Silica-Supported Triosmium Clusters: Catalysts for 1-Butene Isomerization

R. BARTH,* B. C. GATES,*,1 Y. ZHAO,†,2 H. KNÖZINGER,† AND J. HULSE†

*Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19711, and †Physikalisch-chemisches Institut der Universität, Sophienstrasse 11, 8 München 2, West Germany

Silica-supported triosmium carbonyl clusters [HOs$_3$(CO)$_{10}$—O—Si<] were prepared by the reaction of [Os$_3$(CO)$_{12}$] with –OH groups of the silica surface. The supported clusters were catalytically active for isomerization of 1-butene to give 2-butene at 1 atm and 50 to 90°C. The reaction rate was about 10^{-2} molecules/(triosmium cluster · s) at 75°C. The catalytic activity increased slowly with time on stream in a flow reactor, and infrared spectra of the catalyst under reaction conditions (and uv-visible reflectance spectra measured in a separate experiment) indicated that the activity increase was accompanied by a (reversible) loss of CO ligands from the cluster, which were evidently replaced by butene. The spectra indicate that the clusters were maintained intact under reaction conditions, and it is inferred that the clusters themselves provided the catalytic sites.

INTRODUCTION

Supported metal clusters are potentially valuable model catalysts, offering discrete molecular structures and the prospect of providing understanding of the relations between structure and catalytic activity of metals. Only little progress toward this understanding has been made, because only few supported metal clusters with unique structures have been prepared, and most of these are coordinatively saturated and therefore may be regarded as catalyst precursors rather than catalysts themselves (1). Among the supported metal clusters most attractive for determination of structure–catalytic activity relations are triosmium carbonyls, since these are relatively stable and have been anchored intact to a variety of supports, including metal oxides (2–5), phosphine-functionalized silica (6, 7), and phosphine-functionalized poly(styrene-divinylbenzene) (7). Triosmium carbonyl clusters on the phosphine-functionalized supports have been partially decarbonylated to give coordinatively unsaturated clusters, which catalyze olefin isomerization, having activities approximately the same as that of an analogous triosmium cluster in solution, [H$_2$Os$_3$(CO)$_{10}$] (7, 8).

The triosmium clusters supported on unfunctionalized oxides have only begun to be characterized as catalysts or catalyst precursors. The alumina-supported clusters have been reported to be catalysts for olefin isomerization, but quantitative characterization is lacking (9). These alumina-supported clusters, upon heating to ~150–200°C, break up to give mononuclear osmium carbonyl complexes (2–5); electron microscopy, infrared spectroscopy, and XPS indicate these to be present in isolated ensembles of three divalent osmium ions on the support (10). They have been reported to be catalytically active for hydrogenation of olefins (9) and of CO (10).

Our objective was to investigate the catalytic nature of the intact triosmium clusters on an oxide support. Silica was chosen as the support, since the triosmium carbonyl clusters bonded to silica are excellently

1 To whom correspondence should be addressed.
2 Present address: Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, People's Republic of China.

suited to spectroscopic characterization, especially by transmission infrared spectroscopy (2–5). Isomerization of 1-butene was chosen as the catalytic probe reaction, since it occurs at low temperature and has been suggested to be catalyzed by alumina-supported triruthenium clusters (11), by alumina-supported triosmium clusters (9), and by phosphine-anchored triosmium clusters and the analogous soluble cluster [H$_2$Os$_3$(CO)$_{10}$] (7, 8).

EXPERIMENTAL

Catalyst preparation. Silica gel (Cab-O-Sil grade M-5, a gift of Cabot Corporation) was stirred with enough deionized water to give a thick paste, dried at 120°C in air, and heated to 400°C in flowing oxygen for 7 hr. It was then isolated, cooled to room temperature, evacuated, and transferred to an oxygen-free dry box and stored there, under dry nitrogen, until used. This silica gel (12.2 g), with 200 ml of *n*-octane (Fisher, distilled from sodium/benzophenone) and 194 mg of [Os$_3$(CO)$_{12}$] (Strem), was added to a 500-ml flask. The mixture was stirred and refluxed for 2 hr, after which the supernatant liquid was colorless, indicating that almost all of the yellow [Os$_3$(CO)$_{12}$] had reacted with the silica gel. The solid was separated on a glass frit, dried by evacuation, and stored under nitrogen in a dry box until used. All the above operations were carried out with the careful exclusion of air. Osmium analysis (Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.) showed that the sample contained 0.89 wt% Os (in replicate analyses, values of 0.83, 0.88, and 0.97 wt% were obtained; a value of 1.0% would have been expected from complete uptake of Os by the silica gel during preparation).

Nearly identical catalyst preparations were carried out to give samples of different Os contents. One sample was prepared by refluxing an Aerosil 200 silica sample (Degussa)—previously treated at 400°C—in an *n*-octane solution of the [Os$_3$(CO)$_{12}$]. The infrared spectra of the samples prepared from the two silica materials were indistinguishable.

Catalytic reaction rate measurements. The reactant 1-butene (Phillips "pure" grade) flowed through two traps (an activated BASF copper catalyst followed by zeolite A to remove traces of oxygen and water, respectively). Downstream of the traps, the 1-butene flowed through stainless-steel tubing and a Brooks diaphragm-type mass flow controller and into a flow reactor.

The reactor was a vertical stainless-steel tube, 6.3 mm in outside diameter and 20 cm in length, surrounded by a close-fitting cylindrical brass block. The block was wrapped with electrical heating tape; the power input was regulated by a temperature controller, the controlling element being a thermocouple embedded in the block. A sheathed thermocouple inside the reactor provided a measure of the temperature near the sample, which was controlled within ± 1°C.

Catalyst was charged to the reactor as follows: a plug of glass wool was pushed into the reactor until it stopped against the thermocouple. Then 100 to 200 mg of the catalyst (a fine powder) was poured in, followed by quartz chips, then another plug of glass wool.

The reactant stream (1-butene) flowed through the reactor at atmospheric pressure. The product stream flowed through Teflon tubing to an eight-port rotary gas-sampling valve (Valco), where 0.05-cm^3 samples were periodically injected into the He carrier-gas stream of a gas chromatograph equipped with a 3.2-mm × 2-m stainless-steel column packed with 80/100 mesh Carbopak C loaded with 0.19% picric acid. Reactant and product peak areas were measured by electronic integration of the output of a flame ionization detector.

Infrared spectra of catalysts. Spectra of the catalyst samples were recorded with either a Nicolet 7199 Fourier transform infrared spectrometer equipped with a Globar

source and a mercury/cadmium telluride cryogenic detector, or with a conventional dispersive Perkin-Elmer 225 infrared spectrometer; the spectral slit width was typically 4 cm^{-1} in the carbonyl stretching region. The samples were self-supporting pressed disks with geometries chosen according to the beam dimensions in the instruments.

Spectra of the catalysts in the carbonyl stretching region of the spectrum were measured with samples mounted in one of three cells:

(1) For investigation of catalysts during the occurrence of the butene isomerization reaction, a stainless-steel cell with NaCl windows and Viton O-ring seals was used (Fig. 1). Four cartridge heaters provided power to the cell block. A sheathed thermocouple inside the cell provided a measure of the temperature near the sample, which was controlled to within ±1°C.

(2) Spectra were measured with catalyst disks in a quartz cell which could be heated to temperatures as high as 600°C by external nichrome windings. The NaCl windows and Viton sealing surfaces were kept cool by flowing water. The sample holder was made entirely of quartz. The design of this cell is an adaptation of that described by Dent (12).

(3) The third cell [described previously (13)], used in combination with the Perkin-Elmer 225 spectrometer, also permitted in situ heating of the catalyst. It was equipped with CaF$_2$ windows.

The flow of purified gases was provided by a portable gas-handling system. Samples in the quartz cell could be treated in vacuum (2 × 10^{-9} atm), at atmospheric pressure, or under recirculating gases at subatmospheric pressure. A liquid-nitrogen-trapped oil diffusion pump provided vacuum. Traps removed traces of oxygen and water from the flowing gases with copper catalyst and zeolite A, respectively. A separate glass trap containing activated MnO/SiO$_2$ provided a visual indication of gas purity as well as a final purification to bring oxygen concentrations to the parts-per-billion range. A stainless-steel bellows pump (Metal Bellows Corp.) provided circulation of gases at pressures from 0.1 to 1 atm.

Diffuse reflectance spectra. Spectra in the uv-visible region (250–600 nm) were recorded with the diffuse reflectance technique. The spectrometer was a Beckman
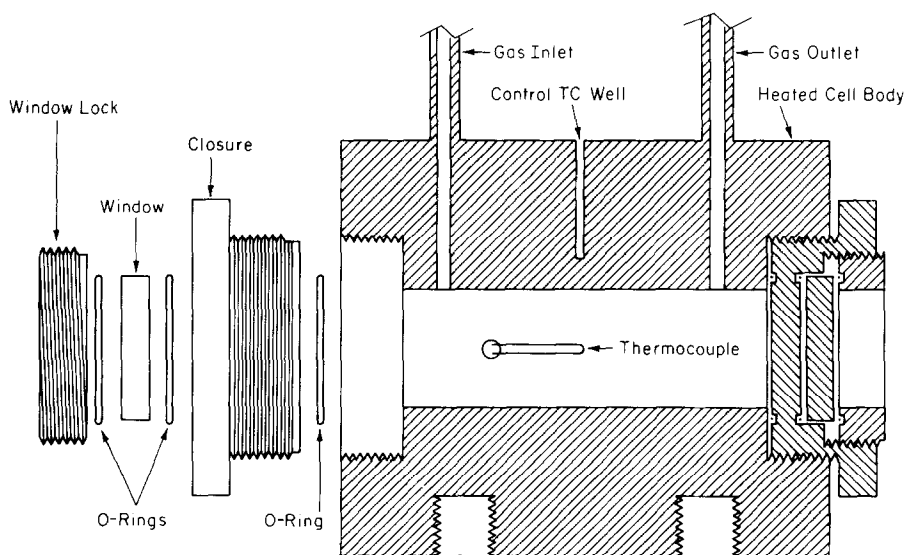

FIG. 1. Infrared cell/flow reactor for measurement of spectra of functioning catalyst wafers.

Spectroreflectometer, type DK2A; the reflectance white standard was BaSO$_4$. The quartz cells provided an effective sample thickness of 2 mm, permitting the determination of R_∞ (the reflectance at infinite sample thickness) in the wavelength region investigated. The spectra were evaluated by means of the Schuster–Kubelka–Munk function $F(R_\infty)$.

RESULTS AND DISCUSSION

Catalytic Reaction Rates

Rates of the catalytic isomerization of 1-butene to give 2-butene were determined at 50 to 90°C from conversions which were so low (0.1 to 0.8%) that they were assumed to be differential. These conversions were an order of magnitude greater than the conversions observed with just silica in the reactor at a much higher temperature (160°C).

In a typical experiment, the flow rate of 1-butene was set at 0.24 cm^3/s, and the catalyst was brought to the desired temperature. Periodic analyses of the product stream demonstrated that the catalytic activity increased for a few hours; after this period (or sometimes less), the temperature of the catalyst was increased, reaching the

new set point in 15 to 30 min. Again, the catalytic activity increased with time onstream, achieving a steady state within a few hours; the data of Fig. 2 are typical.

In several different sets of experiments, each begun with a fresh catalyst sample, the temperature was increased stepwise, and a reaction rate was determined for steady-state operation (or approximate steady-state operation) at each temperature. These catalytic activity data are collected in Fig. 3; the internal consistency of data obtained in separate experiments indicates that the rate of heat-up of the catalyst did not significantly affect the steady-state catalytic activity measurements.

The pattern of increasing activity with time suggests that the structure of the catalyst changed during the course of the reaction. In one experiment, the activity was monitored for 3.3 hr at 75°C, during which steady-state activity was attained. Then the sample was cooled to room temperature in flowing helium, remaining at room temperature for about 100 hr; the temperature was then raised to 75°C with the sample in flowing 1-butene, and catalytic activity measurements were resumed. Again, several hours were required for attainment of a steady-state activity, which was about the
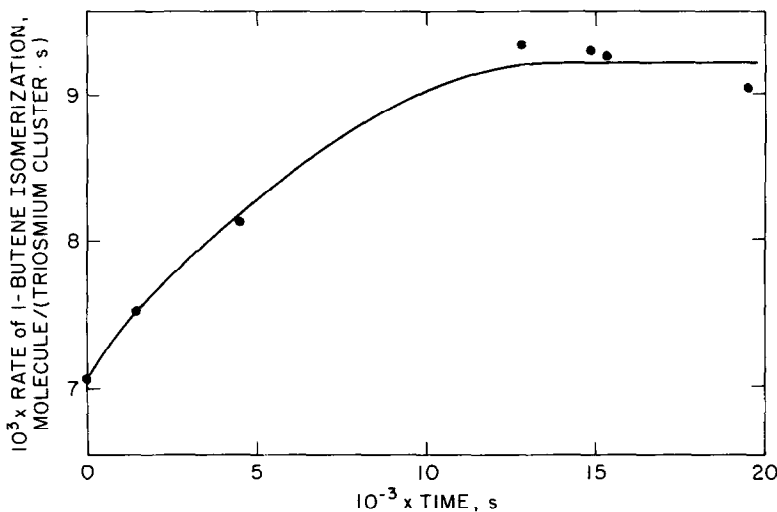

FIG. 2. Break-in of the silica-supported triosmium catalyst for isomerization of 1-butene at 75°C.
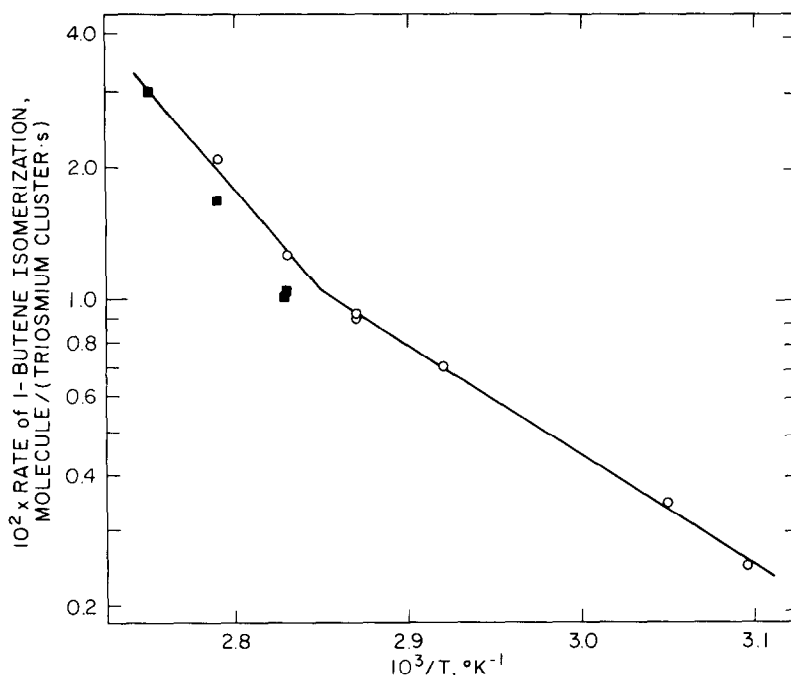
FIG. 3. Rate of 1-butene isomerization catalyzed by silica-supported triosmium clusters.

same as that measured before the interruption of 1-butene flow. This result suggests that upon cessation of the 1-butene flow, desorption of 1-butene occurred, and that upon resumption of 1-butene flow, readsorption of 1-butene occurred slowly as the steady-state activity was approached.
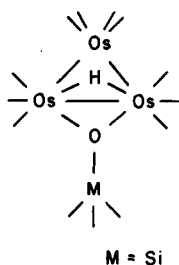
The slow break-in of the catalyst at each temperature suggests a slow formation of the catalytically active species, presumably resulting in part from dissociation of CO (or hydride) ligands and bonding of butene. There is a clear curvature in the plot of Fig. 3, with the apparent activation energy roughly doubling over the range of observed temperatures (50 to 90°C). The increase in apparent activation energy with increasing temperatures is consistent with the suggestion of structural changes in the catalyst as CO ligands were replaced by butene. The pattern is similar to that observed by Brenner et al. (14) for a series of catalysts prepared by deposition of metal carbonyls on oxide supports; these authors observed an increase in catalytic activity associated with removal of CO from the

metal to allow bonding of reactant ligands, such as olefins and hydrogen.

Infrared Spectra

The intense infrared absorption spectrum in the carbonyl stretching region provides an excellent method for characterization of the clusters. For reference, the spectrum of a dilute solution of [Os$_3$(CO)$_{12}$] in cyclohexane is shown in Fig. 4. As predicted by symmetry analysis (15), four bands are present in the carbonyl stretching region. None of these can be associated with any particular carbonyl group; each is a combination of vibrations from within the two sets of symmetry-equivalent carbonyls, axial and equitorial.

The spectrum of the Cab-O-Sil-supported cluster (Fig. 5, spectrum A) is different, indicating that the [Os$_3$(CO)$_{12}$] had reacted with the surface; the results are consistent with those observed previously, which have been interpreted as evidence that the cluster reacted with surface –OH groups to give the following surface-bound cluster (2–5):

$$\begin{array}{c} \backslash\backslash \;\; // \\ Os \\ \backslash \;\; / H \backslash \;\; / \\ -Os \longrightarrow Os- \\ / \;\; \backslash \;\; O \;\; / \;\; \backslash \\ | \\ M \\ / | \backslash \end{array}$$

M = Si

The spectrum remained almost unchanged upon heating of the sample with the surface-bound cluster in vacuum to a temperature of 165°C (Fig. 5, spectrum B). Upon heating to 175°C in vacuum (Fig. 5, spectrum C) changes in the spectrum occurred, indicating breakup of the triangular osmium framework, as observed previously (2–5).

Typical spectra obtained during thermal treatment of an Aerosil-supported cluster are shown in Fig. 6. After heating under vacuum at 150°C for 15 hr, spectrum B was obtained, which still closely resembles that of the freshly prepared material (spectrum A), confirming the relatively high thermal stability of the oxygen-bridged cluster on the support. Cluster breakup to give mononuclear dicarbonyl species is suggested by spectrum C in Fig. 6 (2–5), which was obtained after evacuation at 270°C for 15 hr. No carbonyl bands could be observed after treatment in vacuum at 400°C. Recarbonylation at 100°C under CO at a pressure of 0.13 atm gave two bands, located at 2125 and 2048 cm^{-1} (Fig. 7, spectrum A). These bands are typical of mononuclear tricarbonyl species (2–5). When the sample was heated under CO at 200 to 250°C for extended periods (spectra B and C, Fig. 7), the intensities of the bands indicating the mononuclear tricarbonyl species decreased, and the sharp bands typical of the oxygen-bridged carbonyl cluster reappeared. This result suggests that a triosmium carbonyl cluster was reconstituted from the mononuclear surface species, a behavior analogous to that reported for MgO-supported osmium species (16).

The presence of 1-butene modified the re-

activity of the Cab-O-Sil-supported triosmium cluster. Carbonyl stretching spectra of the sample containing 0.89% Os, measured at various temperatures under flowing 1-butene, are shown in Fig. 8. As the temperature was increased, the first change was evident at 80°C as the growth of new bands at 2108 and 1968 cm^{-1}. These two bands increased in intensity in unison until a temperature of about 140°C was reached, whereupon they began to decline in intensity with increasing temperature. At about 90°C, the bands at 2078 and 2013 cm^{-1} began to decline in intensity, and at about 160°C the bands at 2066 and 2029 cm^{-1} began to decline in intensity. By the time a temperature of 175°C had been reached, the spectrum of silica-supported osmium heated under 1-butene had become similar to that of the same original material which had been heated under vacuum to 175°C to give mononuclear osmium carbonyls (Fig. 5, spectrum D). It appears that, in contrast to the rather abrupt breakup of the cluster heated in vacuum, the breakup in the pres-
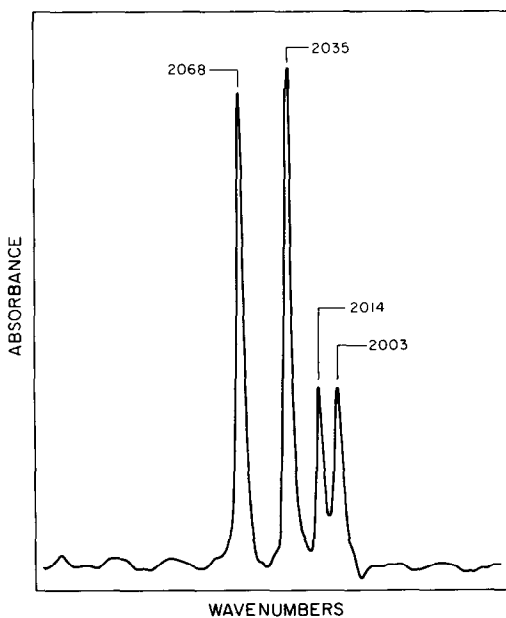

FIG. 4. Infrared spectrum of [Os$_3$(CO)$_{12}$] in cyclohexane.

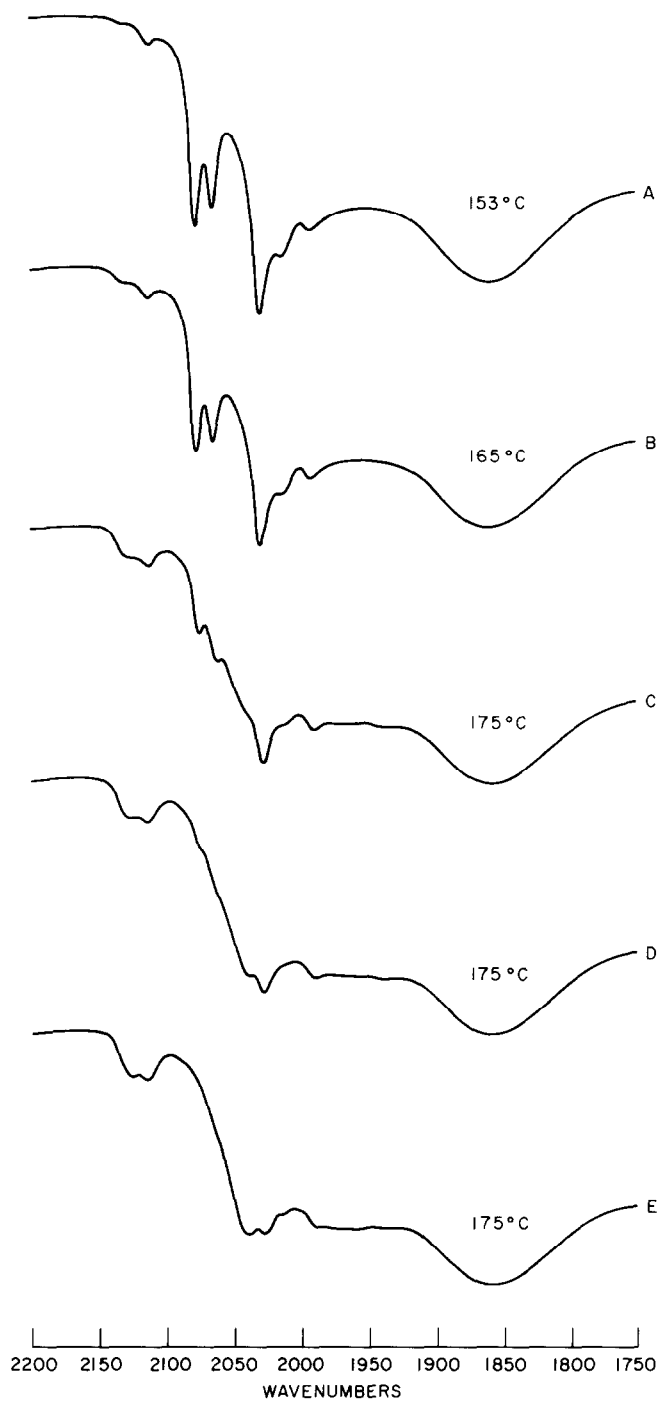FIG. 5. Infrared spectra of Cab-O-Sil-supported cluster prepared by the reaction of [Os₃(CO)₁₂] with surface –OH groups. The sample contained 0.40 wt% Os. It was heated under vacuum to the temperatures shown.
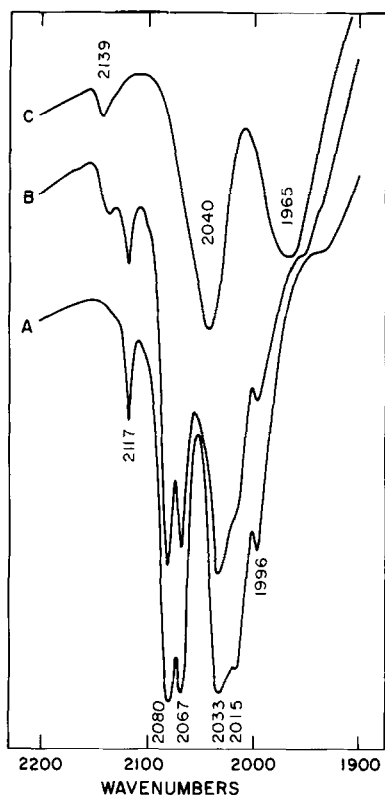
FIG. 6. Carbonyl infrared spectra of an Aerosil-supported sample formed from reaction of $[Os_3(CO)_{12}]$ with surface –OH groups: (A) freshly prepared catalyst; (B) after heating under vacuum to 150°C for 15 hr; (C) after heating under vacuum to 270°C for 15 hr.

FIG. 7. Carbonyl infrared spectra of sample of Fig. 8 after heating under vacuum at 400°C and recarbonylation: (A) CO at 0.13 atm and 100°C for 1 hr; (B) same at 200°C for 8 hr; (C) same at 250°C for 15 hr.

ence of 1-butene was preceded by a complex pattern of decarbonylation.

To allow investigation of the onset of changes in the carbonyl stretching region of the spectrum, a sample was prepared in the form of a thick wafer to provide good definition of the weak bands at 2108 and 1968 cm^{-1}. (It was not possible to follow the more intense bands during the experiments with this sample.) The sample was examined in flowing purified 1-butene, heated to 85°C, and held at that temperature for 1.6 hr. It was then exposed to purified CO and allowed to cool to 70°C in flowing CO (which took 1.3 hr), whereupon the system was purged of CO. Flow of 1-butene was then resumed, and the temperature was raised to 85°C and maintained for about 2

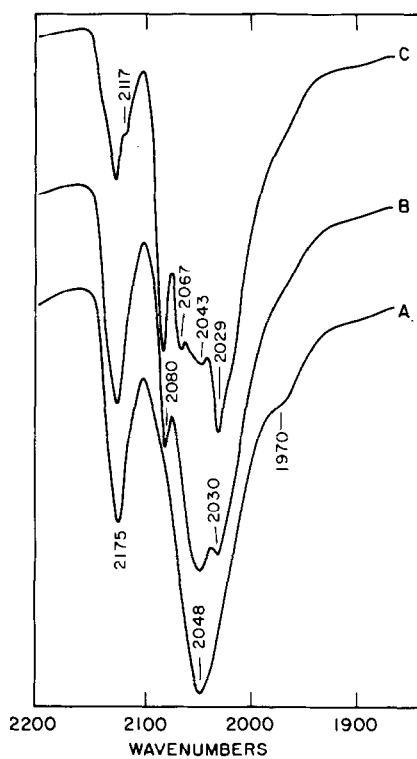hr, after which the system was purged of 1-butene and swept with purified helium. Spectra of the sample in the vicinity of the 2108-cm^{-1} band obtained during this experiment are shown in Fig. 9. The spectra show that the new band increased in intensity with time at 85°C under 1-butene until CO was introduced, whereupon it was immediately effaced. It returned upon heating of the sample in 1-butene, and was unaffected by withdrawal of the 1-butene.[3] The 1968-cm^{-1} band followed the same pattern.

We propose that the bands at 2108 and 1968 cm^{-1} are carbonyl bands resulting from a change in symmetry of the supported cluster arising from bonding of bu-

[3] In the removal of CO, thoroughness was essential; small amounts of CO prevented growth of the new bands associated with bonding of butene to the cluster.

tene. We infer that butene ligands replaced CO and/or hydride ligands; this same inference has already been drawn from the results of the catalysis experiments.

In summary, the spectra of Figs. 8 and 9 show that interaction of 1-butene with the sample at temperatures up to about 90°C leads to no change in the carbonyl bands associated with the supported triosmium clusters—except for the growth of two weak new bands. This change is completely reversed by the treatment with CO at 70°C. These results demonstrate that the cluster framework remained intact under catalytic reaction conditions. We therefore infer that the intact cluster itself provided the catalytic sites.

This inference is consistent with the known catalytic activity of the similar (soluble) cluster [H$_2$Os$_3$(CO)$_{10}$] and a supported analog: Catalytic activities for isomerization of 1-pentene have been reported for [H$_2$Os$_3$(CO)$_{10}$] (7, 17) and for the analogous, coordinatively unsaturated cluster bonded to phosphine-functionalized silica [H$_2$Os$_3$(CO)$_9$PPh$_2$-C$_2$H$_4$-SIL] (7); the reactions were carried out with liquid-phase reactants at 75°C. For a rough comparison, we have assumed that the reaction catalyzed by our silica-supported cluster is first order in the reactant 1-butene. The calculated rate constant is 0.2 liter/(mol of cluster · s) at 75°C for the silica-supported cluster; the observed pseudo-first-order rate constant for the soluble cluster with 1-pentene is 0.026 and that for the cluster supported through phosphine ligands is 0.08 liter/(mol of cluster · s) (7). The order-of-magnitude agreement of the estimated rate constants is consistent with our suggestion that triosmium cluster frameworks provided the catalytic sites in each sample.

Diffuse Reflectance Spectra

In the wavelength range of 250 to 600 nm, [Os$_3$(CO)$_{12}$] exhibits two absorptions (at 330 and 385 nm), which have been assigned to electronic transitions within the molecular orbital structure of the triangular framework (18). The diffuse reflectance spectrum of the sample freshly prepared from the Aerosil 200 support and [Os$_3$(CO)$_{12}$] is shown in Fig. 10. In addition to a blue shift of about 25 nm, the surface-bound cluster exhibited a new low-energy band at 210 nm. The sample was lemon yellow.

When the sample underwent treatment in vacuum similar to that described for the infrared measurements, changes in the uv-visible spectrum became evident, as shown in spectrum B of Fig. 10. The spectrum no longer had the simplicity of that characteristic of the starting material, now consisting of a series of small, poorly resolved bumps. We suggest the following interpretation: first, the overall intensity had been drastically reduced, a result suggesting that some of the cluster had been destroyed or lost from the surface. Second, not all of the original surface-bound species had vanished, as shown by the bands at 302, 360, and 410 nm. Third, new bands appeared at 270, 390, and 470 nm. The sample was now red. Since the sample lost CO upon heating under vacuum, it is tempting to attribute the new set of bands to a partially decarbonylated cluster with an intact metal framework.

When CO was brought in contact with the decarbonylated sample at room temperature, a rapid change in the spectrum was observed (Fig. 10). The two original bands at 305 and 355 nm increased somewhat in intensity, albeit with new relative intensities. The 410-nm absorption of the starting material and the three bands of the presumably decarbonylated species disappeared. The sample was light brownish-yellow. Continued exposure to CO at room temperature led to no further change in the spectrum. Heating the sample under CO only caused it to bleach slowly.

The sample was subjected to further decarbonylation–recarbonylation cycles. The resulting spectrum was virtually identical to spectrum C in Fig. 10.
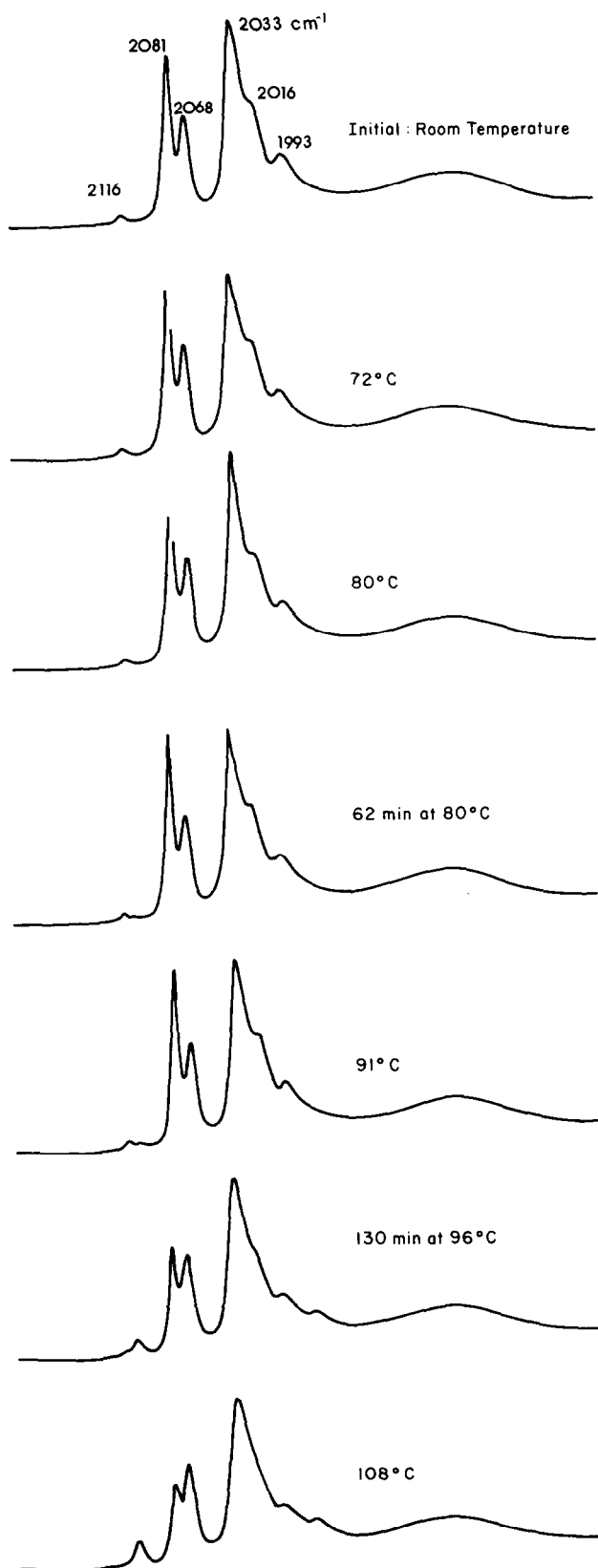
FIG. 8. Infrared spectra (absorbance) of triosmium carbonyl clusters supported on silica: samples in flowing 1-butene at 1 atm and various temperatures.
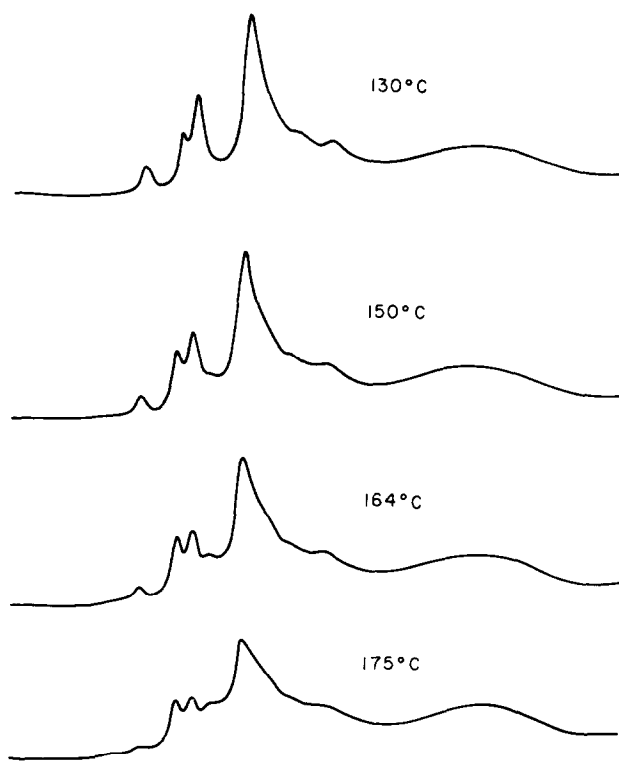
FIG. 8—*Continued.*

The effects of heating a freshly prepared surface-bound cluster under a 1-butene atmosphere were less dramatic. The form of the spectrum (Fig. 10) remained unchanged, but the band intensities decreased considerably; after some 3 hr at 158°C, the band intensities declined twofold. Evacuation of the 1-butene at room temperature brought about a restoration of the original intensities. These results indicate an (unexplained) change in the reflective properties of the sample in the presence of 1-butene at elevated temperatures. Subsequent decarbonylation–recarbonylation proceeded as for the fresh sample described above. We infer that the loss of CO ligands and their replacement by 1-butene is not an important process for the majority of the surface-bound clusters at temperatures up to 158°C. This result is consistent with the infrared results presented above (showing that most of the osmium was present as saturated clusters [$HOs_3(CO)_{10}$—O—Si$\leqslant$]).

We infer that during the decarbonylation–recarbonylation sequence, the triosmium framework remained intact, since the sample remained colored, and the mononuclear surface carbonyls formed on prolonged heating at higher temperatures are colorless (*3*).

In summary, we suggest that carbonyl ligands were lost from the yellow oxygen-bridged cluster [$HOs_3(CO)_{10}$—O—Si$\leqslant$], and a new (red) surface-bound cluster was formed. This could be recarbonylated, giving a yellow sample incorporating a cluster which, however, was not the original cluster. The structures of the new surface-bound clusters remain undetermined.

CONCLUSIONS

The infrared spectra demonstrate that the predominant osmium species on the silica surface under conditions of 1-butene isomerization is a triosmium carbonyl cluster.
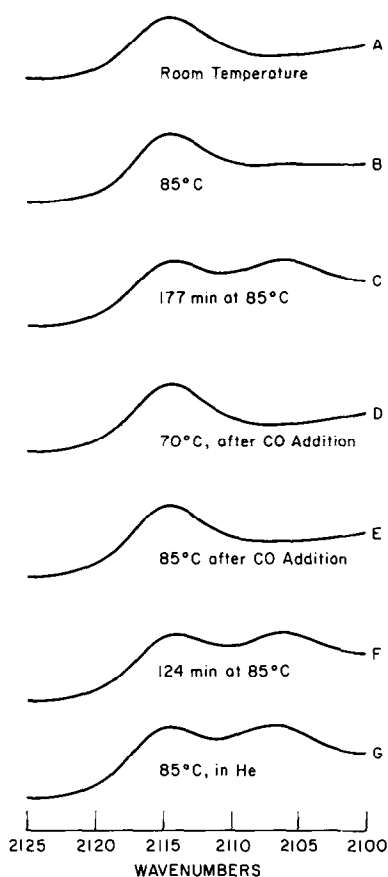
FIG. 9. Infrared spectra (absorbance) of triosmium carbonyl clusters supported on silica: the behavior of the 2108 cm⁻¹ band in 1-butene and the effect of CO addition.

FIG. 10. Diffuse reflectance spectra of a sample prepared from [Os₃(CO)₁₂] and Aerosil silica: (A) freshly reacted; (B) evacuated at 147°C for 94 hr; (C) exposed to CO at 0.92 atm and room temperature.

This cluster reacts with 1-butene, and the change in the spectrum of the original cluster, [HOs₃(CO)₁₀—O—Si≪], is accompanied by the onset of catalytic activity for 1-butene isomerization. The change is reversed by the addition of CO, which probably bonds strongly to the cluster in place of hydrocarbon ligands. All the results point to intact triosmium clusters as the catalytically active species. This conclusion is consistent with the results of earlier investigations showing the catalytic activity of [H₂Os₃(CO)₁₀] and analogous supported triosmium carbonyl clusters (7).

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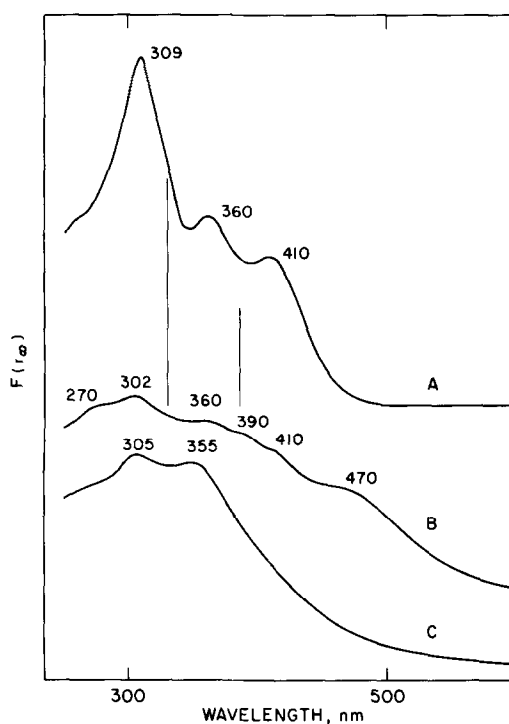
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