the main catalytic species, for both the hydrogenolysis of sulfur compounds and the hydrogenation of olefins. Additionally, it could also explain some part of the isomerization activity. The fact that the optimal Mo/Co atomic ratio in many industrial catalysts is often lower than 4 could be explained by the formation of a solid solution of the Co^{2+} in the Al_2O_3 carrier (*4*). With an appreciable part of the cobalt being thus withdrawn, more cobalt would be necessary to obtain the ideal value in the supported mass, and the overall Mo/Co ratio would be appreciably smaller than 4.

An X-ray crystallographic study, however, does not reveal any mixed sulfide phase no matter what the Mo/Co ratio may be. The only known mixed sulfide, $CoMo_2S_4$ (*7, 8*), has a very low catalytic activity when tested under the same conditions. It does not show up in our catalysts, even in those subjected to a recrystallizing heat treatment at 1100°C under an inert atmosphere. Under these conditions, the X-ray patterns showed the lines of the hexagonal and rhombohedral forms of MoS_2 and those of the cubic form of Co_9S_8.

Our results do not give any conclusive indications concerning the nature of the species or associations forming in the sulfided mass for compositions corresponding to maximum activities. This active species could be a mixed amorphous sulfide, a very poorly crystallized molybdenum sulfide doped with cobalt, or even a composite catalytic mass made of two distinct poorly crystallized phases.

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Received October 26, 1970; revised March 11, 1971

Catalytic Effect of Palladium on Hydrogen Reduction of Metal Oxides

There is considerable experimental evidence (*1–5*) that, for a supported metal catalyst, hydrogen atoms chemisorbed at the metal can (1) migrate to the catalyst support, (2) participate in chemical reactions on the support, and (3) chemically reduce the support. The presence of a metal, such as palladium or platinum, on certain metal oxides has been shown to decrease the reduction temperature of the oxide presumably by the process of hydrogen atom formation on and migration away from the metal. In the studies of platinum on tungsten oxide, qualitative in-formation on the reduction was obtained from the observed color change (*2, 3*). In the case of palladium or platinum on an alumina support containing small amounts of iron oxide, the reduction to metallic iron was noted by means of ESR (*4*). Also, the rate of hydrogen reduction of nickel oxide has been shown to depend on the type of supported metal (*5*).

The present communication is concerned with the catalytic effect of palladium on bulk reduction of metal oxides heated in hydrogen. By means of thermogravimetric analysis (TGA), we investigated the effect of palladium on the rates of hydrogen reduction of three powdered metal oxides, MoO_3, WO_3, and Fe_2O_3 (Matheson, Coleman and Bell, reagent; Sylvania Electric Products; and Baker, reagent; respectively). The TGA was run on about 50-mg samples heated at a rate of 5°C/min in flowing hydrogen (50 cm^3/min) at atmospheric pressure. Palladium was applied to the oxides by slurrying 1 g of each of the metal oxides with 1 ml of a solution of palladium chloride in 0.06 *N* HCl, and by subsequent evaporation of the solution to dryness at 130°C in air for 1 hr. Oxide samples without palladium were slurried only with 0.06 *N* HCl and dried.

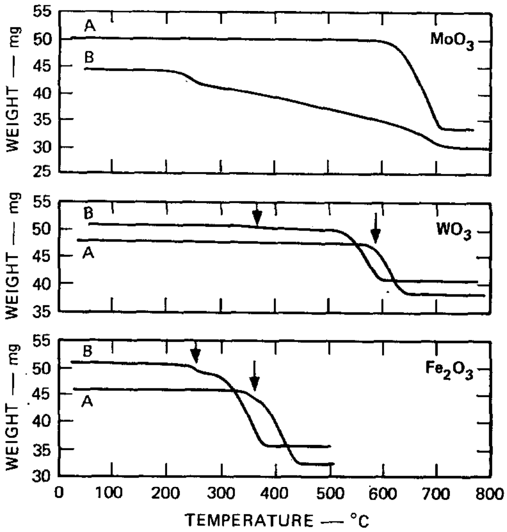

FIG. 1. Thermogravimetric analyses during hydrogen reduction of the metal oxides MoO_3, WO_3, and Fe_2O_3 (Curve A) and of the metal oxides with 1 wt% palladium (Curve B). Arrows indicate inflections in curves.

The TGA curves in Fig. 1 for the three oxides show that the presence of 1 wt% palladium caused a decrease in the temperature required for onset of reduction. The final weight losses measured correspond to complete reduction to metal, within ±0.7% of the theoretical values. At lower temperatures, reduction to intermediate oxidation states is apparent from the inflections in the curves and marked by arrows. By this criterion intermediate oxide reduction of MoO_3 appears to start 400°C lower than it does in the absence of palladium. In the case of Fe_2O_3, the presence of palladium caused a somewhat greater decrease of the reduction temperature to the intermediate oxide (100°C) than to the metal (60°C). In separate experiments it was shown that reduction to the intermediate oxide corresponded essentially to complete conversion to Fe_3O_4. A palladium loading of 0.1 wt% palladium produced about the same result as 1 wt%. In the case of WO_3, the presence of palladium produced a relatively smaller decrease of reduction temperature (30°C) to both the intermediate oxide and the metal.

The relatively rapid bulk reduction to the intermediate oxides (requiring about 5 min for Fe_2O_3 and MoO_3 at about 250°C) may result from hydrogen atom migration throughout the bulk. This mechanism may also apply in the case of reduction to the metal. However, in the latter case, we cannot rule out a nucleation step perhaps provided by palladium metal such as Nowak (*6*) suggests. Alternatively, bulk reduction may be affected by the lability of lattice oxygen which is reported (*7*) to be significant for MoO_3 and WO_3.

The results of the present study have significance to heterogeneous catalysis on such supported metal catalysts. First, certain metal oxide impurities, either indigenous to the catalyst or deposited from the feedstream, may be reduced readily and alter the character of the catalyst. Second, on certain supports the reservoir of hydrogen in the bulk as well as at the surface may make an important contribution to the catalytic reaction.

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Received March 9, 1971