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# Formation of a Supported-Metal Catalyst by Aggregation of Rhodium Complexes

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Catalysts have been prepared incorporating mononuclear Rh bonded to pendant monoamine or phosphine groups linked to silica. $H_2$ at about $7 \times 10^4$ N/m$^2$ and 377°K caused reduction and aggregation of the metal on the monoamine-modified silica; aggregation took place similarly, but more rapidly, on the phosphine-modified silica. In flow-reactor experiments with ethylene hydrogenation, the metal aggregation was evidenced by increases in activity of each catalyst with time on stream. The Rh crystallites formed by aggregation in the presence of $H_2$ were characterized by transmission electron microscopy and found to be nearly uniform in size, being 16–17 and 12–15 Å, respectively, for the amine- and phosphine-containing catalysts.

## INTRODUCTION

Metal catalysts are usually applied as crystallites containing hundreds or thousands of atoms dispersed on a high-surface-area porous metal-oxide support. A distribution of metal crystallite sizes almost always makes it difficult to determine the dependence of catalytic character on the metal crystallite size and surface structure, and there is a need for new methods of preparing supported-metal catalysts to allow systematic experiments with samples having crystallites nearly uniform in size and structure.

The recent literature reports a number of preparative methods whereby catalysts have been formed from materials initially incorporating unique mononuclear complexes or molecular clusters bonded to the support (e.g., *1–6*). With control of the rates of chemical reactions of the attached complexes or clusters and control of the rate of diffusion of the metal species on the support, one might expect to tailor the size distribution of the resulting crystallites; the distribution is expected to be influenced by the metal, the ligands originally bonded to the metal, and the composition of the support.

In the work reported here, we have bonded mononuclear rhodium complexes to silica through pendant phosphine and amine ligands. Under appropriate conditions, the metal has been found to experi-

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ence aggregation on the silica surface, giving small crystallites of nearly uniform size. The supported metals, before and after aggregation, have been characterized by catalytic activity measurements for ethylene hydrogenation, carbonyl infrared spectroscopy, and transmission electron microscopy.

## EXPERIMENTAL METHODS

*Materials.* The modification of the silica support to incorporate pendant $-(CH_2)_3PPh_2$ groups and, alternatively, $-(CH_2)_3NHC_6H_{11}$ groups, and the attachment of Rh species onto each support by contacting it with a solution of $Rh_6(CO)_{16}$ in benzene have been described previously (*7*). The two samples designated (*8*) as P1 (incorporating Rh attached to phosphine-modified silica) and MA1 (incorporating Rh attached to monoamine-modified silica) each contained 1.1 ligands/$nm^2$, and the Rh contents were 0.24 and 0.66 wt%, respectively. These values correspond to ligand-to-$Rh_6$ cluster ratios of 53 and 68, respectively.

For the infrared spectroscopy experiments, carbon monoxide (Linde, 99.99%) and $^{13}CO$-enriched carbon monoxide (Merck, Sharpe, and Dohme, 90 atom% $^{13}CO$) were used without further purification. $H_2$ (Linde) had a purity of 99.999%. For the catalytic activity measurements, cylinder gases ($H_2$ and He; Linde, industrial grade) were purified to remove traces of water and $O_2$ (*9*). Ethylene (Linde, C. P. grade) was used as received.

*Infrared spectroscopy.* Powders of the catalyst material were pressed into self-supporting wafers (20 mg/$cm^2$) between paper discs at pressures of about $6 \times 10^6$ N/$m^2$ and were mounted in an evacuable infrared cell, described previously (*10*). Spectra were recorded with a Perkin-Elmer model 225 spectrometer. An optically equivalent silica wafer was used to compensate the reference beam, and the globar was usually run at about 25% of its maximum power to avoid adverse heating effects. The spectral slit width was about 1.7 $cm^{-1}$ at 2000 $cm^{-1}$.

*Electron microscopy.* Particles of the catalyst material suspended in chloroform were collected on a support using the well-known drop method. The support was a 20-Å carbon film, which was produced by vacuum deposition onto freshly cleaved mica using a special electron impact evaporator (*11*) at $4 \times 10^{-5}$ N/$m^2$. The films were floated off and mounted on 400-mesh copper grids. When prepared in this way, the catalyst showed contrast sufficient to allow recognition of the shapes and dimensions of the Rh species in conventional bright-field electron microscopy. The micrographs were obtained with a Siemens EM 102 electron microscope with an instrumental magnification of 314,000× and an accelerating voltage of 100 kV; an objective aperture of 80 μm and a double condenser illumination were used.

*Catalytic activity measurements.* Conversion data for the ethylene hydrogenation reaction were collected with a conventional steady-state flow reactor interfaced to a gas chromatograph. The apparatus (*12*) and methods (*9*) have been described elsewhere. The conversions initially were differential (typically <1%), determining reaction rates directly, but as the catalyst aged, the conversion rose, no longer falling in the differential range.

## RESULTS AND DISCUSSION

### *Rh-Amine Catalysts*

It has been shown (*8*) that the combination of $Rh_6(CO)_{16}$ with the monoamine-modified silica yielded a solid exhibiting infrared bands at 2085 and 2003 $cm^{-1}$, which were assigned as the symmetric and antisymmetric carbonyl stretching frequencies of a mononuclear rhodium carbonyl complex containing a $Rh(CO)_2$ moiety. This complex may be described formally as $L_nRh(CO)_2$, where $n$ designates an unknown number of surface-bound amine ligands. Decarbonylation of this species led to a decrease in the intensities of these two carbonyl stretching bands and to the simultaneous formation of a new single band at 1943 $cm^{-1}$, which was assigned (*8*) as the terminal carbonyl stretch of a $L_mRhCO$ complex (where *m* is unknown). Decarbonylation–carbonylation $[L_nRh(CO)_2 \underset{+CO}{\overset{-CO}{\rightleftharpoons}} L_mRhCO]$ was completely reversible at temperatures up to about 430°K; at this temperature the surface-bound amine ligands began to experience thermal degradation.

The stability of the amine-bound complexes when exposed to a $H_2$ atmosphere depended strongly on temperature and $H_2$ partial pressure. A sample activated by evacuation at 418°K for 1 hr showed the typical bands at 2085, 2003, and 1943 $cm^{-1}$. During subsequent exposure to $H_2$ at $1.3 \times 10^3$ $N/m^2$ at 393°K for 3 hr, the bands remained unchanged in position, but the 2085 and 2003 $cm^{-1}$ bands decreased in intensity to about 60% of their initial values, whereas the 1943 $cm^{-1}$ band increased in intensity to about 117% of its initial value. These changes were completely reversed by reexposure of the sample to CO. It is therefore clear that $H_2$ at low pressures caused a partial decarbonylation of the solid incorporating the $L_nRh(CO)_2$ and $L_mRhCO$ species. It is not clear whether the latter complex contained Rh-H species; on the one hand we expect that hydrogen had to be bound to the metal center to displace the CO (unless it reacted with CO), but on the other hand the position of the monocarbonyl species is the same as that formed by simple evacuation of the sample. Unfortunately, the low Rh concentrations (and probably a low extinction coefficient of the Rh-H vibration) prevented this group from being detected in the infrared spectra.

Exposure of a slightly decarbonylated sample to an atmosphere of $H_2$ at $6.7 \times 10^4$ $N/m_2$ and 350°K led to only a small reduction of the carbonyl band intensities. As the temperature was raised to 377°K, however, substantial decarbonylation was observed, with only a weak carbonyl spectrum (exhibiting bands at 2083, ~2000, and 1945 $cm^{-1}$) remaining after 20 hr reaction in $H_2$. The spectra observed after recarbonylating this sample are shown in Fig. 1. The bands characteristic of the $Rh(CO)_2$ moiety (at 2083 and 2003 $cm^{-1}$) and that characteristic of the RhCO moiety (at 1943 $cm^{-1}$) can be discerned clearly, although they exhibit much lower intensities than those of the original carbonylated sample. $^{13}CO$ produced the appropriate shifts of these bands to 2038 and 1958 $cm^{-1}$ and to 1900 $cm^{-1}$, respectively, as observed previously (*8*). An additional pronounced shoulder near 2020 $cm^{-1}$, indicated by M(CO) in Fig. 1

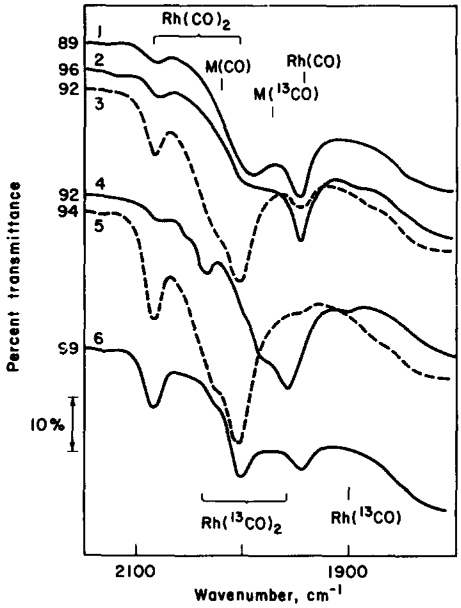

FIG. 1. Carbonyl infrared spectra of the amine-modified silica catalyst containing Rh (sample MA1) after treatment in $H_2$ at $6.7 \times 10^4$ $N/m^2$ at 350°K: (1) after reduction of $H_2$ partial pressure to 67 $N/m^2$; (2) after pumping for 10 min ($1.3 \times 10^{-2}$ $N/m^2$) at cell temperature; (3) 5 min after addition of CO at $1.3 \times 10^3$ $N/m^2$ and cell temperature; (4) after removal of CO and admission of $^{13}CO$ at $6.7 \times 10^2$ $N/m^2$ after 15 min at cell temperature; (5) after recarbonylation by heating in $^{12}CO$ for 0.5 hr at 348°K and 0.5 hr at 368°K in CO at $3.3 \times 10^4$ $N/m^2$; (6) after evacuation for 0.5 hr at cell temperature.

(and absent from the spectrum of the original sample), was pronounced on carbonylation. $^{13}CO$ shifted this band to 1980 cm$^{-1}$. The corresponding carbonyl species was very labile, being removed on evacuation.

A further increase to 390°K in the temperature of the $H_2$ treatment at $6.7 \times 10^4$ N/m$^2$ led to a further decrease in the intensities of the carbonyl bands characteristic of the mononuclear Rh complexes, while the new band at 2020 cm$^{-1}$ simultaneously increased in intensity.

The darker color of the initially light-brown sample after this treatment in $H_2$ suggested that an aggregation of Rh atoms to give metal crystallites had occurred. [The benzene solution of $Rh_6(CO)_{16}$ used for the attachment was light violet.] The new carbonyl stretching band observed near 2020 cm$^{-1}$ (shifted to 1980 cm$^{-1}$ by $^{13}CO$) supports this suggestion, since similar band positions have been reported for CO adsorbed on alumina-supported Rh metal (*13, 14*) and on porous evaporated Rh films (*15, 16*). A band position of 2045 cm$^{-1}$ was reported (*6*) for CO adsorbed on Rh crystallites about 15–20 Å in diameter, which had been formed from aggregation of Rh clusters attached to a phosphine-functionalized polystyrene matrix after controlled oxidation of the phosphine groups. The changes in spectra observed for polymer-supported rhodium as aggregation led to the crystallite formation (*6*) are similar to those reported here, and the present results are also suggestive of the various spectra for very small particles of rhodium on zeolites and larger particles (crystallites) on alumina reported by Primet (*17*).

Electron microscopy confirmed the suggestion of formation of metal crystallites from the silica-supported rhodium complexes. No metal particles could be detected in the original material, and evidently they were not present, since some of the electron micrographs provided so much detail that even the lattice planes of the spherical silica particles (having a separation of 3.7 Å) could be distinguished. [This result confirms the conclusion from the infrared data that the original $Rh_6$-octahedron (having a diameter of about 7 Å) broke up on attachment of the metal to the modified silica.] Figure 2 shows an electron micrograph of the $H_2$-treated material with which the above-mentioned infrared experiments had been carried out. A few metal particles can be clearly identified; the diameters are nearly uniform in the range 16–17 Å. The density of crystallites evident in these micrographs is small, reflecting a result demonstrated by the infrared spectra, namely, that part of the rhodium bound to the support still existed in the form of mononuclear complexes.

The catalysis experiments provided a further, qualitative, confirmation of the aggregation of the Rh in these samples. The activity of the catalyst in the flow reactor (measured as the percentage conversion of ethylene and hydrogen to ethane) at 329°K with partial pressures of ethylene and $H_2$ equal to $1.6 \times 10^4$ and $8.9 \times 10^4$ N/m$^2$, respectively, increased with time on stream from an initial value of about 0.3%. After 27 hr, the conversion had increased to 1%; after 48 hr, to 12%; and after 54 hr, to 87%. As the conversion increased, the temperature rise in the reactor, resulting from the exothermicity of the reaction, became significant. When the conversion was 12% the temperature was 329°K, as it had been for lower conversions, but after the conversion had increased to 87% the temperature had increased to 337°K. The range of conversion for which the temperature was significantly in excess of 329°K is indicated with a dashed line in Fig. 5. The catalyst removed from the reactor had the gray color characteristic of aggregated Rh on silica. We conclude that the increasing activity reflected metal agglomeration.

### *Rh-Phosphine Catalysts*

As described previously (*8*), the combi-

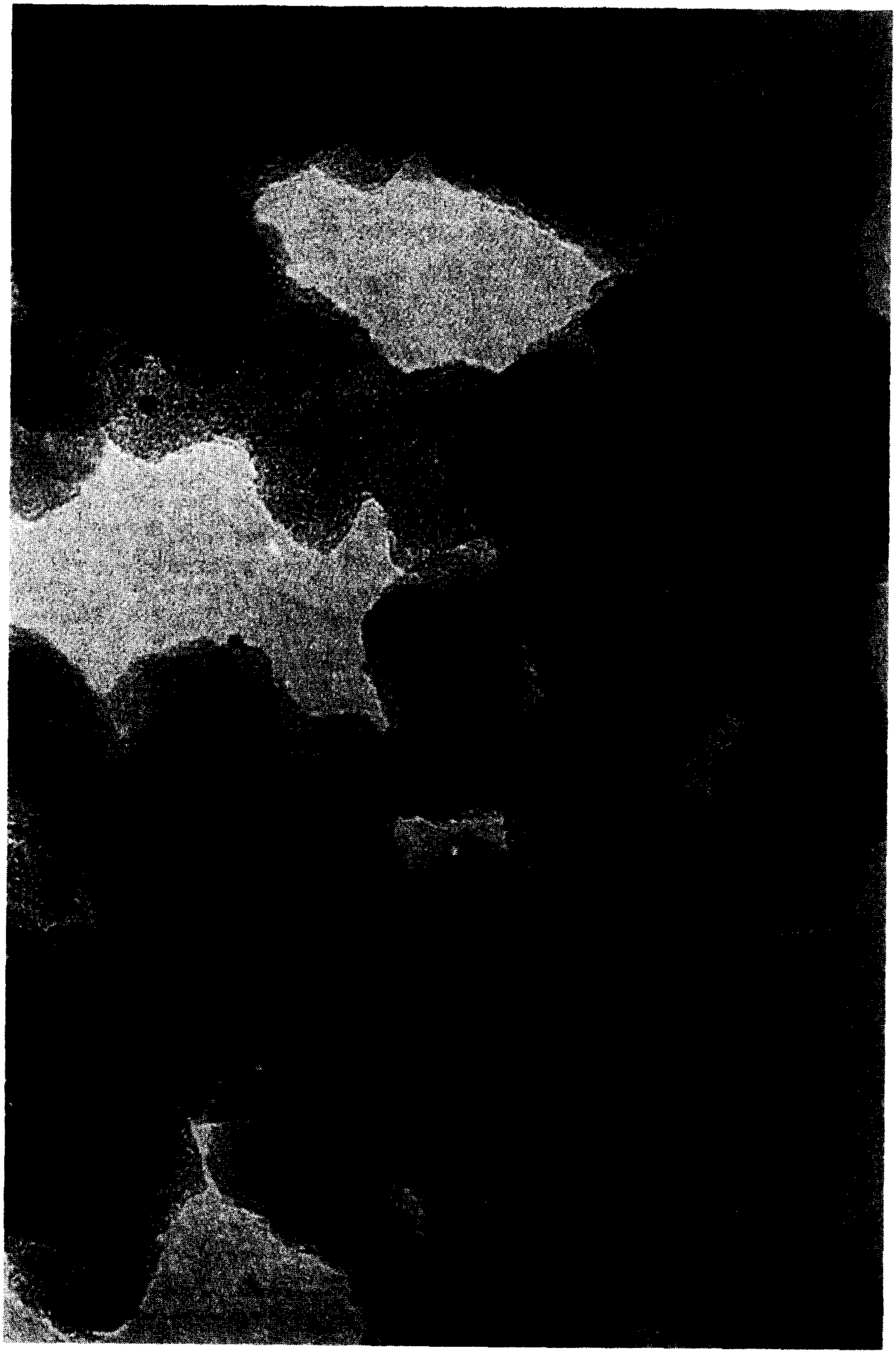

FIG. 2. Electron micrograph of the amine-modified silica catalyst containing Rh (sample MA1) after $H_2$ treatments in infrared experiments. Rh crystallites are clearly visible.

nation of $Rh_6(CO)_{16}$ with the phosphine-modified silica yielded a more complex spectrum than the one observed with the amine-modified sample. Principal carbonyl stretching bands were observed for the fresh carbonylated P1 catalyst at 2069 and 1989 $cm^{-1}$, the latter band being somewhat broader than the former. On evacuation of the sample at 373°K, the bands decreased in intensity, and the 1989 $cm^{-1}$ band also shifted to 1983 $cm^{-1}$. These effects were readily reversed by reexposure to CO at temperatures as high as 470°K. The high-frequency band (at 2069 $cm^{-1}$) has been assigned (*8*) as the symmetric carbonyl stretching vibration in a $Rh(CO)_2$ moiety, and the low-frequency band (1989 $cm^{-1}$) has been identified as a composite, representing contributions from the antisymmetric stretch of a $Rh(CO)_2$ moiety and from the carbonyl stretch of a RhCO moiety. Thus, the infrared spectra show that the $Rh_6$-octahedron was broken up during attachment of Rh onto phosphine-modified silica, as it was during attachment onto amine-modified silica. Decarbonylation analogously led to a RhCO species; the CO ligands in this species seemed to be much more tightly bound in the supported-phosphine than in the supported-amine complex.

A P1 sample activated by evacuation at 370°K showed the typical bands of the $Rh(CO)_2$ and RhCO species. Exposure to an atmosphere of $H_2$ at $1.3 \times 10^3$ $N/m^2$ and 370°K for 45 min led to decreases in intensities of both bands. The 2069 $cm^{-1}$ band remained unchanged in position, but the 1989 $cm^{-1}$ band shifted to approximately 1982 $cm^{-1}$, and this shift was not reversed by subsequent evacuation. After 45 min, the intensities of the 2069 and 1989–1982 $cm^{-1}$ bands had decreased to 21 and 28% of their initial intensities, respectively. Subsequent recarbonylation reversed the decreases in intensity and the frequency shift of the low-frequency band. These results show that the P1 sample behaved in much the same way as the MA1 sample—but only one-third the treatment time under comparable conditions was allowed.

Exposure of the P1 sample to an atmosphere of $H_2$ at $6 \times 10^4$ $N/m^2$ and 320°K for 18 hr led to a reduction in the intensities of the bands at 2069 and 1989 $cm^{-1}$ and to the formation of a pronounced shoulder on the low-frequency band at about 1970–1980 $cm^{-1}$. These effects were completely reversed by evacuation and recarbonylation at cell temperature.

When the temperature was increased to 350°K, reaction in $H_2$ at $6 \times 10^4$ $N/m^2$ caused the carbonyl spectrum to change completely; after 22 hr the spectrum exhibited only a single band at 1975 $cm^{-1}$ and a very weak band at 2070 $cm^{-1}$ (Fig. 3A). Following evacuation and recarbonylation, sharp bands developed at 2095, 2069, and 1989 $cm^{-1}$ (corresponding to the bands of the original mononuclear complexes), and in addition there was a broader, intense band at 2020 $cm^{-1}$; the 1975 $cm^{-1}$ band remained only as a weak shoulder (Fig. 3A). After a brief evacuation, the 2095 and 2020 $cm^{-1}$ bands were removed completely

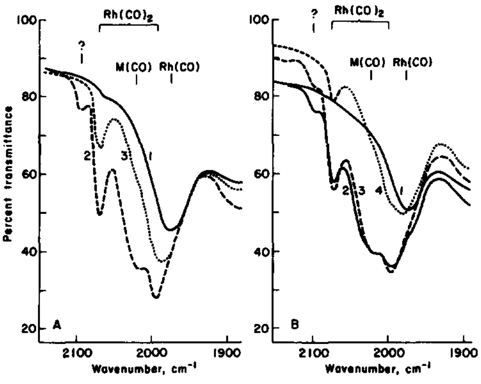

FIG. 3. Carbonyl infrared spectra of the phosphine-modified silica catalyst containing Rh (sample P1) after treatment in $H_2$ at $6.7 \times 10^4$ $N/m^2$ and 330°K (A) and at 380°K (B). A: (1) sample evacuated at cell temperature for 0.5 hr; (2) sample exposed to CO at $2.7 \times 10^3$ $N/m^2$ and 350°K; (3) after evacuation at cell temperature for 0.5 hr. B: (1) sample evacuated 0.5 hr at cell temperature; (2) sample exposed to CO at $1.3 \times 10^4$ $N/m^2$ at cell temperature for 0.5 hr; (3) same as (2) except with CO at $7.8 \times 10^4$ $N/m^2$ for 1 hr; (4) after evacuation for 0.5 hr at cell temperature.

and the 2069 and 1989 cm$^{-1}$ bands were reduced slightly in intensity.

After a further increase in reaction temperature to 380°K, reaction with $H_2$ at 6.7 × $10^4$ N/m$^2$ left only a single band at 1975 cm$^{-1}$ (Fig. 3B). Recarbonylation produced a spectrum (Fig. 3B) very similar to the one described in the preceding paragraph (Fig. 3A), now with the 2020 cm$^{-1}$ band more intense and only a weak band at 2095 cm$^{-1}$. Again, the 2020 and 2095 cm$^{-1}$ bands were removed during a brief evacuation at cell temperature.

Reaction with $H_2$ at 6.7 × $10^4$ N/m$^2$ and an even higher temperature (410°K) left only a very weak band at 1975 cm$^{-1}$. Recarbonylation at cell temperature then produced very weak bands at 2095 and 2069 cm$^{-1}$ and a broad, intense band at 2005 cm$^{-1}$ with a shoulder 1989 cm$^{-1}$. Exposure to $^{13}CO$ shifted the 2005 cm$^{-1}$ band to 1963 cm$^{-1}$, and, after subsequent evacuation, the 1975 cm$^{-1}$ band remained at 1934 cm$^{-1}$ while the 1963 cm$^{-1}$ band was almost removed.

In a separate experiment, it was shown that the 2020 cm$^{-1}$ band had not developed at 380°K after 18 hr in $H_2$ at 6.7 × $10^3$ N/m$^2$, whereas it had become detectable after treatment for the same time at the same temperature in the presence of a higher $H_2$ partial pressure, namely, 2 × $10^4$ N/m$^2$.

Following the reasoning applied in the evaluation of the spectra of the amine-bound Rh sample, we conclude that the 2020 cm$^{-1}$ band is characteristic of CO adsorbed on Rh crystallites which were formed on the catalyst surface during the treatment with $H_2$. The observed change from pale brown of the original sample to dark gray after the final treatment in $H_2$ confirms the metal crystallite formation. The observed intensity changes following the various treatments suggest that an increase in temperature produced an increase in the abundance of metal crystallites at the expense of the mononuclear Rh species. The results for reaction at 410°K, showing a change in the carbonyl band position from 2020 to 2005 cm$^{-1}$, remain unexplained.

Again, in the case of the phosphine-containing samples, electron microscopy provided further confirmation of the conclusions drawn from the infrared spectra, showing that there were no metal species of diameters greater than about 5 Å in the original carbonylated material, whereas there were a large number of Rh crystallites in the above-mentioned materials treated with $H_2$. The crystallites were nearly uniform in size in the 12–15 Å range, as shown in the micrograph of Fig. 4, which was obtained with a P1 sample after prolonged treatment in $H_2$ at 6.7 × $10^4$ N/m$^2$ and 410°K. The higher density of crystallites in this sample than in the MA1 sample indicates the easier aggregation of the original complexes on the phosphine-modified silica support. This behavior was substantiated by the infrared spectra, which show that the bands characteristic of the mononuclear complex had almost completely vanished after the final $H_2$ treatment of the P1 sample, whereas substantial bands were still observed with the MA1 sample after similar treatment.

The catalysis experiments again provide a qualitative confirmation of the spectroscopic and electron microscopic results. When the P1 sample was exposed to the same reaction conditions applied with MA1 (1.6 × $10^4$ N/m$^2$ of ethylene, 8.9 × $10^4$ N/m$^2$ of $H_2$ and 329°K), its activity also increased with time on stream. The rate of increase, however, was less (Fig. 5). The rates of ethylene hydrogenation with P1 and MA1 after short on-stream times were about 0.005 and 0.01 molecules/Rh atom · sec, respectively. A comparison of these rates (and the increases in activity resulting from agglomeration) with those exhibited by similar catalysts suggests the importance of metal–support interactions in determining catalytic activity. Jarrell *et al.* (*6*) studied the aggregation of Rh in catalysts prepared from the reaction of $Rh_6(CO)_{16}$ with poly(styrene-divinylbenzene) functional-

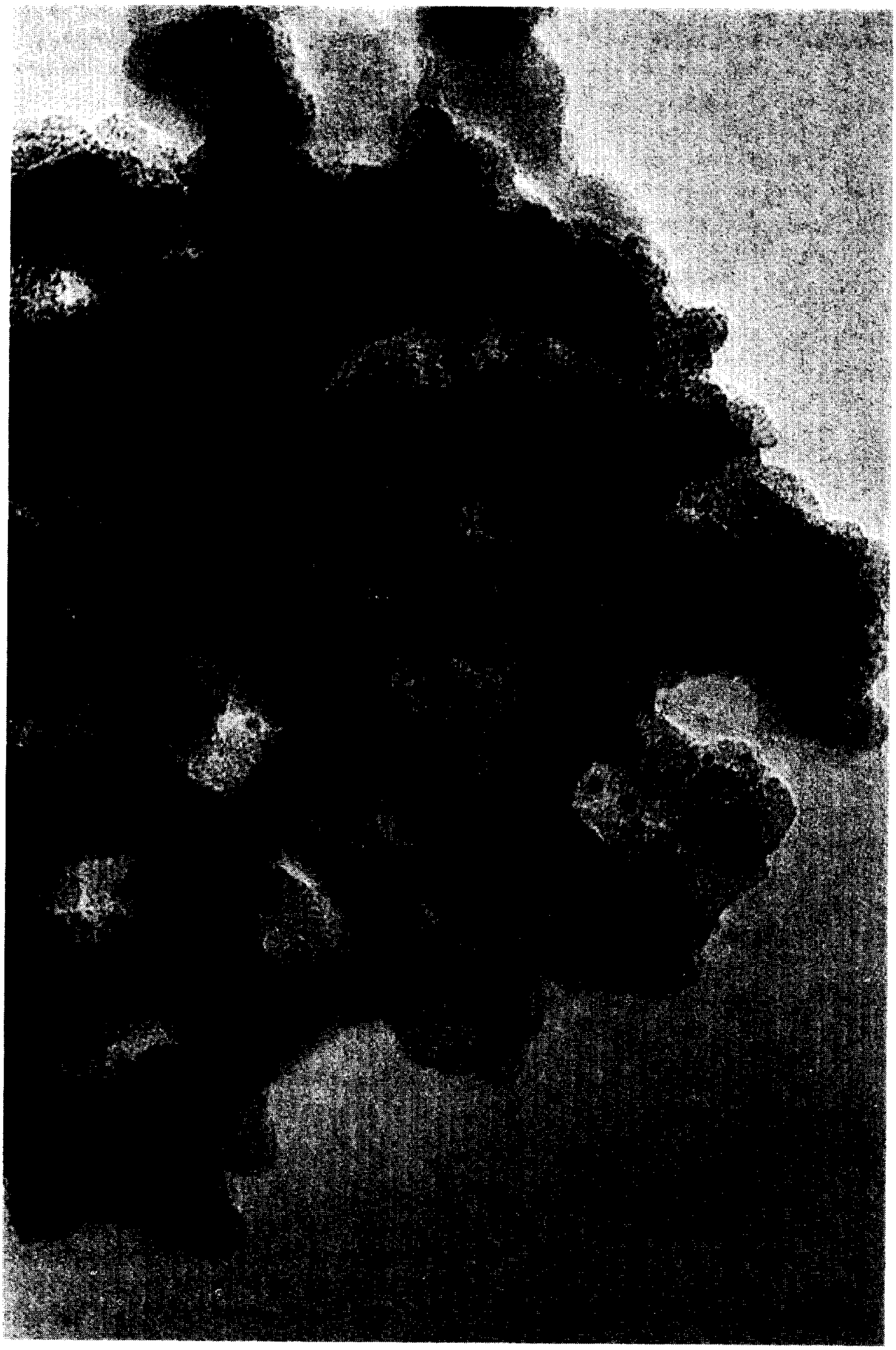

FIG. 4. Electron micrograph of the phosphine-modified silica catalyst containing Rh (sample P1) after $H_2$ treatments in infrared experiments. Rh crystallites are clearly visible.

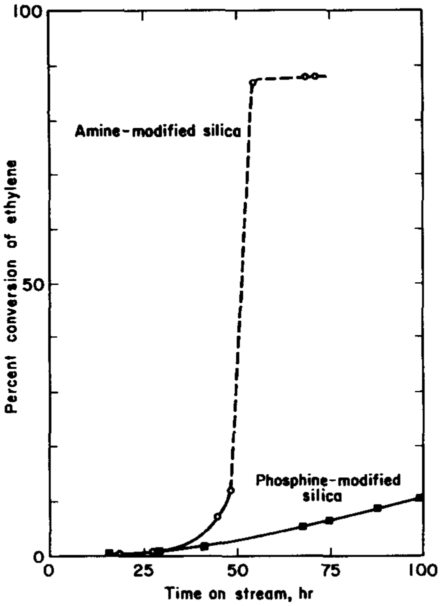

FIG. 5. Ethylene hydrogenation catalyzed by 0.310 g of the phosphine-modified silica containing Rh (■) and by 0.030 g of the amine-modified silica containing Rh (○) at $1.6 \times 10^4$ N/m² of ethylene, $8.9 \times 10^4$ N/m² of $H_2$, and 329°K. The dashed line indicates nonisothermal operation, described in the text. The increases in activities reflect aggregation of the Rh.

ized with phosphine groups. Jarrell's fresh sample, containing decarbonylated Rh clusters of undetermined structure, had an activity of approximately 0.1 molecules/Rh atom · sec under the conditions described above for P1 and MA1, and Jarrell's aged samples, containing Rh crystallites about 20–25 Å in diameter, had nearly the same activity. In contrast to Jarrell's results (*6*), the activities of P1 and especially MA1 increased by several orders of magnitude as the Rh aggregated to form crystallites. The increase in activity may be attributed in part to decarbonylation of the Rh during aggregation. Although differential conversions (hence rates) were not determined for MA1 after the metal had undergone aggregation to form crystallites, the catalytic activity (estimated from the conversion) was very roughly the same as that of Rh/$Al_2O_3$ as measured by Jarrell (*6*).

## CONCLUSIONS

The Rh complexes linked to silica through amine or through phosphine ligands experienced agglomeration to form Rh crystallites which were, respectively, nearly 16–17 or 12–15 Å in diameter. The agglomeration process was accelerated by hydrogen, and the rate was influenced by the nature of the ligands surrounding the metal, with amines hindering the process more than phosphines.

These results suggest that a method of producing supported metal crystallites by slow, controlled reduction of attached mononuclear complexes [or perhaps clusters (*18*)] using hydrogen may be of general applicability for the preparation of metal catalysts with nearly uniform size distributions on inorganic supports. The results are suggestive of those obtained with poly(styrene-divinylbenzene) resins initially incorporating Pd-sulfonate groups (*19*). The method may be applicable to many metals and to the preparation of bimetallic crystallites. Further investigations, for example, by transmission electron microscopy and EXAFS, could provide information about the kinetics of aggregation and the structures of aggregates.

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## REFERENCES

1. Collman, J. P., Hegedus, L. S., Cooke, M. P., Norton, J. R., Dolcetti, G., and Marquardt, D. N., *J. Amer. Chem. Soc.* **94,** 1789 (1972).
2. Anderson, J. R., Elmes, P. S., Howe, R. F., and Mainwaring, D. E., *J. Catal.* **50,** 508 (1977).
3. Ichikawa, M., *Bull. Chem. Soc. Japan* **51,** 2268, 2273 (1978).
4. Brenner, A., paper presented at International Symposium on Relations between Homogeneous and Heterogeneous Catalysis, Lyon, 1977.

5. Bilhou, J. L., Bilhou-Bougnol, V., Graydon, W. F., Basset, J. M., Smith, A. K., Zanderighi, G. M., and Ugo, R., *J. Organometal. Chem.* **153,** 73 (1978).
6. Jarrell, M. S., Gates, B. C., and Nicholson, E. D., *J. Amer. Chem. Soc.* **100,** 5727 (1978).
7. Knözinger, H., and Rumpf, E., *Inorg. Chim. Acta* **30,** 51 (1978).
8. Knözinger, H., Thornton, E. W., and Wolf, M., *J. Chem. Soc. Faraday I* **75,** 1888 (1979).
9. Jarrell, M. S., and Gates, B. C., *J. Catal.* **54,** 81 (1978).
10. Knözinger, H., *Acta Cien. Venezolana* **24,** Suppl. 2, 76 (1973).
11. Tesche, B., *Vak.-Tech.* **24,** 104 (1975).
12. Jarrell, M. S., and Gates, B. C., *J. Catal.* **40,** 255 (1975).
13. Yang, A. C., and Garland, C. W., *J. Phys. Chem.* **61,** 1504 (1957).
14. Arai, H., and Tominaga, H., *J. Catal.* **43,** 131 (1976).
15. Garland, C. W., Lord, R. C., and Troiano, P. F., *J. Phys. Chem.* **69,** 1188 (1965).
16. Queau, R., and Poilblanc, R., *J. Catal.* **27,** 200 (1972).
17. Primet, M., *J. Chem. Soc. Faraday I* **74,** 2570 (1978).
18. Lieto, J., Rafalko, J. J., Minkiewicz, J. V., Rafalko, P. W., and Gates, B. C., *in* "Fundamental Research in Homogeneous Catalysis," Vol. 3, M. Tsutsui, Ed. Plenum, New York, 1979.
19. Hanson, D. L., Katzer, J. R., Gates, B. C., Schuit, G. C. A., and Harnsburger, H. F., *J. Catal.* **32,** 204 (1974).