JOURNAL OF CATALYSIS 90, 147–149 (1984)

NOTES

Heterogeneous Hydrodeoxygenation of Ketones and Alcohols on Sulfided NiO–MoO_3/γ-Al_2O_3 Catalyst

The conversion of ketones and alcohols into the corresponding hydrocarbons is an important reaction in organic chemistry. This transformation often requires multistep procedures and new improved methods are always of interest.

Methods based on heterogeneous hydrodeoxygenation (HDO) of ketones and alcohols on a Ni/Al_2O_3 catalyst were recently proposed by Maier *et al.* (*1, 2*), but, as mentioned by the authors, the major drawback was a lack of reactivity of strained or sterically hindered ketones. Single-metal sulfides can also be used as heterogeneous catalysts (*3*) for the transformation of ketones and alcohols into hydrocarbons, but they require drastic experimental conditions (temperature ≥ 300°C, hydrogen pressure ≥ 100 bar).

Taking into account this previous work on the catalytic properties of supported metals and metal sulfides, we have tested the hydrodesulfurization catalyst, sulfided NiO–MoO_3/γ-Al_2O_3, in HDO of a representative collection of ketones and alcohols and have used a temperature of 250°C and a hydrogen pressure of 40 bar. Experiments were carried out in a 0.3-liter stirred autoclave (Autoclave Engineers type Magne-Drive), operating in a batch mode and equipped with a system for sampling of liquid during the course of the reaction. The HDS catalyst used was Procatalyst HR 346, which has the composition: 3% NiO, 14% MoO_3, and 83% Al_2O_3. It was sulfided at atmospheric pressure using a fluidized-bed technique with a gas mixture of 15% H_2S and 85% H_2 by volume (gas flow 120 ml/min) with temperature being raised from 20 to 400°C at 8°C/min and then held at 400°C for 4 h. Analyses were performed on a Girdel 3000 gas chromatograph equipped with a flame ionization detector and using nitrogen as carrier gas. Three types of column were used: OV 17 (3% on Chromosorb Q 80/100, 3 m × ⅛ in.); SE 30 (10% on Chromosorb WHMDS 80/100, 3 m × ⅛ in.), and squalane (20% on Chromosorb PANDMCS, 5 m × ⅛ in.). Products were identified by comparison with authentic samples. Rate constants were deduced from experimental curves by curve fitting and simulation using an HP computer equipped with an HP 9826 A tracing table.

The experimental results (see Table 1) show that an industrial catalyst such as sulfided NiO–MoO_3 supported on γ-alumina can achieve transformation of ketones and alcohols into corresponding hydrocarbons in nearly quantitative yield, with a better reactivity than that observed by Maier *et al.* (*2*) in the case of cyclopentanone and 2-norbornanone and under less drastic experimental conditions than those reported by Weisser and Landa (*3*).

The first step for the conversion of ketones into hydrocarbons is the hydrogenation of the ketone to the corresponding alcohol which was shown to be the rate-determining step of the overall process. For the transformation of alcohols into final hydrocarbons, two ways have to be considered depending on the possibility of alcohol dehydration:

(i) If alcohols can undergo dehydration (entries **1** to **4** in Table 1), they are dehydrated to an olefin which is then reduced to a saturated hydrocarbon. This mechanism is usually postulated in hydrotreating processes, particularly in the hydrogenation of alcohols on polyfunctional sulfided catalysts, the source of protons needed for the

0021-9517/84 $3.00

TABLE 1

Hydrodeoxygenation of Ketones and Alcohols on Sulfided NiO–MoO_3/γ-Al_2O_3 Catalyst (T = 250°C; p_{H_2} = 40 bar)

Entry	Compound	k_I[a] (min^{-1} g · cat.$^{-1}$)	Final product	Yield %
1	2-Octanone	5.1×10^{-2}	*n*-Octane	95
2	Cyclopentanone	5.4×10^{-2}	Cyclopentane	90
3	Cyclohexanone	5.3×10^{-2}	Cyclohexane	95
4	2-Norbornanone	2.6×10^{-2}	Norbornane	95
5	Adamantanone	6.6×10^{-2}	Adamantane	90
6	Benzophenone	4.4×10^{-2}	Diphenylmethane	90
7	1-Adamantanol	91×10^{-2}	Adamantane	90
8	2-Adamantanol	28×10^{-2}	Adamantane	90
9	Diphenylmethanol	39×10^{-2}	Diphenylmethane	95

[a] Rate constants of disappearance of ketones (entries **1** to **6**) or alcohols (entries **7** to **9**).

process being the acid surface of the sulfided catalyst (*3*). Under the experimental conditions reported in this work, olefin is barely detectable; however, at lower temperature (175°C), olefin was shown to be an intermediate. From our results, the possibility of direct hydrogenolysis of the C–OH bond cannot be definitely ruled out.

(ii) If alcohols cannot undergo dehydration (entries **5** to **9** in Table 1) because of the implications of Bredt's rule, the C–OH bond is directly hydrogenolyzed to give the corresponding hydrocarbon.

Numerous investigations have aimed at establishing the mechanism of hydrogenation of ketones in the liquid phase leading to an overall conception based on the general scheme represented by the Horiuti–Polanyi type of reaction mechanism (*4–7*). Most of these investigations were carried out by using supported metals or metal sulfides and, to our knowledge, no kinetic data are available on supported bimetallic sulfided catalysts.

From this preliminary study, three points are noteworthy:

(i) The rate constants of hydrogenation of ketones on a supported bimetallic sulfided catalyst do not vary significantly for the compounds studied. This behavior contrasts with the hydrogenation of ketones on Pt/SiO_2 or Ru/SiO_2 where the rates of hydrogenation depend on the ring size (*5*).

(ii) We have observed a lesser selectivity in the hydrogenation of 2-norbornanone into endo- and exo-2-norbornanols (65% endo and 35% exo) on sulfided NiO–MoO_3/γ-Al_2O_3 than in reduction on metal catalyst (*4*). Such a lesser selectivity is frequently observed with sulfided catalysts (*3*).

(iii) The rate constants of direct hydrogenolysis of alcohols are of the same order of magnitude. This reaction is expected to behave like hydrogenolysis of alcohols on oxide-supported metals (*2, 8, 9*), i.e., through the formation of carbenium ion intermediates, because of the relative acidity of the catalysts. There is no evident relationship between the rate constants and the stability of carbenium ion intermediates in the rate-determining step because diphenylmethanol should give a more stable carbenium ion than either 1- or 2-adamantanol and the rate of hydrogenolysis is not particularly enhanced.

Experimental work is under way to obtain results which should enable the mechanism of hydrodeoxygenation of ketones and alcohols to be defined. Nevertheless, the main feature to be noted is the easy conversion of ketones and alcohols into corresponding hydrocarbons on a sulfided industrial catalyst in nearly quantitative yield.

REFERENCES

1. Maier, W. F., Bergman, K., Bleicher, W., and Schleyer, P. von R., *Tetrahedron Lett.* **22,** 4227 (1981).
2. Maier, W. F., Thies, I., and Schleyer, P. von R., *Z. Naturforsch.* **37b,** 392 (1982).
3. Weisser, O., and Landa, S., "Sulphide Catalysts, their Properties and Applications," p. 150, Pergamon, Oxford, 1973.
4. Rylander, P. N., "Catalytic Hydrogenation in Organic Synthesis," p. 82. Academic Press, New York, 1979.
5. Geneste, P., Bonnet, M., and Rodriguez, M., *J. Catal.* **57,** 147 (1979).
6. Bonnet, M., Geneste, P., and Rodriguez, M., *J. Org. Chem.* **45,** 40 (1980).
7. Teratani, S., Tanaka, K., Ogawa, H., and Taya, K., *J. Catal.* **70,** 347 (1981).
8. Bonnet, M., Geneste, P., and Lozano, Y., *C.R. Acad. Sci. Paris, Ser. C,* **282,** 1009 (1976).
9. Hall, W. K., *Acc. Chem. Res.* **8,** 257 (1975).

R. DURAND
P. GENESTE[1]
C. MOREAU
J. L. PIRAT

Laboratoire de Chimie Organique Physique Appliquée
UA 418.CNRS
Ecole Nationale Supérieure de Chimie de Montpellier
8, rue Ecole Normale
34075 Montpellier Cedex
France

Received June 24, 1983

---

[1] To whom correspondence should be addressed.