or gases, nor did they report measurement of the O_2 content of the reactant mixture at the catalyst.

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