JOURNAL OF CATALYSIS 44, 320–323 (1976)

Parameters Affecting the Reorganization of Supported Metals

Sintering of supported metal catalysts under reaction conditions is particularly undesirable in that it usually leads to permanent deactivation by loss of metal area and gain in crystallite size. Recent studies have shown that low temperature sintering of silver and of nickel results from surface diffusion of these metals (*1*). Agreement has been observed between experimental observations and the theoretical predictions of the dependence of the kinetics of sintering on temperature, metal thickness, and the nature and pressure of the ambient gas.

The theory also predicts that the rate of sintering should be dependent on the chemical and physical state of the support surface and on the difference in surface energy between the support and the metal. Recent quantitative studies have confimed this prediction for silver sintering in oxygen (*2*, *3*): the present note reports preliminary measurements to show that the same processes are important for other metals (*4*, *5*).

Studies have been carried out using copper, nickel, and silver films in the presence of hydrogen or oxygen. Four supports were used for each metal; namely, flame blown silica, quartz, magnesia, and sapphire. Approximately 1000 Å of metal was evaporated onto the surface of the clean support, and the sample was then placed in a reactor through which the appropriate gas was passed. The sample was then brought to the required temperature (±1°C) as rapidly as possible, left for some time, and then cooled. The extent of reorganization was then checked by electron optical examination in a JEOL Jem 7 transmission electron microscope and a Cambridge Instruments Stereoscan scanning microscope.

No reorganization was observed with the Ni/O_2 and Ag/H_2 systems, but extensive reorganization occurred in all other cases. Some of the results obtained with silica and sapphire, the two supports that showed most difference in behavior, are shown in Figs. 1 and 2. In all cases, hydrogen-accelerated reorganization occurred at considerably higher temperatures than oxygen-accelerated reorganization, as would be expected from the known effects of oxygen on rates of surface diffusion (*1*, *6*).

It is known that reorganization of metals in these types of systems proceeds in a sequence of hillock formation, hole formation, island formation, and final equilibration of the islands (*1*, *2*). In these terms, reorganization of silica-supported metals had occurred to a greater extent than sapphire-supported metals in the presence of both gases. Comparison of Fig. 1C and 1D shows that silica-supported nickel had reorganized to the point of producing islands, while sapphire-supported nickel had reorganized to the point of hole formation only. Although copper had reorganized almost completely over both supports (Fig. 1E and 1F), the islands were closer to their equilibrium shape over silica (*1*).

Again, in the presence of oxygen, hillock formation had occurred to a much greater extent for copper on silica as compared to copper on sapphire (Fig. 2a and 2b),

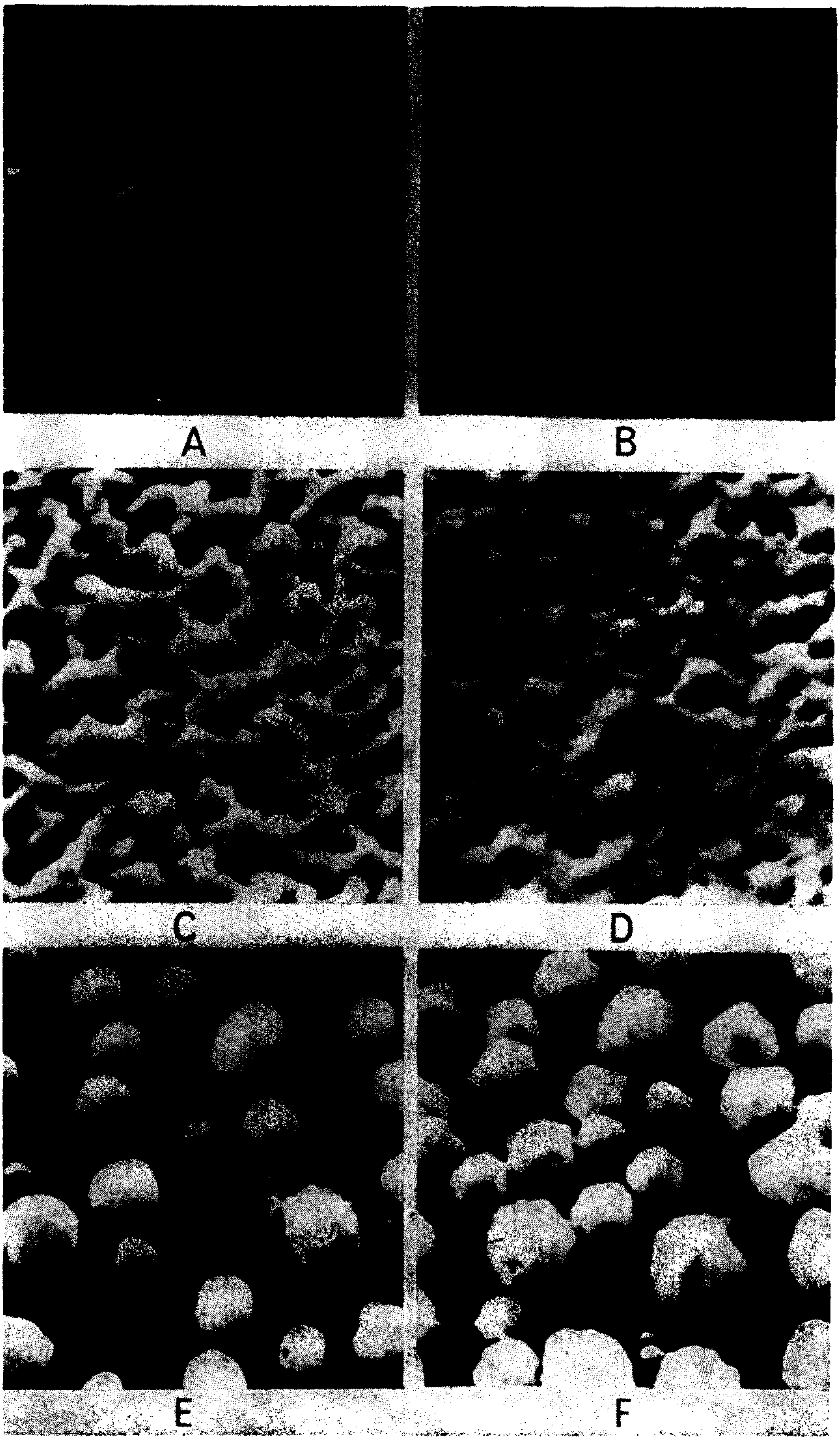

FIG. 1. Hydrogen-accelerated sintering. (A) Ni/SiO_2: as deposited; × 5200. (B) Ag/SiO_2: as deposited; × 5200. [Cu/SiO_2 is indistinguishable from this.] (C) Ni/SiO_2: 600°C; 60 min; × 9600. (D) Ni/Sapphire: 600°C; 60 min; × 9600. (E) Cu/SiO_2: 680°C; 20 min; × 9600. (F) Cu/Sapphire: 680°C; 20 min; ×9600.

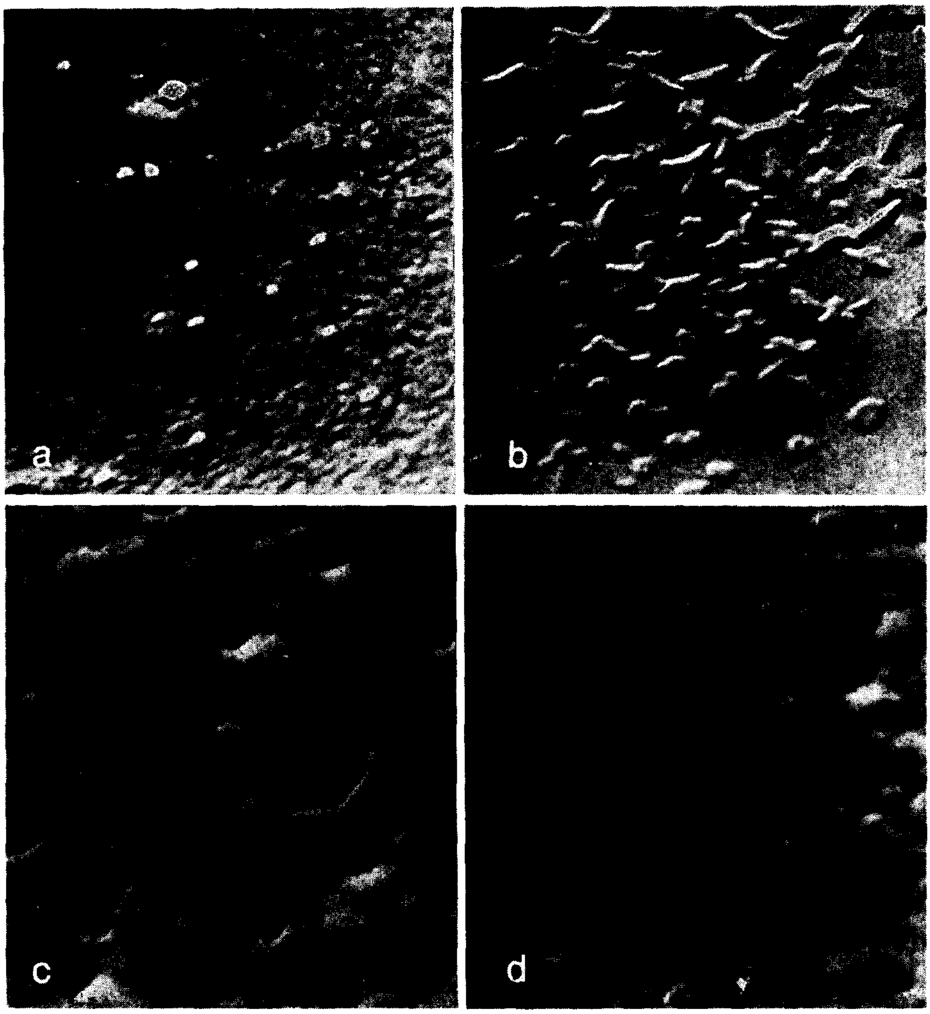

FIG. 2. Oxygen-accelerated sintering. (a) Cu/SiO_2: 270°C; 50 min; × 5200. (b) Cu/Sapphire: 270°C; 50 min; × 5200. (c) Ag/SiO_2: 245°C; 45 min; × 8800. (d) Ag/Sapphire: 245°C; 45 min; × 8800.

while hole formation was more advanced for silver on silica than for silver on sapphire (Fig. 2c and 2d).

The results show that the rate of reorganization of the metal is dependent on the nature of the metal (cf. Fig. 1C and 1E), on the support (cf. Fig. 1C and 1D) and on the ambient gas (cf. Figs. 1E and 2a). Quantitative assessment of the relative importance of these different factors has been obtained for silver (*1*, *2*), and further work is in progress to elucidate the nickel–hydrogen, copper–oxygen, and platinum–oxygen systems.

ACKNOWLEDGMENT

The authors wish to thank Pilkington Brothers for valuable financial support.

REFERENCES

1. Presland, A. E. B., Prince, G. L., and Trimm, D. L., *in* "Progress in Surface Science" (S. G. Davison, Ed.), Vol. 3. Pergamon, New York, 1973.

2. Riassian, M., Trimm, D. L., and Williams, P. M., *J.C.S. Faraday I*, **72**, 925 (1976).
3. Riassian, M., Trimm, D. L., and Williams, P. M., submitted to *J. Catal.*
4. Ponsolle, L., Wrobel, G., Debut, D., and Mutte, J. C., *in* "Microscopie Electronique" (P. Favard, Ed.), Vol. 2, p. 355. 1970.
5. Dalmai-Imelik, G., and Leclerq, C., *in* "Microscopie Electronique" (P. Favard, Ed.), Vol. 2, p. 359. 1970.
6. Gjostein, N. A., *in* "Surfaces and Interfaces" (J. J. Burk, N. L. Read, and V. Weiss, Eds.), Syracuse Univ. Press, Syracuse, New York, 1967.

M. RIASSIAN
D. L. TRIMM
P. M. WILLIAMS

Department of Chemical Engineering and Chemical Technology
Imperial College
London S. W. 7, England

Received September 3, 1975