JOURNAL OF CATALYSIS 23, 295–300 (1971)

NOTES

Catalytic Activity of Cobalt and Molybdenum Sulfides in the Hydrogenolysis of Thiophene, Hydrogenation of Cyclohexene, and Isomerization of Cyclohexane*

The catalysts used for the hydrogen treating of petroleum fractions (hydrodesulfurization, hydrocracking, etc.) combine, as active elements, a Group VIb metal (molybdenum or tungsten) with a Group VIII metal (cobalt, nickel, or sometimes iron) supported on a carrier. These catalysts have several chemical functions, e.g., hydrogenolysis of sulfur and organic nitrogen compounds, hydrogenation, dehydrogenation, and isomerization. The atomic ratio of the Group VIb metal to the Group VIII metal, for which maximum activity of the first two functions has been observed, differs with different authors and varies between 1 and 5 (*1*). According to results obtained by Ahuja, Derrien, and Le Page (*2*), the optimum ratio is close to 3.5–4. Cooperation clearly exists between both metals. This cooperation has received no satisfactory explanation up to now (*3*).

In standard hydrotreating catalysts, the carrier, usually alumina, partially combines with the Group VIII metal, thereby changing the concentration of the active metals. We decided to simplify the catalytic system by taking unsupported masses.

All studies carried out previously were made on oxides and their associations (*4, 5*), although hydrotreating catalytic masses always operate under more or less sulfiding conditions. We set ourselves the goal of making sulfides directly.

EXPERIMENTAL PROCEDURE

The catalysts were prepared by reacting molybdenum oxide MoO_3 (obtained by the air decomposition of ammonium paramolybdate at 600°C) and cobalt oxide Co_3O_4 (obtained by air roasting the nitrate at 600°C) in the right proportions in a 20% aqueous solution of ammonium sulfide. The slurry, maintained at 70°C, was continuously stirred for 6 hr until evaporation to dryness. The solid mass obtained was treated for 4 hr at 500°C by a sulfiding mixture of 20% H_2S and 80% Ar. A subsequent vacuum treatment (400°C, 10^{-2} mm Hg) produced the experimental catalysts.

The sulfur content was determined by the combustion of the prepared masses in a quartz tube, adsorption of the combustion gases in a diluted aqueous solution of H_2O_2, and determination of the sulfate content of this solution.

The preparation method applied to pure MoO_3 yielded a compound with a composition corresponding to MoS_2. Applied to Co_3O_4, it produced a compound with a composition corresponding to Co_9S_8.

The X-ray patterns of the catalytic masses showed only three or four very broad lines corresponding to the most intense reflections of MoS_2. The strongest line of Co_9S_8 ($d = 1.76$) appeared when the ratio $Co/Co + Mo$ was greater than 0.50.

The catalytic samples were sieved to produce particles having a diameter of be-

---

* This paper is part of a doctoral thesis by G. Hagenbach.

TABLE 1
SURFACE AREA DATA

Co/Co + Mo	Surface area (m^2/g)
0	26
0.05	25
0.1	23
0.15	23
0.20	21
0.25	21
0.40	23
0.5	22.5
0.6	24.3
0.8	23.6
1.0	29

tween 0.6 and 1 mm. Their surface area was measured by the BET method (Table 1). Their activity was determined by treating a feed containing 70% by weight of cyclohexane, 30% of cyclohexene, and 5000 ppm of thiophene. The fixed-bed reactor was maintained at 300°C by a regulated electric furnace. The feed, at a rate of 1 cm^3/min, and the hydrogen, at a rate of 600 cm^3/min were mixed and run through the reactor by downflow at 20 vol/vol/hr.

The start-up procedure consisted of charging the catalyst, flushing the equipment with argon to remove air, and heating under argon to the desired temperature. Hydrogen was then substituted for argon and the pressure adjusted to 30 kg/cm^2 by a Grove regulator. An initial 1-hr period was considered to be sufficient for bringing the reactor and the product recovery system to a steady state and the catalyst to equilibrium.

Activity data were obtained by gas-chromatographic analysis of the products, which consisted of methylcyclopentane, cyclohexene, cyclohexane, and thiophene. No tetrahydrothiophene was obtained. Before analysis, the liquid product was stripped countercurrently with nitrogen to rid it of the hydrogen sulfide formed in the hydrogenolysis of the thiophene.

Conversion was defined as follows: *Hydrogenation of cyclohexene (wt%):* 100 (initial cyclohexene *minus* remaining cyclohexene)/initial cyclohexene; *isomerization of cyclohexane (wt%):* 100 (methylcyclopentane formed)/(initial cyclohexane *plus* initial cyclohexene); *hydrogenolysis of thiophene (wt%):* 100 (initial thiophene *minus* remaining thiophene)/initial thiophene.

RESULTS AND DISCUSSION

A simple mechanical mixture of the pure sulfides MoS_2 and Co_9S_8, prepared independently as indicated above, gives a catalyst whose activity in the hydrogenolysis of thiophene, for instance, is exactly the sum of the activities of each part of the mixture (Fig. 1).

On the other hand, if a *blend* of the oxides is subjected to the treatment, the mixed sulfide mass has an activity which is considerably greater than the sum of the activities of the simple sulfided masses. This conclusion holds for the hydrogenolysis of thiophene (Fig. 1), the hydrogenation of cyclohexene (Fig. 2), and the isomerization of cyclohexane to methylcyclopentane (Fig. 3). The result is obtained when the specific activities (activities

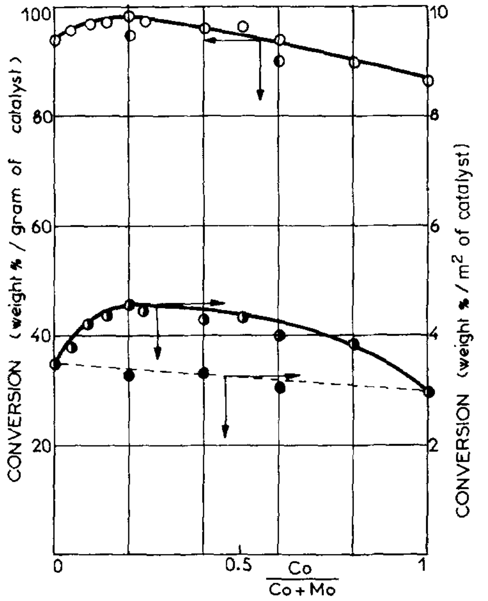

FIG. 1. Hydrogenolysis of thiophene at 300°C. ○, ◑, sulfided catalysts obtained from the blend of the oxides; ●, catalysts obtained by blending the individually prepared sulfides; and ◐, industrial catalysts.

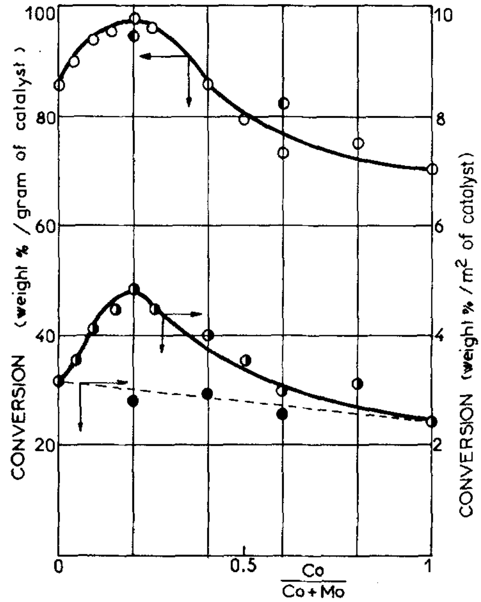

FIG. 2. Hydrogenation of cyclohexent at 300°C. ○, ◑, sulfided catalysts obtained from the blend of the oxides; ●, catalysts obtained by blending the individually prepared sulfides; and ◐, industrial catalysts.

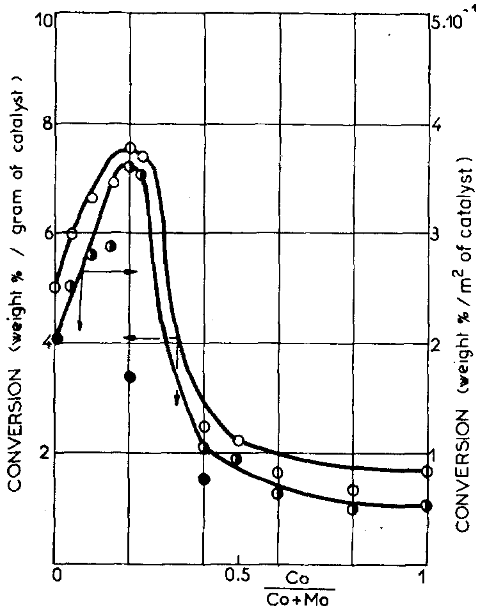

FIG. 3. Isomerization of cyclohexane at 300°C. ○, ◑, sulfided catalysts obtained from the blend of the oxides; ●, catalysts obtained by blending the individually prepared sulfides; and ◐, industrial catalysts.

per gram) are considered. When taking into account the specific surface area of the samples, it is possible to calculate the intrinsic activities (activities per unit surface area). Figures 1, 2, and 3 show that the same conclusion is valid when intrinsic activities are considered.

The cooperative effect of molybdenum and cobalt observed in supported industrial catalysts (*3*) is retained in mixed sulfided masses. Cooperation exists for thiophene hydrogenolysis, olefin hydrogenation, and hydrocarbon-chain isomerization. The conclusion with regard to isomerization suggests that the association of the sulfides themselves possesses a surface acidity. If the catalytic consequences are considered, it can be concluded that the acidity is quite appreciable. This acidity is completely independent of the acidity contributed by the carrier in industrial catalysts. This result agrees with that of Kolboe and Amberg (*6*) who, by studying a MoS_2 catalyst, concluded in the existence of weakly acid sites, which are not of the Brønsted type.

It is interesting to try and compare the activities of the sulfided masses with those of industrial catalysts. For a comparison of specific activities, the most sensible basis is the activity *per weight of deposited sulfides* (instead of the total weight of the catalyst). For computation, it is assumed that 65% of the deposited oxides are converted to sulfides (*2*). The activity thus defined will be called the "specific" activity. The specific activities of the sulfided masses in hydrogenolysis and hydrogenation are very similar to the "specific" activities of industrial catalysts with the same Co/Co + Mo ratio (Figs. 1, 2). A comparison of the intrinsic activities is much more difficult, because the fraction of the total surface area contributed by the sulfides is not known with sufficient accuracy.

Maximum activity, either specific or intrinsic, is observed for a Mo/Co ratio very close to that observed for certain supported catalysts (*2*). This result could suggest that it is the intimate association of molybdenum and cobalt in sulfided form which, in some hydrotreating catalysts, constitutes 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.

References

1. Mitchell, P. C. H., "The Chemistry of Some Hydrodesulfurization Catalysts Containing Molybdenum," Climax Molybdenum Co. Ltd., London, 1967.
2. Ahuja, S. P., Derrien, M. L., Le Page, J. F., *Ind. Eng. Chem. Prod. Res. Develop.* **9**, 272–281 (1970).
3. Richardson, J. T., *Ind. Eng. Chem. Fund Am.* **3**, 154–158 (1964).
4. Lipsch, J. M. J. G., Schuit, G. C. A., *J. Catal.* **15**, 163–189 (1969).
5. Ashley, J. H., Mitchell, P. C. H., *J. Chem. Soc.* (A) **11**, 2821–2827 (1968).
6. Kolboe, S., Amberg, C. H., *Can. J. Chem.* **44**, 2623–2630 (1966).
7. Van den Berg, J. M., *Inorg. Chim. Acta* **2**, 216–218 (1968).
8. Chevrel, R., Sergent, M., Prigent, J., *C. R. Acad. Sci. Ser. C* **267**, 1135–1136 (1968).

G. Hagenbach
Ph. Courty
B. Delmon*

Institut Francais du Pétrole
Laboratoire de Catalyse et de Chime du Solide
92-Rueil-Malmaison, France
(*) *Professor, Univ. of Louvain, Belgium*

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-