

Hexene-1 Isomerization Catalyzed by Alumina-Supported Osmium Complexes Derived from $[\text{Os}_3(\text{CO})_{12}]$

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Supported osmium catalysts were prepared by the reaction of $[\text{Os}_3(\text{CO})_{12}]$ with the surface —OH groups of $\gamma\text{-Al}_2\text{O}_3$ to form $\text{HOs}_3(\text{CO})_{10}\text{—O—Al}$. The catalyst was initially active for hexene-1 isomerization at 120°C and 1 atm; the activity decreased rapidly, becoming almost constant after 2 h on stream in a flow reactor. Infrared spectra of the catalyst indicated that the decline in activity was accompanied by a breakup of the initial supported clusters $[\text{HOs}_3(\text{CO})_{10}\text{—O—Al}]$ and the formation of mononuclear Os(II) carbonyl complexes, which are evidently present in ensembles of three complexes. The isomerization reaction catalyzed by this stable form of the catalyst was inhibited strongly and reversibly by CO. Hydrogen in the reactant stream increased the rate of the isomerization reaction, and we infer that hydride ligands on the osmium played a role in increasing the catalytic activity.

INTRODUCTION

Research with supported-metal catalysts having simple structures is motivated by the goal of determining relations between structure, reactivity, and catalytic activity. There is also a practical goal—the discovery of catalysts having new activities and selectivities, the latter, in prospect, being associated with the uniqueness of structure of the metal species.

Many oxide-supported metal catalysts with simple structures are known (1); most of these do not include group VIII metals, a notable exception being osmium. Osmium complexes on metal oxides appear to be unusual in their offering simple structures stable under conditions of hydrocarbon conversion catalysis.

Osmium carbonyl compounds, especially $[\text{Os}_3(\text{CO})_{12}]$, have been used to prepare supported-metal catalysts consisting of trios-

mium clusters bonded to surfaces of oxides through bridging oxide ligands (2-7) and through pendant phosphine ligands (8). These supported clusters have been reported to be catalytically active for isomerization of olefins at temperatures $<90^\circ\text{C}$ (3, 7), but at higher temperatures the clusters evidently break apart to give supported mononuclear osmium complexes, which are less active for olefin isomerization (7). The breakup of the clusters on the supports evidently leads to the formation of three-atom ensembles of mononuclear Os carbonyl complexes (6), which, upon recarbonylation, may react to reconstitute a cluster (7, 9).

We report here results contrasting the above-mentioned osmium species on $\gamma\text{-Al}_2\text{O}_3$. The catalytic isomerization of hexene-1 was chosen as a simple test reaction, since it occurs under mild conditions in the presence of supported osmium clusters and complexes (3, 7-9). The effects of hydrogen, carbon monoxide, and oxygen on the catalytic activity have been determined, and infrared spectra in the carbonyl region have been used to characterize the struc-

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tures of the supported osmium species; the evidence is consistent with the identification of the ensembles of osmium complexes as the stable catalytically active species formed from the supported triosmium clusters.

EXPERIMENTAL METHODS

Materials. The support, γ - Al_2O_3 (Ketjen, surface area: $185 \text{ m}^2/\text{g}$), was dehydroxylated to varying degrees under flowing oxygen for 4 h at 120, 250, 400, or 550°C. Most of the experiments were done with the sample treated at 400°C. *n*-Heptane solvent was dried and distilled under nitrogen. $[\text{Os}_3(\text{CO})_{12}]$ (Strem) and hexene-1 (Aldrich) were used as received. Helium (Airco, 99.99%), hydrogen (Airco, 99.995%), and carbon monoxide (Matheson, 99.99%) were purified by flow through traps containing supported copper catalyst and zeolite 5A, respectively, to remove traces of oxygen and water.

Catalyst preparation. Each catalyst was prepared by refluxing a solution of $[\text{Os}_3(\text{CO})_{12}]$ in *n*-heptane with γ - Al_2O_3 for 2 h under nitrogen. The supernatant liquid was drawn off, and the solid was washed with *n*-heptane to remove physically adsorbed $[\text{Os}_3(\text{CO})_{12}]$; the washing was repeated until the supernatant liquid no longer had the yellow color indicative of $[\text{Os}_3(\text{CO})_{12}]$. The light-yellow solid was dried in flowing nitrogen and then under vacuum. The Os content was varied by changing the amount of $[\text{Os}_3(\text{CO})_{12}]$ in the slurry containing the γ - Al_2O_3 . The solid samples were analyzed for Os by Schwartzkopf Microanalytical Laboratory, Woodside, N.Y.; the results are summarized in Table 1. The catalyst samples were stored in a desiccator over anhydrous CaSO_4 .

Catalytic reaction experiments. The catalytic reaction experiments were carried out with a flow microreactor interfaced to a gas chromatograph. The reactor was an 28-cm stainless-steel tube (6.4 mm o.d.) downstream of a 1.2-m preheater tube (3.2 mm

TABLE 1
Analysis of Alumina-Supported Osmium Catalysts

Sample number	Pretreatment temperature of alumina (°C)	Osmium content (wt%)
1	120	1.26
2	250	0.92
3	400	0.91
4	550	0.93

o.d.). These were immersed in an oil bath, with the temperature controlled within $\pm 1^\circ\text{C}$ by a thermometer (Sargent). The liquid reactant, hexene-1, was held in a thermostated evaporator; the reactant was vaporized into a stream of dried and deoxygenated carrier gas (helium, hydrogen, or carbon monoxide), which bubbled through the hexene-1. Analysis by GLC indicated that when the flow rate of carrier gas was $< 60 \text{ cm}^3/\text{min}$, the helium was saturated with hexene-1. The partial pressure of hexene-1 in the reactant stream was calculated from the vapor pressure of hexene-1 at the vaporizer temperature. Usually, 0.5 g of catalyst powder (< 100 mesh) was placed in the reactor (the handling being done in air) and held in place with glass wool. To avoid high flow rates of helium or hydrogen in the measurement of the lower conversions of hexene-1, sometimes only 0.25 g of catalyst was used.

In a typical catalysis experiment, the product stream was sampled periodically for the on-line GLC analysis. Products were separated in a 3.7-m \times 3.2-mm o.d. column packed with bis-2-methoxyethyladipate (16%) on chromosorb P-AW; the column was held at 35°C. A flame ionization detector was used, and peak areas were determined electronically.

Infrared spectra of catalysts. Samples were prepared for infrared spectroscopy as follows: an alumina wafer, pressed at 12,000 psi and having a diameter of 20 mm

and a mass of about 30 mg, was placed in a quartz infrared cell interfaced to a vacuum and gas-handling system [described previously (7)] and heated to an assigned temperature (namely, 120, 250, 400, or 550°C) under vacuum (10^{-4} Torr) for 3 h. After the alumina wafer had cooled to room temperature, a solution of $[\text{Os}_3(\text{CO})_{12}]$ in *n*-heptane at about 98°C was introduced by pipet onto the wafer surface under a helium atmosphere; the solvent was then removed by evacuation of the cell. The purpose of this preparation was to prevent contamination of the catalyst by contact with air.

Infrared spectra were measured with a Nicolet Model 7199 Fourier transform infrared spectrometer in the range 400 to 4000 cm^{-1} ; the resolution was 4 cm^{-1} . Spectra of the physically adsorbed $[\text{Os}_3(\text{CO})_{12}]$ were measured at room temperature, and the sample was then heated to 100°C, and spectra of the resulting (chemisorbed) osmium species were recorded and monitored during the heating. Used catalyst samples were also characterized with this apparatus.

RESULTS AND DISCUSSION

Catalytic Activity and Catalyst Structure

The catalysts prepared from $\gamma\text{-Al}_2\text{O}_3$ and $[\text{Os}_3(\text{CO})_{12}]$ were active for isomerization of hexene-1 to give a mixture of *cis*- and *trans*-hexene-2 at 120°C and 1 atm, as expected (7–9). The alumina support was found to have a negligible activity under these conditions.

The catalytic activity declined with time on stream in the flow reactor. To characterize the changes in the catalyst, the activity was monitored in transient experiments. After the sample had been heated to 120°C in flowing helium (in a period of about 30 min), the hexene-1 was introduced into the helium carrier gas stream, and periodic analysis of the product stream was begun 10 min later. The results (Fig. 1) show that the hexene-1 conversion decreased significantly for the first 2 h and then declined only slightly during the remainder of the ex-

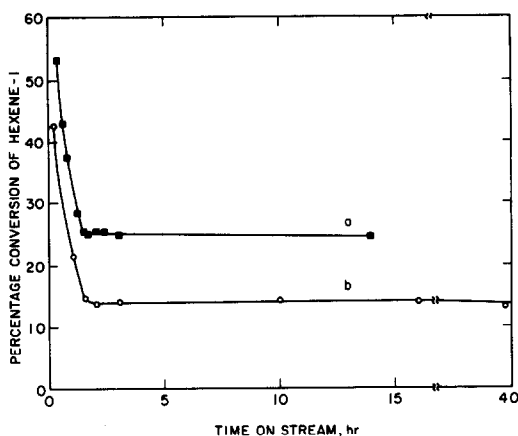
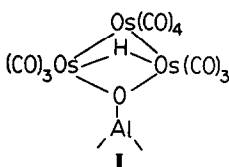


FIG. 1. Change of activity of the supported osmium catalyst (sample 3, Table 1) with time on stream in a flow reactor at 1 atm and 120°C. The catalyst initially incorporated triosmium clusters (Structure I). The mass of catalyst was 0.50 g. Curve a, $P_{\text{hexene-1}} = 0.076$ atm; feed flow rate = 19.6 cm^3/min . Curve b, $P_{\text{hexene-1}} = 0.23$ atm; feed flow rate = 17.4 cm^3/min .

periment. Results of a separate experiment showed that when the catalyst was heated to 200°C in flowing helium for 4 h prior to the beginning of hexene-1 flow at 120°C, the initial activity was approximately equal to the steady-state activity measured in the aforementioned experiment. We infer that the same catalytic species formed ultimately in all these experiments.

Some insight into the evolution of the catalytic activity and the structure of the catalytic species is provided by infrared spectra measured under conditions similar to those of the catalytic reaction—but in the absence of the hexene-1 reactant. The spectrum of the initially prepared catalyst (spectrum A, Fig. 2) [2125(w), 2106(m), 2068(vs), 2053(s), and 2026(vs) cm^{-1}] is similar to those reported (3, 4) and is in agreement with our observations of the catalysts prepared in the infrared cell (Table 2). These and other spectroscopic results have been interpreted as evidence that in the catalyst synthesis $[\text{Os}_3(\text{CO})_{12}]$ reacted with —OH groups of the alumina surface, splitting off two CO ligands and forming structure I (2–5, 11, 12):



When the sample incorporating this structure was heated to 120°C, the original carbonyl bands located at 2053, 2068, and 2125 cm^{-1} disappeared over a 2-h period, and the bands located at 2026 and 2106 cm^{-1} shifted to 2024 and 2118 cm^{-1} , respectively (Fig. 2). After 1 h, a new band at 1960 cm^{-1} began to appear (spectrum D); then its intensity gradually increased as it shifted to 1940 cm^{-1} . After 4 h, there were only three carbonyl bands, located at 1940, 2024, and 2118 cm^{-1} (spectrum H). Further

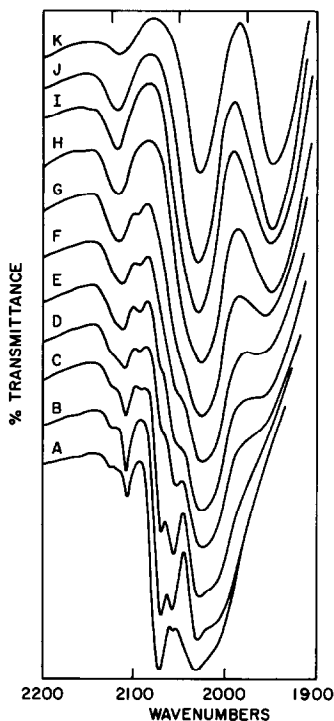


FIG. 2. Breakup of the Al_2O_3 -supported triosmium clusters indicated by changes in the infrared spectrum (sample 3). (A) sample at 25°C; (B) sample heated to 120°C in flowing helium; samples held at 120°C in helium for various times: (C) 0.5 h; (D) 1 h; (E) 1.5 h; (F) 2 h; (G) 3 h; (H) 4 h; (I) 5 h; (J) 10 h; (K) after use in hexene-1 isomerization at 120°C for 30 h.

heating caused an increase in the intensity of the 1940- cm^{-1} band relative to that of the 2118- cm^{-1} band. These results are in agreement with earlier observations indicating that the supported cluster I broke apart on the surface, giving supported mononuclear Os(II) carbonyl complexes (2-7, 12). The sample was finally light gray.

After a sample had been used to catalyze the hexene-1 isomerization for 30 h at 120°C, it was removed from the reactor, pressed into a wafer, and characterized spectroscopically (the sample came in contact with air) (spectrum K, Fig. 2). This spectrum also indicates the presence of the Os(II) carbonyl complexes. The intensities of the bands at 2118 and 2024 cm^{-1} were less than those of the sample heated to 120°C in helium for only a few hours, indicating that partial decarbonylation had occurred slowly during the catalysis experiment (Fig. 2).

We conclude from these spectroscopic results that the clusters initially present on the catalyst surface broke up during the catalysis experiment, giving surface-bound mononuclear Os(II) complexes. The changes in the infrared spectra of the surface osmium carbonyl species took place in two stages: The first change was fast, being completed in about 2 h; it is characterized by the disappearance of bands representative of structure I, located at 2053, 2068, and 2125 cm^{-1} . The second stage, lasting much longer, is characterized by a slow variation of the relative intensities of the new bands at 1940, 2024, and 2118 cm^{-1} .

We associate the rapid changes of the infrared spectrum in the first stage with the initial rapid decline in the catalytic activity (shown in Fig. 1), which also occurred in about 2 h—this was the period required for the catalyst to become nearly stable. This correspondence suggests that the initial catalytic species were the triosmium clusters and that the final catalytic species were the Os(II) complexes—which are less active than the clusters. During the second stage, the relative intensities of the three carbonyl

TABLE 2
Infrared Frequencies of Alumina-Supported Triosmium Clusters

Pretreatment temperature of Al ₂ O ₃ (°C)						ν_{CO} (cm ⁻¹)	Ref.
Physically adsorbed [Os ₃ (CO) ₁₂] at 25°C ^a							
120		2069vs	2035s	2010vs			This work
250		2069vs	2035vs	2014m		2003w(sh)	This work
400		2069vs	2034vs	2016m		2003w(sh)	This work
550		2069vs	2034vs	2015m		2001w(sh)	This work
300		2069vs	2035vs	2015m		2000m	(3)
400	2109vw	2068vs	2033s	2020s	2011sh	2000sh	(2)
Alumina-supported osmium cluster at 100°C							
120		2106m	2067vs	2054s		2019vs	This work
250		2107w	2067vs	2054m		2020vs	This work
400		2106m	2067vs	2054s		2021vs	This work
550		2106m	2069vs	2054s		2029vs	This work
300		2107w	2068s	2056s		2023vs	(3) ^b
400		2109w	2070s	2058s		2030vs	(4) ^b

^a The carbonyl stretching frequencies of [Os₃(CO)₁₂] in cyclohexane solution are 2069vs, 2035vs, 2015m, and 2000m cm⁻¹ (3).

^b These spectra were measured at room temperature.

bands (at 1940, 2024, and 2118 cm⁻¹) changed slowly, and the catalytic activity also changed slowly; only after about 40 h had a noticeable decline in catalytic activity occurred (Fig. 1). These results suggest that after some fraction of the CO ligands on the osmium complexes had been lost, further decarbonylation did not have a significant effect on the activity; we infer that the catalytic species present finally were osmium carbonyl complexes.

The complexes formed by breakup of the supported clusters have been characterized by high-resolution transmission electron microscopy (6, 13); the results demonstrate that the osmium was finally present in ensembles consisting of three neighboring Os(II) complexes. The cluster may lie on the surface so that the three osmium atoms are all bonded at different surface oxygen atoms; breaking of the Os–Os bonds and oxidation of the osmium to give Os(II) species would complete the formation of the ensembles. The CO ligands on the osmium

may be attacked by surface —OH groups to form CO₂ and H₂—products that were observed by several authors (2, 4, 5, 14). The hydrogen formed initially in this process may promote the catalytic isomerization, being responsible in part for the initial high activity of the catalyst—this inference is drawn from the results (mentioned below) indicating that the hexene-1 isomerization rate increased in the presence of hydrogen in the reactant stream.

Effect of Alumina Pretreatment Temperature on the Catalytic Properties

To determine the influence of the surface structure of the alumina on the catalytic properties, we investigated physisorption and chemisorption of [Os₃(CO)₁₂] on alumina samples calcined at various temperatures and measured their catalytic activities for isomerization of hexene-1. The infrared data summarized in Table 2 show that the carbonyl frequencies of physically ad-

sorbed $[\text{Os}_3(\text{CO})_{12}]$ and the structures formed by reaction of $[\text{Os}_3(\text{CO})_{12}]$ with the surfaces were about the same for all the alumina samples. The physically adsorbed $[\text{Os}_3(\text{CO})_{12}]$ had three major bands (at 2069, 2035, and 2015 cm^{-1}), the same as those observed for $[\text{Os}_3(\text{CO})_{12}]$ in solution (Table 2). When the $[\text{Os}_3(\text{CO})_{12}]$ reacted with each of these surfaces, the four major bands mentioned previously appeared (at 2106, 2067, 2054, and 2020 cm^{-1}). These results are in good agreement with those reported earlier (2-4, 10).

The data of Table 3 show that the spectra in the carbonyl region of the several catalysts which had been used in isomerization of hexene-1 were all nearly the same. There were only three major bands, located at 1928-1938, 2016-2026, and 2116-2124 cm^{-1} . These bands are in agreement with spectra G-K in Fig. 2, namely, the spectra of the ensembles of Os(II) carbonyls.

These results suggest that the chemical interaction between $[\text{Os}_3(\text{CO})_{12}]$ and the surface —OH groups of alumina was not significantly influenced by the density of

surface —OH groups or by other details of the surface chemistry. The results appear to be consistent with the few results presented in the literature for triosmium clusters bonded to other oxides, including SiO_2 and TiO_2 (2-4, 10). All these supports, except, probably, MgO (10), evidently react in the same way with $[\text{Os}_3(\text{CO})_{12}]$, forming structure I.

Although the infrared spectra of all the used catalysts were almost the same (Table 3), the activity of one of the catalysts (the one prepared with the alumina dried at 120°C), was higher than the activities of the other three catalysts, which were treated at higher temperatures and which were all nearly equal in activity (Fig. 3). It is expected that the support of the more active catalyst had much more adsorbed water than the other three, and we attribute the higher activity to the water. After this catalyst had been held in flowing helium at 200°C for 2 h, its activity became nearly the same as the activities of the other catalysts (Fig. 3, curve B); this result is consistent with results indicating that when the calcin-

TABLE 3
Comparison of the Infrared Spectra of Fresh and Used Catalysts^a

Catalyst sample	ν_{CO} (cm^{-1})					
Fresh						
1	2010sh	2025vs	2052s	2066vs	2105m	2126vw
2	2007sh	2025vs	2051m	2067vs	2104m	2126w
3	2004sh	2026vs	2056s	2067vs	2106m	2126w
4	2010sh	2027vs	2055s	2067vs	2107m	2125w
Used						
1	1928vs	2016vs	2116m			
2	1934vs	2026vs	2118m			
3	1943vs	2026vs	2126m			
4	1934vs	2026vs	2118sh	2125m		
Thermally decomposed cluster ^b						
1	1940vs	2022vs	2116s			
2	1948s	2026vs	2112s			
3	1942vs	2028vs	2114s			
4	1948vs	2028vs	2118s			

^a Infrared spectra were measured at 25°C and atmospheric pressure.

^b Infrared spectra were measured after the fresh catalysts had been held at 140°C and 10^{-3} Torr for 30-60 min.

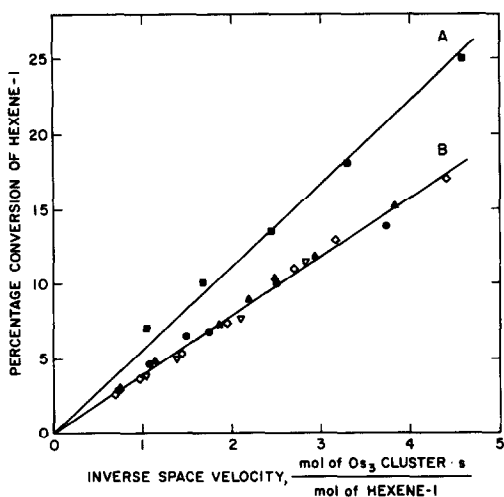


FIG. 3. Dependence of the catalytic activity for hexene-1 isomerization on the pretreatment temperature of the alumina. Reaction temperature = 120°C; $P_{\text{hexene-1}} = 0.23$ atm; $P_{\text{He}} = 0.77$ atm. Data were collected after the clusters initially present on the surface had broken up into complexes. (A) catalyst sample 1; (B) catalyst samples 2 (\blacktriangle), 3 (\diamond), and 4 (\bullet), and sample 1 (∇) after heating to 200°C under He for 2 h.

ing temperature of alumina is higher than 200°C, the water is desorbed almost completely (15). We suggest, therefore, that the adsorbed water did not perturb the interaction between $[\text{Os}_3(\text{CO})_{12}]$ and surface —OH groups in the synthesis of the catalyst, and the effect of water on the carbonyl bands was weak.

Influence of H_2 , CO , and O_2 on Catalytic Activity

Investigations of homogeneous reactions catalyzed by transition metal carbonyl complexes have indicated that metal hydrides often have higher catalytic activities for olefin isomerization than the transition metal carbonyls (16–19); this result applies, in particular, to triosmium cluster catalysts (17, 18), and it is inferred to pertain also to triosmium clusters supported on phosphine-functionalized silica and polymers (8, 9, 20). The high initial activity of the alumina-supported osmium catalysts may be related to hydride ligands on the osmium. To test this notion, we performed

experiments with hydrogen in the feed to the flow reactor. The results of Fig. 4 demonstrate that inclusion of hydrogen in the feed in place of helium led to an increase in the activity of the catalyst. At the same time, the activity of the catalyst for hydrogenation of the olefin became apparent (curve C). The results are similar to those of Sánchez-Delgado *et al.* (19) for catalysts derived from silica-supported ruthenium carbonyl clusters.

Further evidence of the acceleration of the isomerization reaction by hydrogen was obtained when a pulse of hydrogen was injected into the feed stream (Fig. 5, curve II). When 10 cm³ of hydrogen was injected into the stream of helium and hexene-1, the reaction rate immediately underwent a sharp increase, followed by a decrease as the hydrogen was purged out of the reactor. Presumably a surface osmium hydride complex formed which was unstable in the absence of hydrogen.

When a fresh supported triosmium cluster catalyst was used for hexene-1 isomerization in the presence of hydrogen at 100°C, the initial activity was higher than that of the fresh catalyst used in the pres-

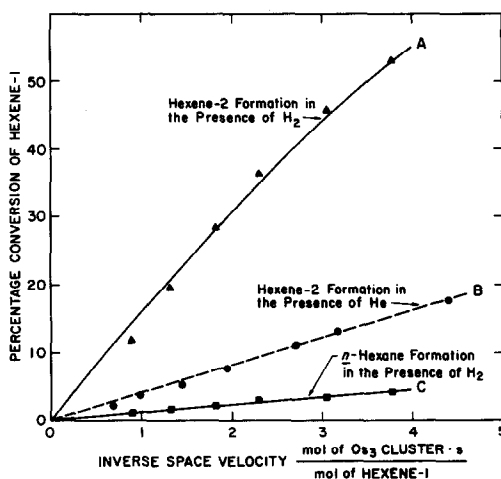


FIG. 4. Influence of hydrogen on the activity of the supported osmium catalyst (sample 3). Temperature = 120°C; total pressure = 1 atm; $P_{\text{hexene-1}} = 0.23$ atm. Data were collected after the clusters initially present on the surface had broken up into complexes.

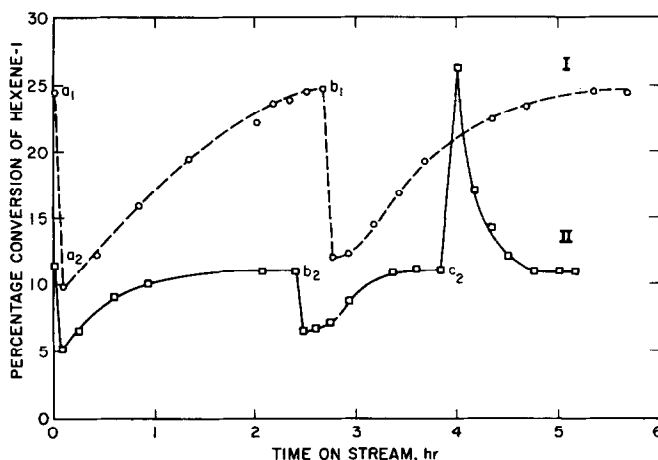


FIG. 5. Effects of air and hydrogen on the activity of the catalyst which had undergone deactivation resulting from breakup of the supported triosmium clusters as illustrated in Fig. 1. Temperature = 120°C ; $P_{\text{hexene-1}} = 0.076$ atm; $P_{\text{He}} = 0.92$ atm. Curve I, catalyst sample 1 (0.50 g); feed flow rate = 12.8 cm^3/min . Curve II, sample 4 (0.50 g), feed flow rate = 21.6 cm^3/min . Pulses of air (10 cm^3) were introduced at points a_1 , a_2 , b_1 , and b_2 . A pulse of H_2 (10 cm^3) was introduced at point c_2 .

ence of helium (Figs. 1 and 6). Moreover, in contrast to the performance of the catalyst used without hydrogen in the feed, the isomerization and hydrogenation activities of the fresh supported cluster catalyst did not decrease in 10 h of operation (Fig. 6). To provide a structural characterization of the catalyst after the isomerization reaction had been carried out under hydrogen for various times, fractions of the sample (about 50 mg) were removed, pressed into wafers, and characterized spectroscopically; the results are shown in Fig. 7. The infrared bands in the carbonyl region show that the catalyst had undergone some decarbonylation. Comparing the carbonyl spectra of Fig. 7 with those of Fig. 2, we see the similarity between curves A and B of Fig. 7 and curves F and J of Fig. 2, respectively. This comparison suggests that the degree of decarbonylation of the catalysts was about the same under hydrogen and under helium. The difference in the catalytic activities is therefore suggested to be a consequence of different (and still undetermined) structures of the surface osmium species, the more active species perhaps being aggregates of osmium metal.

The influence of CO as a reaction inhibitor provided some further evidence of the nature of the catalyst. When hexene-1 flowed over the catalyst at 1 atm and 120°C in the presence of CO at a partial pressure

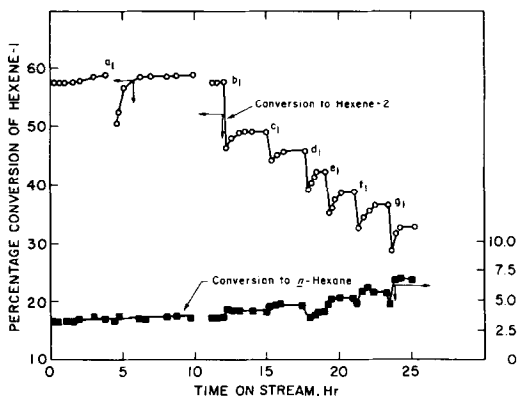


FIG. 6. The influence of air on the activity of the catalyst at 100°C and 1 atm. The catalyst (0.50 g, sample 3) was initially present in the form of the supported triosmium cluster. $P_{\text{hexene-1}} = 0.076$ atm; $P_{\text{H}_2} = 0.92$ atm; feed flow rate = 24.2 cm^3/min . At point a_1 , the catalyst was taken off stream and exposed to air at room temperature for 45 min. After an interruption of the experiment at 10 h on stream, a sequence of tests was done with pulses of air introduced into the feed stream at points b_1 , c_1 , etc.

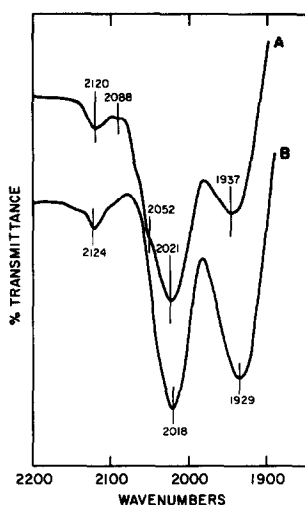


FIG. 7. Infrared spectra of catalysts used for hexene-1 isomerization at 120°C in the presence of H₂. (A) used for 3 h; (B) used for 25 h.

of 0.78 atm, the rate of the isomerization reaction was nil. The infrared spectra of the catalyst used under these conditions for 5 h showed that the locations and intensities of the carbonyl bands were almost the same as those of the fresh catalyst (Fig. 8). These results indicate that CO completely inhibited the decarbonylation of the catalyst and prevented the breakup of the triosmium

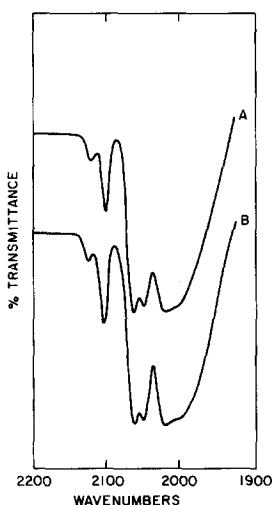


FIG. 8. Infrared spectra of fresh and used catalysts: (A) catalyst used in hexene-1 isomerization at 120°C in the presence of CO; (B) fresh catalyst.

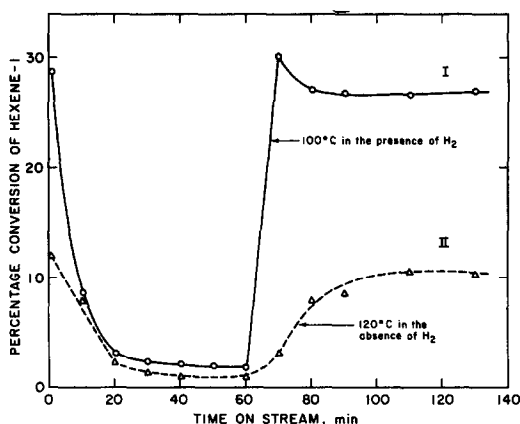


FIG. 9. Inhibition of the hexene-1 isomerization by CO; the catalyst was 0.50 g of sample 3. Curve I: temperature = 100°C; $P_{\text{hexene-1}} = 0.21$ atm; $P_{\text{H}_2} = 0.75$ atm; $P_{\text{CO}} = 0.035$ atm; feed flow rate = 23.9 cm³/min. Curve II: temperature = 120°C; $P_{\text{hexene-1}} = 0.21$ atm; $P_{\text{He}} = 0.73$ atm; $P_{\text{CO}} = 0.054$ atm; feed flow rate = 11.5 cm³/min. Prior to introduction of CO into the feed stream, the catalyst had been in operation in the presence of hexene-1 and helium long enough to have undergone deactivation associated with breakup of the initial supported triosmium clusters.

clusters, which otherwise occurred rapidly under these conditions.

Transient experiments with CO introduced into the feed stream containing hexene-1 and helium (or hydrogen) confirmed that CO was a strong reaction inhibitor (Fig. 9). After cessation of the CO flow, the activity of the catalyst was restored in 10 min (Fig. 9). The changes were similar with either helium or hydrogen in the reactant stream, but the activity was restored more rapidly after the cessation of CO flow when hydrogen was the second component present with the hexene-1, rather than helium (Fig. 9). In every case, an increase in the partial pressure of CO led to a decrease in the rate of the catalytic reaction. We conclude that CO inhibited the decarbonylation of the initial surface osmium clusters and the formation of the catalytically active ensembles, and it also inhibited catalytic reaction by binding to coordinatively unsaturated Os centers in competition with hexene-1 (and possibly hydrogen).

The results of Fig. 6 show that after the catalyst initially present in the form of supported triosmium cluster had been exposed to air at room temperature, its activity returned to its initial value in the presence of hydrogen. This lack of sensitivity of the catalyst to air at room temperature is in agreement with the results of Hunt *et al.* (21) for catalytic hydrogenation of ethylene. But when a pulse of 10 cm³ of air was introduced into the reactant stream containing hexene-1 and hydrogen at 100°C, the activity decreased, and each succeeding pulse caused the hexene-1 conversion to decrease about 4 to 7% (Fig. 6). In this experiment, introduction of air might have led to oxidation of the surface osmium complex, giving a species which was difficult to reduce with hydrogen to its original state. Therefore, we infer that new catalytic sites (of undetermined structure) were formed by the oxidation-reduction process; the newly formed sites were more active for hydrogenation of hexene-1 (Fig. 6).

In contrast to these results, when the hexene-1 isomerization was carried out at 120°C in the absence of hydrogen with a catalyst consisting of the complexes formed by breakup of the clusters, the introduction of air into the reactant stream caused only a temporary decrease in the catalytic activity, which was restored to its original value in about 2 h (Fig. 5). This period was evidently associated with removal of adsorbed oxygen, as described by Hunt *et al.* (21). We suggest that the surface complex was an Os(II) complex (2, 5) on which the oxygen adsorption was weak and reversible.

ACKNOWLEDGMENT

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REFERENCES

1. Yermakov, Yu. I., Kuznetsov, B. N., and Zakharov, V. A., "Catalysis by Supported Complexes." Elsevier, Amsterdam, 1981.
2. Smith, A. K., Besson, B., Basset, J. M., Psaro, R., Fusi, A., and Ugo, R., *J. Organometal. Chem.* **192**, C31 (1980).
3. Deeba, M., and Gates, B. C., *J. Catal.* **67**, 303 (1981).
4. Psaro, R., Ugo, R., Zanderighi, G. M., Besson, B., Smith, A. K., and Basset, J. M., *J. Organometal. Chem.* **213**, 215 (1981).
5. Knözinger, H., and Zhao, Y., *J. Catal.* **71**, 337 (1981).
6. Knözinger, H., Zhao, Y., Tesche, B., Barth, R., Epstein, R., Gates, B. C., and Scott, J. P., *Faraday Discuss. Chem. Soc.* **72**, 53 (1981).
7. Barth, R., Gates, B. C., Zhao, Y., Knözinger, H., and Hulse, J., *J. Catal.* **82**, 147 (1983).
8. Freeman, M. B., Patrick, M. A., and Gates, B. C., *J. Catal.* **73**, 82 (1982).
9. Nguini Effa, J.-B., Lieto, J., and Aune, J.-P., *J. Mol. Catal.* **15**, 367 (1982).
10. Deeba, M., Scott, J. P., Barth, R., and Gates, B. C., *J. Catal.* **71**, 373 (1981).
11. Besson, B., Moraweck, B., Smith, A. K., Basset, J. M., Psaro, R., Fusi, A., and Ugo, R., *J. Chem. Soc. Chem. Commun.* 569 (1980).
12. Deeba, M., Streusand, B. J., Schrader, G. L., and Gates, B. C., *J. Catal.* **69**, 218 (1981).
13. Schwank, J., Allard, L. F., Deeba, M., and Gates, B. C., *J. Catal.* **84**, 27 (1983).
14. Thomas, T. J., Hucul, D. A., and Brenner, A., *ACS Symp. Ser.* **192**, 267 (1982).
15. Peri, J. B., and Hannan, R. B., *J. Phys. Chem.* **64**, 1529 (1960).
16. Castiglioni, M., Milone, L., Osella, D., Vaglio, G. A., and Valle, M., *Inorg. Chem.* **15**, 394 (1976).
17. Keister, J. B., and Shapley, J. R., *J. Amer. Chem. Soc.* **98**, 1056 (1976).
18. Deeming, A. J., and Hasso, S., *J. Organometal. Chem.* **114**, 313 (1976).
19. Sánchez-Delgado, R. A., Duran, I., Montfort, J., and Rodríguez, E., *J. Mol. Catal.* **11**, 193 (1980).
20. Goldwasser, J., and Hall, W. K., Proceedings Inter. Iberian Cong. Catal. (Madrid), 1982.
21. Hunt, D. J., Jackson, S. D., Moyes, R. B., Wells, P. B., and Whyman, R., *J. Chem. Soc. Chem. Commun.* 85 (1982).