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Support Effects in Hexene-1 Isomerization Catalyzed by Oxide-Supported Osmium Complexes

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Oxide-supported osmium was prepared from [$Os_3(CO)_{12}$] and MgO, γ-Al_2O_3, SiO_2, TiO_2, ZrO_2, CeO_2, Cr_2O_3, and ThO_2. The samples were tested as catalysts for hexene-1 isomerization with vapor-phase reactant at 1 atm and 120°C. The activities of the catalysts supported on MgO, Al_2O_3, and SiO_2 were approximately the same and at least an order of magnitude greater than those of the catalysts on the other supports. Infrared spectra indicate the presence of mononuclear osmium carbonyl complexes on the surfaces of all the used catalysts, and these are suggested to be the catalytic sites. The support effects may indicate differences in osmium-surface coordination, degree of coordinative unsaturation, or coverage by carbon.

INTRODUCTION

There has been a surge of interest in supported osmium catalysts motivated by indications that many of them are structurally simple (*1–5*). Most of the recent work has been devoted to catalysts prepared from triosmium carbonyl clusters, since the intact clusters can be bonded to surface oxygens of a variety of metal-oxide supports. Silica- and alumina-supported triosmium carbonyl clusters evidently maintain their framework structures at low reaction temperatures, and they have been inferred to be catalytically active for olefin isomerization (*6–8*) and hydrogenation (*9*). But the supported clusters are not very stable; when the temperature increases beyond roughly 100°C (depending on the support), the clusters are partially decarbonylated with breaking of the Os–Os bonds (*1–8*); the resulting species on alumina have been described as ensembles consisting of three Os atoms bonded adjacent to each other on the support (*5*), evidently in the divalent state and typically having 2 or 3 carbonyl ligands each (*1, 2, 4*). The ensembles and their cluster precursors have been observed by transmission electron microscopy (*5, 10*).

The work reported here was an attempt to take advantage of the structural simplicity of the oxide-supported ensembles of osmium; these were prepared with a series of metal-oxide supports and compared as catalysts for a simple test reaction, the isomerization of hexene-1. The objective was to compare a set of catalysts with equivalent structures, differing only in the interactions between the support and the catalytically active metal species—and to determine how the catalytic activity depends on the nature of the support.

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TABLE 1

Supported Osmium Catalysts Prepared from $[Os_3(CO)_{12}]$

Sample no.	Support	Support pretreatment temperature (°C)	Support area (m^2/g)	Osmium content (wt%)
1	Al_2O_3	120	185	1.26
2	Al_2O_3	250	185	0.92
3	Al_2O_3	400	185	0.93
4	Al_2O_3	550	185	0.91
5	SiO_2	400	200 ± 25	0.93
6	MgO	400	30	0.99
7	ZrO_2	400	55	0.71
8	TiO_2	400	50 ± 15	0.83
9	CeO_2	400	80	3.87
10	ThO_2	400	35	0.56
11	Cr_2O_3	400	44	1.25

EXPERIMENTAL

Materials and Catalysts

Each of the following supports [SiO_2 (Cab-O-Sil, grade M-5, <325 mesh), γ-Al_2O_3 (Ketjen, <100 mesh), MgO (Matheson, Coleman, and Bell), and TiO_2 (Degussa, 30 nm)] was prepared with enough deionized water to give a thick paste followed by drying at 120°C in air. The ZrO_2 and Cr_2O_3 were used as supplied by Degussa; the CeO_2 was prepared by thermal decomposition of $Ce(NO_3)_3 \cdot 6H_2O$ in oxygen at 500°C for 3 h (the sample was heated to 500°C at a rate of 10°C/min). ThO_2 was prepared by thermal decomposition of the oxalate at 400°C in air for 7 h, as described previously (*11, 12*). The BET surface areas of the supports are listed in Table 1.

The γ-Al_2O_3 was dehydroxylated to varying degrees by treatment with flowing oxygen for 4 h at 120, 250, 400, or 500°C; SiO_2, MgO, and TiO_2 were dehydroxylated at 400°C in flowing oxygen for 4 h; ZrO_2, Cr_2O_3, CeO_2, and ThO_2 were treated in oxygen at 400°C for 3 h and then evacuated at 400°C (at $<10^{-3}$ torr) for 6 h.

n-Heptane was dried and distilled under nitrogen; *n*-octane was dried over $MgSO_4$ under nitrogen. $[Os_3(CO)_{12}]$ (Strem), hexene-1 (Aldrich, 99%, chemically pure), and *trans*-hexene-2 (Aldrich, 99%, Gold Label) were used as received. Helium (Airco, 99.995%), hydrogen (Airco 99.995%), and carbon monoxide (Matheson, 99.99%) flowed through beds of active copper catalyst and zeolite 5A to remove traces of oxygen and water, respectively.

The catalysts were prepared by refluxing a solution of $[Os_3(CO)_{12}]$ with the pretreated oxide support under nitrogen (*3–5*). *n*-Heptane solvent was used with Al_2O_3, SiO_2, MgO, and TiO_2, and *n*-octane was used with ThO_2, ZrO_2, CeO_2, and Cr_2O_3. The samples were analyzed for Os by Schwartzkopf Microanalytical Laboratories, Woodside, New York; the results are given in Table 1.

Catalytic Reaction Rate Measurements

The catalytic reaction experiments were carried out with a flow microreactor interfaced to a gas chromatograph. The reactor was a stainless-steel tube (6.35-mm o.d. × 2.8-cm length) connected to a preheater tube (3.2-mm o.d. × 1.22-m length). These were immersed in an oil bath, with the temperature controlled to ±1°C. In a typical experiment, 0.5 g of catalyst powder mixed with glass wool was loaded into the reactor, which was then packed with glass wool plugs at the inlet and outlet.

The reactant liquid was held in a thermostated vaporizer; vaporized hexene-1 was carried into the reactor in a stream containing helium, and/or hydrogen, and/or carbon monoxide. Analysis by glc indicated that when the flow rate of carrier gas was <60 cm^3/min, the stream was saturated with hexene-1. The product stream was sampled periodically for on-line glc analysis; products were separated in a 3.2-mm o.d. × 3.7-m column packed with bis-2-methoxyethyladipate on Chromosorb P-AW and held at 35°C.

Infrared Spectroscopy of Catalysts

Spectroscopic characterization of the catalysts was carried out with samples in a quartz cell interfaced to a vacuum and gas handling system (*6*). The spectra were recorded with a Nicolet 7199 Fourier trans-form infrared spectrometer in the carbonyl stretching range (1800–2200 cm^{-1}) with a 4-cm^{-1} resolution.

RESULTS AND DISCUSSION

Hexene-1 Isomerization with γ-Al_2O_3-Supported Catalysts

Experiments were conducted at 1 atm and 90–140°C with hexene-1 in the presence of helium; the partial pressure of hexene-1 varied from 0.072 to 0.22 atm. The activity of the Al_2O_3 support was negligible under these conditions. The catalysts were pretreated at 120°C in flowing helium for 2 h before the hexene-1 was introduced. The hexene-1 was converted into a mixture of *cis*- and *trans*-hexene-2. The activity was initially high, decreasing in a short time to a steady-state value at each temperature, as observed previously (*7*). Kinetics data were collected after the catalytic activity became time-invariant.

The kinetics results show that conversions varied linearly with inverse space velocity, determining reaction rates directly. The isomerization reactions of hexene-1 to give *cis*- and *trans*-hexene-2 were both found to be zero order in the partial pressure of hexene-1. The observed ratio of cis to trans isomers was approximately 0.4 in all these experiments.

The rates of formation of *cis*- and *trans*-hexene-2 from hexene-1 were large in comparison with the rate of interconversion of the latter two isomers. We therefore represent the catalytic activity with the zero-order rate constants for formation of these isomers from hexene-1. The activation energy for the formation of the cis isomer was found to be 21.5 ± 1.3 kcal/mol and that for the formation of the trans isomer 17.9 ± 1.0 kcal/mol in the temperature range 100–140°C.

To compare the activities of catalysts pretreated at various temperatures, measurements of rates and activation energies were made under the conditions stated above. The results (Table 2) show that the rate constant for hexene-1 isomerization in the presence of the γ-Al_2O_3 catalyst pretreated at 120°C is about 1.4 times greater than that for the reaction in the presence of each of the other three γ-Al_2O_3 catalysts (which had approximately equal activities), and the activation energy is about 5 kcal/mol lower. The higher activity of the former catalyst may be related to the adsorbed water and/or surface —OH groups.

TABLE 2

Effect of the Pretreatment Temperature of Alumina on Catalytic Properties

Sample no.	Pretreatment temperature of alumina (°C)	10^2 × Rate constant for hexene-2 formation[a] (mol/(mol of Os_3 · s))			Activation energy[b] (kcal/mol)
		Cis	Trans	Total	
1	120	1.86	4.03	5.89	14.1 ± 0.7
2	250	1.28	2.91	4.19	19.8 ± 1.3
3	400	1.12	2.73	3.85	19.6 ± 1.1
4	550	1.37	3.02	4.39	18.5 ± 1.0

[a] The rate constants were measured at 120°C.

[b] The values are the activation energy for total hexene-2 formation.

Hexene-1 Isomerization with SiO_2- and MgO-Supported Catalysts

The hexene-1 isomerization was also investigated with catalysts prepared from $[Os_3(CO)_{12}]$ and the supports MgO and SiO_2. The conversions of hexene-1 observed with the supports themselves were about 1% of the values observed with the supported osmium catalysts under the same conditions. The kinetics results are summarized in Table 3. The rate of formation of hexene-2 was found to be independent of the partial pressure of hexene-1, as for the Al_2O_3-supported catalysts. The rate constant characterizing the MgO-supported catalyst is about 3 times greater than that characterizing the SiO_2-supported catalyst, which is approximately equal to that of the Al_2O_3-supported catalyst at 120°C (Tables 2 and 3). The activation energy for hexene-1 isomerization in the presence of the SiO_2-supported catalyst was found to be about 8 kcal/mol greater than that characteristic of the other two catalysts.

TABLE 3

Influence of the Support on Performance of Supported Osmium Catalysts Prepared from $[Os_3(CO)_{12}]$

Sample no.	Support	10^2 × Rate constant for hexene-2 formation[a] (mol/(mol of $Os_3 \cdot s$))			Activation energy[b] (kcal/mol)
		Cis	Trans	Total	
3	Al_2O_3	1.12	2.73	3.85	19.6 ± 1.1
5	SiO_2	1.58	2.76	4.34	27.7 ± 1.3
6	MgO	4.11	7.53	11.6	20.1 ± 1.5

[a] The rate constants were measured at 120°C.

[b] Activation energy for total hexene-2 formation.

The relatively high activity of the MgO-supported catalyst may be related to the basicity of the MgO surface. In the catalyst preparation, the MgO is far more reactive toward $[Os_3(CO)_{12}]$ than the γ-Al_2O_3 and SiO_2, as evidenced by the rapid uptake of the cluster from the solution—this solution became colorless after refluxing for about 1 h, whereas the solutions in contact with the other two supports were still light yellow after 2 h. When the MgO-supported sample was washed with *n*-heptane at 98°C, the solution did not take on the yellow color indicative of extracted $[Os_3(CO)_{12}]$. The MgO-supported sample is sensitive to air and undergoes structural changes upon heating, as observed previously (*13, 14*). The infrared spectra (Fig. 1) show that when the sample was heated to 120°C in flowing helium, the frequencies and intensities of the carbonyl bands changed so rapidly that the shoulders at 1954, 1983, and 2102 cm^{-1} disappeared and the intensities of the bands at 2005 and 2074 cm^{-1} decreased markedly after 10 min. There were only two strong bands (at 1911 and 2003 cm^{-1}) and a very weak band (at 2072 cm^{-1}) detectable after 1 h. The spectra of the catalyst after it had been used in the isomerization reaction at 120°C for 25 h (and transferred in air to the infrared cell) also had only two strong bands in the carbonyl region (at 1916 and 2007 cm^{-1}). These results suggest that the $[Os_3(CO)_{12}]$ adsorbed on MgO is easily attacked by basic —OH groups to form (partially) decarbonylated surface osmium species, which are different from the species on γ-Al_2O_3 and SiO_2 and are catalytically more active.

The olefin isomerization reaction occurring in the presence of the MgO-supported catalyst was promoted by hydrogen. [This promotion was also observed with the γ-Al_2O_3-supported catalyst (*8*).] For example, the rates observed for isomerization of hexene-1 in the presence of H_2 were 9.4×10^{-2} and 19.8×10^{-2} mol/(mol of $Os_3 \cdot s$) at 100 and 110°C, respectively. These rates are 4.3 and 3.8 times greater than those ob-

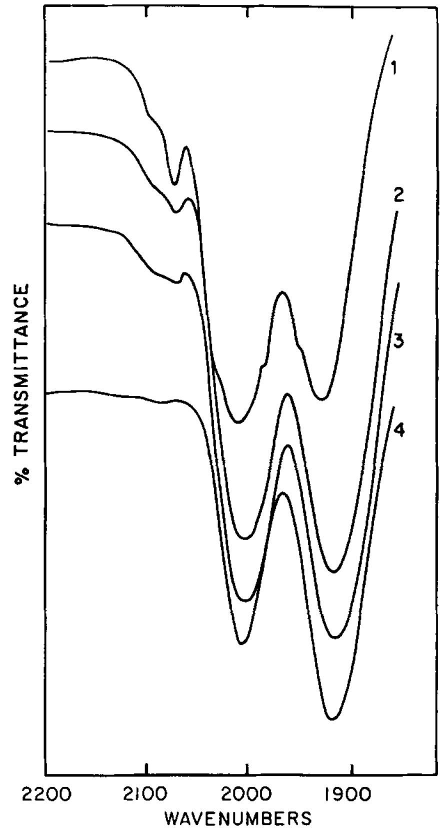

FIG. 1. Infrared spectra taken at 120°C of the MgO-supported catalyst prepared from $[Os_3(CO)_{12}]$: 1, fresh catalyst; 2, catalyst in helium for 10 min; 3, catalyst in helium for 1 h; 4, catalyst after use in hexene-1 isomerization for 25 h.

served in the absence of hydrogen at 100 and 110°C, respectively.

The rates of hydrogenation of hexene-1 in the presence of hydrogen and the MgO-supported catalyst were 2.6×10^{-2} and 3.9×10^{-2} mol/(mol of $Os_3 \cdot s$) at 100 and 110°C, respectively. The high hydrogenation activity was not observed with the γ-Al_2O_3- and SiO_2-supported catalysts. The effect of hydrogen suggests a role of osmium hydride intermediates (*7, 8*), but the role of the MgO support is unexplained.

Strong inhibition of the isomerization reaction by CO was observed with the MgO-supported catalyst, as it had been with the Al_2O_3-supported catalyst (*8*); when hydrogen in the feed stream was replaced by CO, the activity of the catalyst decreased rapidly to an undetectably low value. Even after the deactivated catalyst had been treated at 100°C in flowing hydrogen for 3 h, it did not have any detectable activity.

The catalytic properties of the SiO_2-supported osmium are similar to those of the Al_2O_3-supported osmium, but the promotion of the isomerization reaction by hydrogen was found to be greater with the SiO_2-supported material. On the other hand, the hydrogenation activity of the SiO_2-supported catalyst was less than that of the Al_2O_3-supported catalyst, being too low to measure.

The isomerization rates of hexene-1 in the presence of hydrogen and the SiO_2-supported catalyst were 1.1×10^{-1} and 1.7×10^{-1} mol/(mol of $Os_3 \cdot s$) at 100 and 110°C, respectively. These values are 14.6 and 11.3 times greater than those observed in the presence of helium at 100 and 110°C, respectively.

The high activity of the SiO_2-supported catalyst in the presence of hydrogen may be associated with the relative stability of the osmium cluster on the SiO_2 surface. We have observed from the infrared spectra (Fig. 2) that the changes in the carbonyl bands indicative of triosmium carbonyl clusters on SiO_2 are much slower than the changes observed with the Al_2O_3- and MgO-supported catalysts at 120°C in flowing helium.

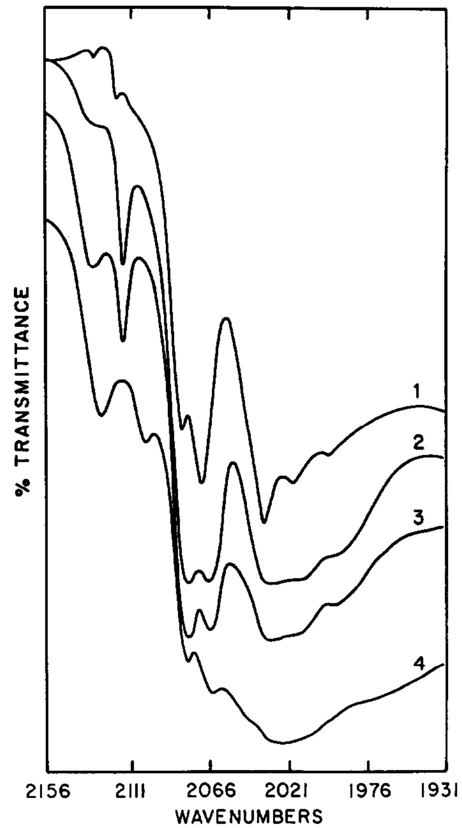

FIG. 2. Infrared spectra taken at 120°C of the SiO_2-supported catalyst prepared from $[Os_3(CO)_{12}]$: 1, fresh catalyst; 2, catalyst in helium for 2 h; 3, catalyst in helium for 6 h; 4, catalyst after use in hexene-1 isomerization for 20 h.

We infer that the high activity of the SiO_2-supported catalyst in the presence of hydrogen might be an indication of preservation of the original cluster framework, which (on Al_2O_3 at least) is more highly active for olefin isomerization in the presence of hydrogen than is the ensemble (*8*).

The strong inhibition of the isomerization reaction by CO was also demonstrated with the SiO_2-supported catalyst. But the isomerization activity of the catalyst was not suppressed completely in the presence of

CO at a partial pressure of 0.77 atm. This result is similar to that observed with the Al_2O_3-supported catalyst.

Hexene-1 Isomerization with ZrO_2-, TiO_2-, CeO_2-, ThO_2-, and Cr_2O_3-supported Catalysts

The rates of hexene-1 isomerization in the presence of osmium-cluster-derived species on ZrO_2, TiO_2, Cr_2O_3, CeO_2, and ThO_2 were measured at 1 atm and 120°C with a hexene-1 partial pressure of 0.22 atm; the remainder of the reactant stream was helium. The supports alone (except TiO_2, which was not tested) had approximately the same activities as the supported osmium under these conditions. The results therefore indicate that the catalytic activities attributable to the osmium were too low to determine accurately. (This statement may not pertain to the ZrO_2-supported catalyst, which was roughly 3 times as active as its support.) Comparing these results with those described in the preceding sections, we recognize that the activities of the catalysts supported on the three nontransition metal oxides are at least an order of magnitude greater than those of the catalysts supported on ZrO_2, TiO_2, Cr_2O_3, CeO_2, and ThO_2.

Nature of the Catalytic Species

High-resolution electron microscopy did not give evidence of metal particles or aggregates in any of the freshly prepared catalysts (*15*). This result is supported by the infrared spectra of the fresh catalysts, which either showed the characteristic set of bands of the triosmium carbonyl cluster edge-bridged by an oxygen (ZrO_2 and TiO_2) or the three-band pattern indicating a mixture of mononuclear osmium tri- and dicarbonyl species (on CeO_2, ThO_2, and Cr_2O_3). These mononuclear species alone were detected by infrared spectroscopy on all five metal oxides after their use in the catalytic activity tests. Therefore, the osmium species present on these metal oxides after use (and presumably during the catalytic tests) must be considered to be similar, if not identical, to those present on Al_2O_3 and MgO. And yet their specific activities are lower by at least an order of magnitude than those of the comparable osmium species supported on Al_2O_3 and MgO.

This result indicates a significant support effect. Its origin, however, remains unexplained. The mode of coordination of the osmium species to surface oxide ions may play a role, but the differing acid-base properties of the oxides and the variability of cation oxidation states may be more important. Moreover, carbon can be deposited as a result of CO disproportionation during cluster breakup at low temperatures (*15*) and may block osmium sites or alter the properties of the osmium species.

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