

MgO-Supported $[\text{Ir}_6(\text{CO})_{15}]^{2-}$: Catalyst for CO Hydrogenation

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Received February 7, 1994; revised June 14, 1994

Neutral and anionic iridium carbonyl clusters were synthesized from $[\text{Ir}(\text{CO})_2(\text{acac})]$ adsorbed on $\gamma\text{-Al}_2\text{O}_3$ and on MgO surfaces, respectively. The samples were characterized as CO hydrogenation catalysts and found to have low activities at 21.4 atm, 250°C, and H_2/CO molar ratios of 1–3. Both catalysts gave Schulz–Flory distributions of hydrocarbon products. At low conversions (<2%), the $\gamma\text{-Al}_2\text{O}_3$ -supported catalyst gave mainly paraffins, whereas the MgO-supported catalyst gave hydrocarbon products with relatively high olefin to paraffin ratios. The $\gamma\text{-Al}_2\text{O}_3$ -supported catalyst that had been used for 1 day in a flow reactor was dark gray, indicating the formation of metallic iridium aggregates. However, the used MgO-supported catalyst was reddish brown, and its infrared spectrum showed that the predominant iridium-containing species was $[\text{Ir}_6(\text{CO})_{15}]^{2-}$, which could be extracted from the surface by cation metathesis. © 1994 Academic Press, Inc.

EXPERIMENTAL METHODS

Materials and Catalyst Preparation

Syntheses and sample transfers were conducted with exclusion of air and moisture on a double-manifold Schlenk vacuum line and in a Vacuum Atmospheres drybox. N_2 , He, and H_2 with purities of 99.999% (Matheson) passed through traps containing particles of Cu_2O and particles of activated 4A zeolite to remove traces of oxygen and moisture, respectively. CO (Matheson, UHP grade) passed through a trap containing particles of activated alumina heated to a temperature exceeding 250°C to remove traces of iron carbonyl contaminants and through a trap containing particles of activated 4A zeolite to remove moisture. All solvents were deoxygenated by purging with N_2 for several hours prior to use. Bis(triphenylphosphine)iminium chloride, $[\text{PPN}][\text{Cl}]$, (Aldrich) was used without purification. Extraction of surface organometallic species from supports was performed with a suspension of $[\text{PPN}][\text{Cl}]$ in methanol or tetrahydrofuran (THF).

$[\text{Ir}(\text{CO})_2(\text{acac})]$ (Strem) was used without purification. The MgO support (MX-65-1 powder, MCB reagents) was treated by evacuation (pressure < 10^{-3} Torr) at 25°C for 4 h, and then stored in the drybox. This treatment did not remove all the carbonates from the MgO surface. The $\gamma\text{-Al}_2\text{O}_3$ support (Degussa, Aluminum Oxide C) was first made into a paste by adding deionized distilled water, followed by drying in an oven at 120°C overnight. The solid was then ground, evacuated (pressure < 10^{-3} Torr) at 25°C for 4 h, and stored in the drybox.

In the preparation of the supported samples, $[\text{Ir}(\text{CO})_2(\text{acac})]$ (0.036 g) was brought in contact with 2.0 g of the preevacuated MgO or $\gamma\text{-Al}_2\text{O}_3$ by slurring in hexane for 24 h. The resulting supported samples contained 1.0 wt% Ir. Each sample was dried by evacuation (pressure < 10^{-3} Torr) for 14 h at room temperature. The sample was then stored in the drybox.

Catalytic Hydrogenation of CO

CO hydrogenation kinetics measurements were performed with a copper-lined stainless-steel tubular flow

INTRODUCTION

Metal carbonyl clusters have been suggested to be potentially useful catalysts for reactions such as CO hydrogenation (1, 2), but most of these clusters are too unstable to even be involved in catalysis. They are easily converted into fragments such as mononuclear metal carbonyls or into colloidal metal, and these are often the actual catalysts. Our goal was to evaluate the potential and limitations of supported metal carbonyl clusters as catalysts. The clusters were chosen from among the most robust known metal carbonyls, and they were tested as catalysts under conditions that maximize their stability. Specifically, experiments were done with iridium carbonyl clusters in the presence of CO at elevated pressures, because CO is a ligand that helps to stabilize the clusters. Furthermore, because a number of metal carbonyl cluster anions are stabilized by basic media, strongly basic MgO support was used.

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reactor having an inside diameter of 1/4 in. Typically, 1.0 g of catalyst was loaded into the central (isothermal) zone of the reactor in the drybox; the upstream and downstream reactor sections were packed with glass wool. The gases used as feeds, CO (Matheson, UHP grade) and H₂ (Matheson, UHP grade), passed through a trap containing particles of activated 4A zeolite; H₂ also flowed through a trap containing particles of Cu₂O to remove residual O₂. CO flowed through a trap containing particles of activated carbon at 300°C to remove residual metal carbonyls.

The reactor was first pressurized to 21.4 atm in H₂ + CO (equimolar). The sample was then heated at a rate of 2.5°C/min to 250°C in flowing H₂ + CO [12 min]. Time zero on-stream was defined as the time when this temperature was reached. The effluent stream flowed through a heated line (ca. 140°C) to prevent condensation of products, which were intercepted periodically for analysis in an Antek 300 gas chromatograph equipped with a flame ionization detector. The products were separated in a Porapak Q column (4 ft in length and 1/8 in. in outside diameter) with the column heated at a rate of 4°C/min from 85 to 125°C and held at 125°C for 50 min. The C₁–C₆ hydrocarbon (paraffin and olefin) as well as oxygenated (methanol, ethanol, and dimethyl ether) products were identified and quantified by use of calibration gas mixtures. Measurements of CO₂ and water were not made. Conversions (<2%) were measured as a function of time on stream for 24 h to provide data characterizing catalyst deactivation. At the conclusion of each experiment, the catalyst was cooled to room temperature in flowing H₂ and CO (equimolar), and the pressure was reduced to 1 atm. The sample was unloaded in the drybox in preparation for further characterization experiments.

Catalyst Characterization by Infrared Spectroscopy

Each of the freshly supported samples was pressed into a thin self-supporting wafer in the drybox and mounted in a controlled-atmosphere quartz cell equipped with NaCl windows for examination with infrared spectroscopy. Samples were treated in flowing CO + H₂ (equimolar) at 1 atm and temperatures ranging from 25 to 250°C. The spectrum in the ν_{CO} region was recorded for each sample.

Wafers were brought in contact with solutions containing an excess of [PPN][Cl] in THF under N₂. The soluble products of the cation metathesis were identified by infrared spectroscopy of the extract solution. Similarly, the used catalysts were pressed into thin wafers in the drybox and characterized by infrared spectroscopy and cation metathesis.

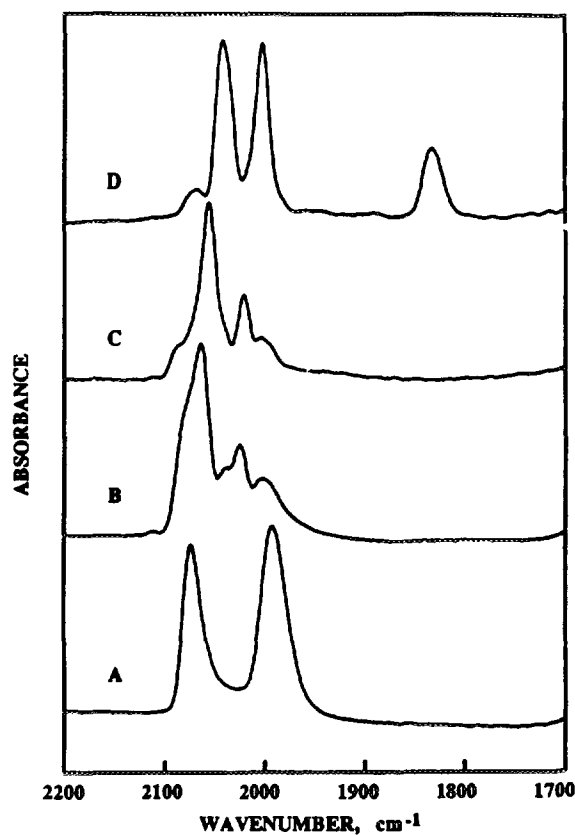


FIG. 1. Infrared spectra of the sample prepared by adsorption of [Ir(CO)₂(acac)] on γ -Al₂O₃ followed by treatment in CO + H₂ at 1 atm and room temperature: (A) freshly supported sample; (B) after 3 days. (C) [Ir₄(CO)₁₂] sublimed onto the infrared cell windows; (D) extract solution formed by treating the sample of spectrum B with [PPN][Cl] in THF.

RESULTS

Reactivity of γ -Al₂O₃-Supported Iridium Carbonyl Clusters in CO + H₂ at 1 atm

A sample prepared by adsorption of [Ir(CO)₂(acac)] from hexane solution onto γ -Al₂O₃ was loaded in a Schlenk flask and treated in CO + H₂. After exposure of the sample to CO + H₂ at room temperature, the ν_{CO} band at 2000 cm⁻¹ decreased in intensity, and a new band appeared at 2030 cm⁻¹ and increased in intensity (Fig. 1A). After 3 days in CO + H₂ at 25°C, the sample was brownish yellow and characterized by the ν_{CO} spectrum 2111 w, 2082 sh, 2062 vs, 2040 m, 2024 s, and 2003 m cm⁻¹ (Fig. 1B). This spectrum is similar to that of [Ir₄(CO)₁₂] sublimed onto the cell windows (Fig. 1C) and that of [Ir₄(CO)₁₂] in a KBr disc (Table 1). The results suggest that [Ir₄(CO)₁₂] had been formed by carbonylation of the adsorbed [Ir(CO)₂(acac)] on γ -Al₂O₃ (3).

Attempts to extract the surface species with THF were not successful; however, addition of [PPN][Cl] to the

TABLE 1

Infrared Spectra in the Carbonyl Stretching Region of γ -Al₂O₃-Supported Iridium Carbonyl Clusters Formed by Treatment of Adsorbed [Ir(CO)₂(acac)] in CO + H₂

Sample	ν_{CO} , cm ⁻¹	Ref.
[Ir(CO) ₂ (acac)] on Al ₂ O ₃	2072 vs, 1990 vs	This work
Carbonylated iridium on Al ₂ O ₃ (1A)	2111 w, 2082 sh, 2062 vs, 2040 m, 2024 s, 2003 m	This work
[Ir ₄ (CO) ₁₂] on cell windows	2111 w, 2086 sh, 2056 vs, 2040 sh, 2020 s, 2004 m	This work
[Ir ₄ (CO) ₁₂] in KBr disc	2108 w, 2085 sh, 2058 vs, 2040 m, 2022 s, 2002 m	(15)
Extraction of 1A/[PPN][Cl]/THF	2076 w, 2044 vs, 2002 vs, 1833 ms	This work
[Ir ₄ (CO) ₁₁ Cl ⁻] in THF	2080 w, 2040 vs, 2005 vs, 1960 vw, 1835 s, 1830 sh	(4, 14)

slurry gave a yellow solution, and the immediately recorded infrared spectrum of the extracted species (ν_{CO} : 2076 w, 2044 vs, 2002 vs, 1833 ms cm⁻¹) (Fig. 1D) is essentially the same as that of [Ir₄(CO)₁₁Cl]⁻, which is formed by reaction of [Ir₄(CO)₁₂] with [PPN][Cl] in THF solution (Table 1) (3, 4). These results are consistent with the suggestion that [Ir₄(CO)₁₂], formed by carbonylation of adsorbed [Ir(CO)₂(acac)] on γ -Al₂O₃ (3), was extracted from the surface and reacted with [PPN][Cl] in THF solution to form [Ir₄(CO)₁₁Cl]⁻.

A wafer of the brownish-yellow sample was treated in flowing CO + H₂ (equimolar) in an infrared cell. After treatment at 150°C for 2 h, the initial infrared absorptions decreased in intensity, and a band grew in at around 2060 cm⁻¹. This band frequency has been reported to be characteristic of CO chemisorbed on iridium metal particles (5). Further treatment at 250°C for 2 h in flowing CO + H₂ did not change the spectrum. The wafer unloaded in the drybox was dark gray, consistent with the formation of metallic particles. These results indicate that iridium carbonyl clusters on γ -Al₂O₃ are readily converted into metallic iridium aggregates during CO treatment.

Reactivity of MgO-Supported Iridium Carbonyl Clusters in CO + H₂ at 1 atm

A sample prepared by adsorption of [Ir(CO)₂(acac)] from hexane solution onto MgO was examined by infrared spectroscopy in the presence of flowing equimolar CO + H₂ at 1 atm. A few minutes after exposure of the sample to CO + H₂ at room temperature (Fig. 2A), new ν_{CO} bands appeared at 2019 w, 1931 m, and 1878 m cm⁻¹; the intensities of these bands increased in proportion to each

other, and the bands at 2058 and 1975 cm⁻¹ decreased in intensity. The appearance of these three carbonyl bands has been shown before when CO, instead of equimolar CO + H₂, was used in the carbonylation; the new species has been suggested to be [Ir(CO)₄]⁻ (6).

With continuing CO flow over the sample at room temperature, additional new bands appeared at 2072, 2038, 2022, and 1994 cm⁻¹, and the bands at 2058, 1975, 1931 and 1878 cm⁻¹ decreased in intensity. Continuation of the CO + H₂ flow for 8 h led to a spectrum with bands at 2072 sh, 2038 sh, 2022 s, 1994 m, 1975 sh, and 1790 w cm⁻¹ (Fig. 2B). Again, the spectrum is similar to that observed previously when CO alone was used as the treatment gas, and it has been assigned to [Ir₈(CO)₂₂]²⁻ (Table 2) (6). When the wafer was removed from the cell in the drybox, it was reddish pink, consistent with the formation of [Ir₈(CO)₂₂]²⁻ (6-9).

The sample treatment in flowing CO + H₂ was continued at higher temperatures. The infrared spectrum was

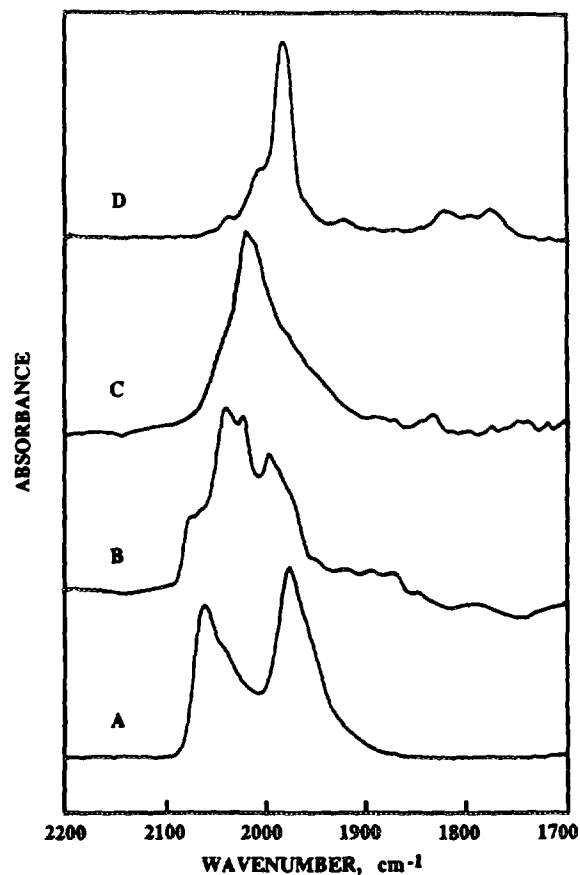


FIG. 2. Infrared spectra of the sample prepared by adsorption of [Ir(CO)₂(acac)] on MgO followed by treatment in CO + H₂ at 1 atm: (A) freshly prepared supported sample; (B) sample A after 8 h at 25°C; (C) sample B after 2 h at 200°C; (D) extract solution formed by bringing sample C in contact with [PPN][Cl] in THF.

TABLE 2

Infrared Spectra in the Carbonyl Stretching Region of MgO-Supported Iridium Carbonyl Clusters Formed from Treatment of Adsorbed $[\text{Ir}(\text{CO})_2(\text{acac})]$ in $\text{CO} + \text{H}_2$

Sample	ν_{CO} , cm^{-1}	Ref.
$[\text{Ir}(\text{CO})_2(\text{acac})]$ on MgO (1A)	2058 vs, 1975 vs	This work
1A, then $\text{CO} + \text{H}_2$, 25°C, 8 h (1B)	2072 sh, 2038 vs, 2022 s, 1994 ms, 1790 vw	This work
1B, then $\text{CO} + \text{H}_2$, 200°C, 2 h (1C)	2016 vs, 2010 s, 1830 w, 1771 w, 1740 w	This work
Extract of 1C/[PPN][Cl]/THF	2004 vw, 1980 vs, 1920 vw, 1818 w, 1790 w, 1773 mw	This work
$[\text{Ir}_8(\text{CO})_{22}]^{2-}$ on MgO	2072 sh, 2038 sh, 2021 s, 1995 m, 1975 sh, 1830 w	(6, 9)
$[\text{PPh}_4]_2[\text{Ir}_8(\text{CO})_{22}]$ in THF	2070 vw, 2040 m, 2020 vs, 1970 m, 1820 m	(8)
$\text{Na}_2[\text{Ir}_8(\text{CO})_{22}]$ in THF	2067 w, 2023 s, 2017 vs, 1985 m, 1920 w	(9)
$[\text{Ir}_6(\text{CO})_{15}]^{2-}$ on MgO	2056 w, 2008 s, 1831 w	(6, 10)
$\text{Na}_2[\text{Ir}_6(\text{CO})_{15}]$	1993 s, 1984 s, 1928 w, 1788 m, 1735 m	(10)
$[\text{NMe}_4]_2[\text{Ir}_6(\text{CO})_{15}]$	2030 sh, 1970 s, 1910 sh, 1775 s, 1735 s	(7)

maintained after treatment of the sample at 75°C for 30 min, indicating the stability of MgO-supported $[\text{Ir}_8(\text{CO})_{22}]^{2-}$ in $\text{CO} + \text{H}_2$. However, after the sample had been treated in $\text{CO} + \text{H}_2$ at 200°C for 2 h, the spectrum included bands at 2016 vs, 2010 s, 1830 w, 1771 w, and 1740 w cm^{-1} (Fig. 2C) (6, 10). The sample removed from the cell in the drybox was reddish brown; extraction with [PPN][Cl] in THF gave a reddish-brown solution, and the immediately recorded infrared spectrum (ν_{CO} : 2004 vw, 1980 vs, 1920 vw, 1818 w, 1790 w, 1773 mw cm^{-1}) (Fig. 2D) is virtually identical to that of $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ (Table 2) (7, 11, 12).

Comparison of the infrared spectra of $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ on MgO and $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ in THF solution shows a shift of the terminal carbonyl bands of the supported cluster of about 22 cm^{-1} to higher energy and a shift of the bridging carbonyl band of about 40 cm^{-1} to lower energy. The shifts are explained by the ion pairing of $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ with the Mg^{2+} ions of the surface, similar to that observed for $\text{Na}_2[\text{Ir}_6(\text{CO})_{15}]$ in solution (6, 10, 12).

Another sample prepared from $[\text{Ir}(\text{CO})_2(\text{acac})]$ and MgO was placed in the infrared cell and treated in flowing $\text{CO} + \text{H}_2$ at 25°C for 2 h and then at 75°C for 2 h. The temperature was then slowly increased to 200°C. After 2 h at 200°C, the sample was characterized by an infrared

spectrum that again included bands at 2016 s, 2010 s, 1830 w, 1771 w cm^{-1} . The sample was then treated at 250°C, and after 6 h at this temperature, the carbonyl bands were broadened at around 2030 cm^{-1} . The wafer was dark gray, indicating the formation of iridium aggregates. These results indicate that iridium carbonyls on MgO were not stable in $\text{CO} + \text{H}_2$ at 1 atm and at high temperature; they tend to form iridium metal particles.

Catalytic Hydrogenation of CO

All the iridium-containing samples were found to catalyze CO hydrogenation at temperatures of 225°C or greater. Conversions were measured as a function of time on stream. Catalytic activities are represented by rates of reaction calculated from low-conversion data and are expressed in units of [mol CO converted to hydrocarbons/(mol total Ir · s)]. All the experiments were conducted with CO conversions between 0.1 and 2.0%. The standard conditions were chosen to be 250°C, 21.4 atm, space velocity = 20 ml (NTP) (g catalyst · min) $^{-1}$ and CO/H_2 feed molar ratio = 1.0. In a blank test with the reactor packed with 1 g of MgO or $\gamma\text{-Al}_2\text{O}_3$, hydrocarbon formation was not observed under the standard operating conditions.

Typical product distributions with the $\gamma\text{-Al}_2\text{O}_3$ - and MgO-supported catalyst on stream for 1 day are shown in Figs. 3 and 4, respectively. The catalyst supported on $\gamma\text{-Al}_2\text{O}_3$ gave relatively high yields of $\text{C}_1\text{-C}_4$ hydrocarbons, predominantly paraffins. The catalyst supported on MgO also gave high yields of $\text{C}_1\text{-C}_4$ hydrocarbons, but they were predominantly olefins. Products with >5 carbon atoms were formed only in very low yields at the low conversions observed (0.1–2.0%). The MgO-supported catalyst showed major changes in activity during the first 8 h on stream; after 8 h, the activity was almost un-

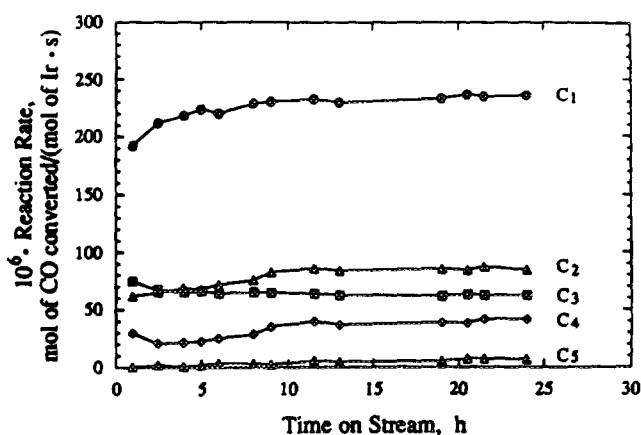


FIG. 3. CO hydrogenation catalyzed by $\gamma\text{-Al}_2\text{O}_3$ -supported iridium: dependence of product distribution on time on stream in a flow reactor. Reaction conditions: 250°C, 21.4 atm, $\text{CO}/\text{H}_2 = 1.0$ (molar).

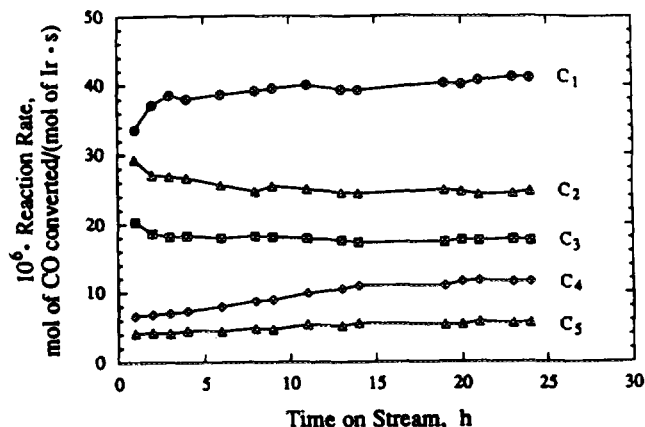


FIG. 4. CO hydrogenation catalyzed by MgO-supported iridium carbonyl clusters: dependence of product distribution on time on stream in a flow reactor. Reaction conditions: 250°C, 21.4 atm, CO/H₂ = 1.0 (molar).

changed. The activity of the γ -Al₂O₃-supported catalyst continued to increase slightly as long as it was on stream.

The hydrocarbon product distributions after 1 day on stream are shown in the nearly linear Schulz-Flory plots of Fig. 5.

The catalysts that had been on stream for 1 day were removed from the reactor in the absence of air. The γ -Al₂O₃-supported catalyst was dark gray, indicating the formation of metallic iridium. However, the MgO-supported catalyst was brown, with no visible indication of metallic iridium.

The good stability of the MgO-supported catalyst provided an opportunity for investigation of the effects of process variables on the catalyst performance. The effects of space velocity and feed composition were measured under nearly steady-state conditions. The conversion to

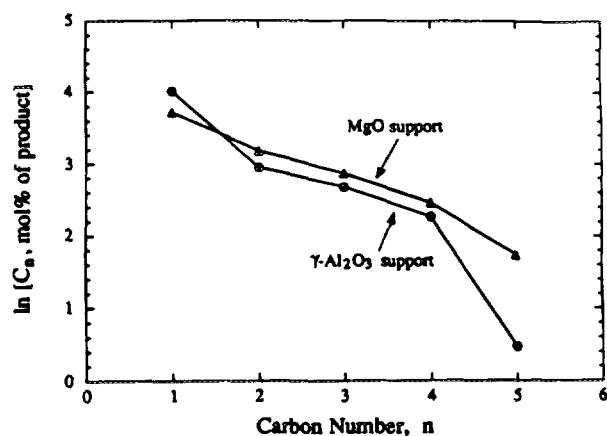


FIG. 5. Hydrocarbon product distributions in CO hydrogenation (after 24 h) catalyzed by supported iridium samples.

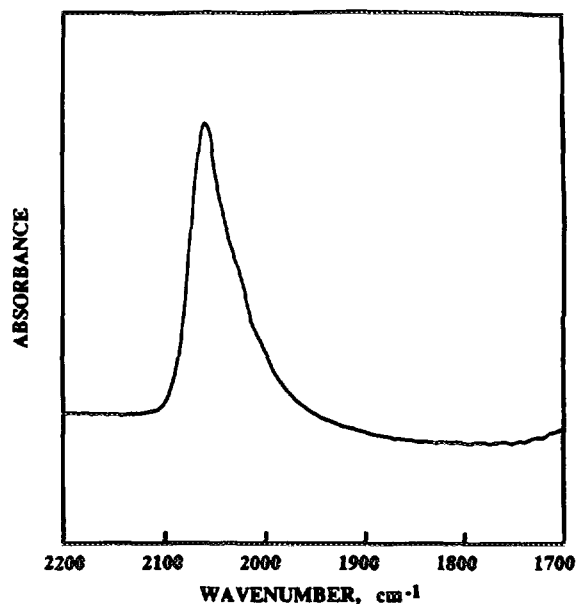


FIG. 6. Infrared spectrum characterizing the used γ -Al₂O₃-supported iridium catalyst after being on stream for CO hydrogenation (equimolar CO + H₂ feed, 250°C, 21.4 atm) for 24 h.

hydrocarbons was observed to be proportional to the inverse space velocity, confirming that the conversions were differential, determining reaction rates directly.

To determine the effect of high H₂ partial pressures on catalyst stability, a sample of catalyst prepared from [Ir(CO)₂(acac)] on MgO was treated for 24 h at 250°C and 21.4 atm in flowing CO + H₂ with a CO/H₂ molar ratio of 1 : 3. The activity of this catalyst was about six times higher than that observed for the catalyst used in equimolar CO + H₂. When the former catalyst sample was removed from the reactor, it was dark gray, indicating that iridium metal particles had formed on the surface after treatment at the relatively high H₂ partial pressure. The catalyst containing iridium metal is evidently more active than that not treated at the high H₂ partial pressure.

Characterization of Used Catalysts by Infrared Spectroscopy

The used catalysts were pressed into thin wafers without exposure to air and examined by infrared spectroscopy. The infrared spectrum in the ν_{CO} region of the used catalysts prepared from [Ir(CO)₂(acac)] adsorbed on γ -Al₂O₃, which was dark gray, had one ν_{CO} absorption band, at 2060 (s) cm⁻¹ (Fig. 6). Contacting of the solid with excess [PPN][Cl] in THF led to no extraction of metal carbonyls, as shown by the lack of carbonyl species in the extract, as indicated by infrared spectroscopy.

The used catalyst derived from [Ir(CO)₂(acac)] adsorbed on MgO was brown. The infrared spectrum of this

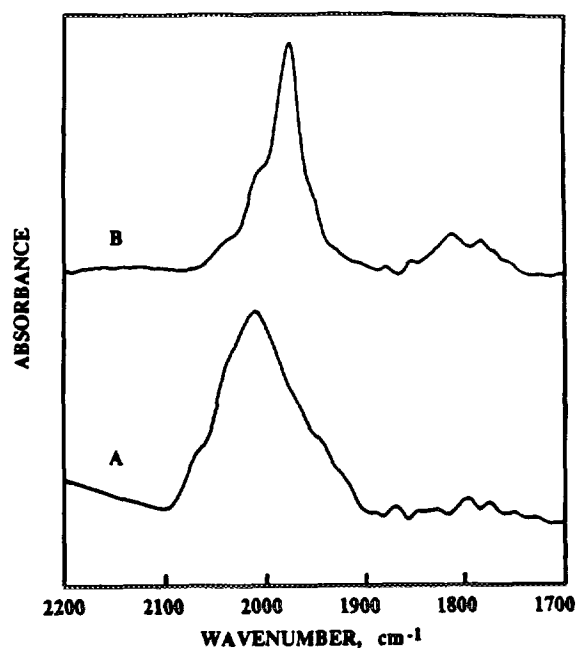


FIG. 7. Infrared spectra characterizing (A) the used MgO-supported iridium catalyst after being on stream for CO hydrogenation (equimolar CO + H₂ feed, 250°C, 21.4 atm) for 24 h; (B) extract solution formed by bringing sample A in contact with [PPN][Cl] in THF.

catalyst had ν_{CO} bands at 2063 sh, 2013 s, and 1785 w cm^{-1} (Fig. 7A). These bands are almost the same as those attributed to $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ on the MgO surface (6, 10). The extraction of the MgO-supported catalyst with excess [PPN][Cl] in THF gave a reddish-brown solution with ν_{CO} absorptions at 2010 sh, 1980 s, 1818 w, and 1785 w cm^{-1} (Fig. 7B). These correspond to $[\text{Ir}_6(\text{CO})_{15}]^{2-}$.

DISCUSSION

Parallels between Iridium Carbonyl Chemistry in Solution and on Metal Oxide Surfaces

The chemistry of the formation of iridium carbonyl clusters on metal oxide surfaces can be understood by comparison with the chemistry of the formation of iridium carbonyl clusters in solution. $[\text{Ir}_4(\text{CO})_{12}]$ is synthesized in solution by carbonylation of iridium salts (13, 14, 15) or by carbonylation of $[\text{Ir}(\text{CO})_2(\text{acac})]$ (3). In basic solutions, the treatment of $[\text{Ir}_4(\text{CO})_{12}]$ with KOH in methanol under CO gives first $[\text{HIr}_4(\text{CO})_{11}]^-$ (13, 16), then $[\text{Ir}_8(\text{CO})_{22}]^{2-}$ (8, 13), and finally $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ (11, 13). The latter is the most stable of these anionic species formed in the treatment of iridium precursors in basic solutions (7, 12).

The organometallic chemistry of iridium carbonyl clusters on the strongly basic MgO surface parallels that in basic solutions. Reductive carbonylation of $[\text{Ir}(\text{CO})_2(\text{acac})]$ adsorbed on partially dehydroxylated MgO ini-

tially gives $[\text{HIr}_4(\text{CO})_{11}]^-$, then $[\text{Ir}_8(\text{CO})_{22}]^{2-}$, and finally $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ (6). When the MgO is hydrated, reductive carbonylation of adsorbed $[\text{Ir}(\text{CO})_2(\text{acac})]$ in CO gives $[\text{Ir}_8(\text{CO})_{22}]^{2-}$ directly and then $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ (6). When CO + H₂ is used, as shown in this work, similar surface organometallic chemistry takes place on the basic MgO surface. A similar parallel between organometallic chemistry in basic solutions and on basic MgO surfaces has been observed with osmium carbonyls (17).

On the weakly basic $\gamma\text{-Al}_2\text{O}_3$ surface, however, the chemistry of iridium carbonyls is different, being similar to that occurring in neutral solutions. For example, iridium precursors react on the $\gamma\text{-Al}_2\text{O}_3$ surface in the presence of CO or CO + H₂ to give $[\text{Ir}_4(\text{CO})_{12}]$ (3). This iridium carbonyl cluster was not stable on the $\gamma\text{-Al}_2\text{O}_3$ surface; it was easily converted into metallic aggregates by treatment in flowing CO + H₂ at temperatures >150°C.

Structures of the Used Catalysts

The iridium catalyst supported on weakly basic $\gamma\text{-Al}_2\text{O}_3$, after being used for CO hydrogenation at 250°C and 21.4 atm for 24 h, was dark gray. The infrared spectrum of the catalyst showed one ν_{CO} band at 2060 cm^{-1} ; this band is typical of CO chemisorbed on iridium metal particles (5). These results indicate that iridium metal particles had been formed on the support. The formation of these metal particles on the weakly basic $\gamma\text{-Al}_2\text{O}_3$ in the presence of high-pressure CO + H₂ is not surprising, because the present results show that $[\text{Ir}_4(\text{CO})_{12}]$, which had formed on the support at low temperature, agglomerated in the presence of CO + H₂ to form metal aggregates at temperatures >100°C. Iridium carbonyl clusters are not stable on the weakly basic $\gamma\text{-Al}_2\text{O}_3$ at relatively high temperatures; they tend to form metal particles even under high partial pressures of CO.

In contrast, on the more strongly basic MgO support, the anionic cluster $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ was formed and maintained intact, even after being on stream in the CO hydrogenation reactor for 24 h. At temperatures >200°C in the presence of CO + H₂ at 1 atm, this iridium carbonyl cluster agglomerated to form metal particles. However, at the high CO + H₂ pressure used in the CO hydrogenation catalysis experiment, $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ was maintained as the predominant iridium-containing species on the MgO surface even at higher temperatures. These results indicate that the high CO partial pressure was needed to stabilize the iridium carbonyl cluster at the higher temperatures.

The catalytic activity of the MgO-supported catalyst containing $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ is lower than that of the $\gamma\text{-Al}_2\text{O}_3$ -supported catalyst containing iridium metal, and we suggest that $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ could be the catalytically active species or the precursor of the catalytically active species in the former. However, the results do not exclude the

possibility of catalysis by undetected small iridium metal clusters or crystallites present with the iridium carbonyl clusters in the MgO-supported catalyst. Because the activity of this catalyst containing the iridium carbonyl cluster anions is relatively low and the activity of the catalyst containing iridium metal is relatively high, the observed activity of the former catalyst could be explained by the presence of only a small amount of metal. However, the product distribution observed with the MgO-supported catalyst (a high olefin:paraffin ratio) suggests that the catalytically active species were different from those in the catalyst containing iridium metal, which is consistent with the suggestion that the catalytically active species or their precursors were $[\text{Ir}_6(\text{CO})_{15}]^{2-}$.

Catalyst Performance

High pressure was found to be crucial for stable performance of the MgO-supported iridium catalyst. The results show that at a pressure of 21.4 atm, the catalyst performance was maintained for at least 24 h. The high partial pressure of CO was also needed to maintain the iridium carbonyl clusters intact during catalytic CO hydrogenation. The infrared results show that the hexairidium carbonyl clusters were not stable at temperatures of about 250°C when the pressure of CO + H₂ was only 1 atm; they agglomerated to form metal particles. The stabilization of $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ on MgO during catalytic hydrogenation of CO is attributed to (1) the strength of the Ir–Ir bonds in the octahedral metal frame, (2) the CO ligands provided by the gas phase reactants, which help to keep the frame intact, and (3) the basic character of the MgO surface, which stabilizes the anionic clusters (18).

The used MgO-supported catalyst that had been treated under high H₂ partial pressures was dark gray, suggesting that iridium metal particles had formed on the surface. We infer that under the high H₂ partial pressure, the MgO-supported iridium carbonyl species migrated and agglomerated to form metallic iridium. The product distribution data measured in the catalysis experiments show that the metallic aggregates behave like the $\gamma\text{-Al}_2\text{O}_3$ -supported iridium catalyst, giving the Schulz–Flory distribution of hydrocarbon products consisting mainly of paraffins.

Comparison with Catalytic Performance of Other Supported Metal Clusters

The iridium in the MgO-supported catalyst reported here was present predominantly as iridium carbonyl cluster anions. There are a number of reports of supported CO hydrogenation catalysts in which the metal is present predominantly in the form of metal carbonyl clusters. Performance data characterizing a number of these catalysts are summarized in Table 3. The catalysts included in Table 3 were all derived from metal carbonyl precursors

on metal oxide and zeolite supports, and all were investigated for CO hydrogenation under approximately the same conditions. Table 3 is not an exhaustive compilation of the supported CO hydrogenation catalysts derived from organometallic precursors, but it includes almost all of the catalysts in this class that were tested in flow reactors under conditions similar to those used in the present work, with the CO/H₂ ratios being sufficient to minimize formation of metal aggregates in the catalysts.

The activities of all these catalysts are equal to each other within two orders of magnitude, and they are all low in comparison with the activities of conventional Fischer–Tropsch catalysts. In low-conversion experiments, all these catalysts were selective for formation of hydrocarbons, and the sample containing supported rhodium also catalyzed the formation of oxygenated products. The hydrocarbons formed in the presence of catalysts with basic supports (those on which metal carbonyl cluster anions were stable under catalytic reaction conditions) were characterized by greater olefin/paraffin ratios than the hydrocarbons formed in the presence of the other catalysts. Thus the basic supports favor the formation of olefins relative to paraffins, and this pattern in the selectivity is correlated with the presence of metal carbonyl cluster anions on the support; this pattern remains to be explained (25). These results are consistent with the hypothesis that metal carbonyl clusters are either catalysts or catalyst precursors in all the materials listed in Table 3, but the data are not sufficient to rule out other possible catalytic species.

The hydrocarbons formed in the presence of catalysts with zeolitic supports were characterized by non-Schulz–Flory distributions, whereas those formed in the presence of catalysts with nonzeolitic supports were characterized by Schulz–Flory distributions. These results support the generalization that the pore structures of the zeolites are somehow responsible for the non-Schulz–Flory distributions of hydrocarbon products, but it is not known how.

CONCLUSIONS

$[\text{Ir}(\text{CO})_2(\text{acac})]$ adsorbed on the strongly basic MgO surface in the presence of CO + H₂ was converted into $[\text{Ir}_8(\text{CO})_{22}]^{2-}$ and then into $[\text{Ir}_6(\text{CO})_{15}]^{2-}$. The formation of these clusters on the basic MgO surface parallels the solution chemistry of iridium carbonyl cluster synthesis. $[\text{Ir}(\text{CO})_2(\text{acac})]$ adsorbed on the less basic $\gamma\text{-Al}_2\text{O}_3$ surface was converted in the presence of CO + H₂ into $[\text{Ir}_4(\text{CO})_{12}]$; however, this cluster was not stable on $\gamma\text{-Al}_2\text{O}_3$ at high temperature and was easily converted into iridium metal crystallites. Strongly basic metal oxides and high CO partial pressures help to stabilize metal carbonyl clusters; $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ supported on MgO was stable during cata-

TABLE 3

CO Hydrogenation in the Presence of Supported Catalysts Prepared from Metal Carbonyls

Sample ^a (precursor/support)	Reaction conditions ^b	CO conversion, (%)	Activity, (mol of CO converted/ mol of metal · s)	Products ^b	Hydrocarbon product distribution	Predominant metal species in the used catalyst	Ref.
[Ir(CO) ₂ (acac)]/MgO	CO/H ₂ = 1, 250°C, 21 atm	0.1–2.0	9.8 × 10 ⁻⁵ (avg. over 24 h)	C ₁ –C ₅ , mostly C ₁ , no oxygenates ole- fin/paraffin = 3.1	Schulz–Flory	[Ir ₆ (CO) ₁₅] ²⁻ /MgO	This work
[Ir(CO) ₂ (acac)]/Al ₂ O ₃	CO/H ₂ = 1, 250°C, 21 atm	0.1–2.0	4.4 × 10 ⁻⁴ (avg. over 24 h)	C ₁ –C ₅ , mostly C ₁ , no oxygenates, olefin/paraffin = 0.6	Schulz–Flory	Ir aggregates/Al ₂ O ₃	This work
[Ir(CO) ₂ (acac)]/NaY	CO/H ₂ = 1, 250°C, 21 atm	0.1–2.0	9.0 × 10 ⁻⁵ (avg. over 192 h)	C ₁ –C ₅ , mostly C ₁ , no oxygenates, olefin/paraffin = 0.2	non-Schulz–Flory	[Ir ₆ (CO) ₁₆]/NaY	19
[Ir(CO) ₂ (acac)]/NaX	CO/H ₂ = 1, 250°C, 21 atm	0.1–2.0	7.2 × 10 ⁻⁵ (avg. over 72 h)	C ₁ –C ₅ , mostly C ₁ , no oxygenates, olefin/paraffin = 2.0	non-Schulz–Flory	[Ir ₆ (CO) ₁₅] ²⁻ /NaX	20,21
[H ₂ Os(CO) ₄]/MgO	CO/H ₂ = 0.33, 275°C, 10 atm	0.7	1.5 × 10 ⁻⁴ (after 12 h on stream)	C ₁ –C ₄ , mostly C ₁ , olefin–paraffin ratio not reported	Schulz–Flory	[Os ₁₀ C(CO) ₂₄] ²⁻ /MgO	18
[Os ₆ (CO) ₁₈]/MgO	CO/H ₂ = 1, 300°C, 70 atm	0.2	6.3 × 10 ⁻⁵ (after 24 h on stream)	C ₁ –C ₄ , mostly C ₁ , no oxygenates, no olefins	Schulz–Flory	[H ₃ Os ₄ (CO) ₁₂] ⁻ /MgO	22,23
[Os ₆ (CO) ₁₈]/Al ₂ O ₃	CO/H ₂ = 1, 300°C, 70 atm	1.8	8.5 × 10 ⁻⁴ (after 1 h on stream)	C ₁ –C ₄ , mostly C ₁ , no oxygenates, olefin/paraffin = 0.02	Schulz–Flory	[HOs(CO) ₄] ⁻ /Al ₂ O ₃	23
[H ₂ Os(CO) ₄]/NaY made basic with NaN ₃	CO/H ₂ = 1, 300°C, 19 atm	0.9–1.8	8.0 × 10 ⁻⁶ (avg. over 480 h)	C ₁ –C ₅ , mostly C ₁ , no oxygenates, olefin/paraffin = 2.0	non-Schulz–Flory	[Os ₃ (CO) ₁₁] ⁻ /NaY	24,25,29
[H ₄ Ru ₄ (CO) ₁₂]/MgO	CO/H ₂ = 1, 275°C, 10 atm	0.06	1.10 × 10 ⁻⁵ (after 20 h on stream)	C ₁ –C ₅ , no oxygen- ates	Schulz–Flory	[Ru ₆ C(CO) ₁₆] ²⁻ /MgO	26
[Rh(CO) ₂ (acac)]/NaY made basic with NaN ₃	CO/H ₂ = 1, 300°C, 20 atm	0.1–0.3	9.0 × 10 ⁻⁵ (avg. over 300 h)	C ₁ –C ₅ , mostly C ₁ , trace of CH ₃ OH, C ₂ H ₅ OH, CH ₃ OCH ₃ , olefin/ paraffin >7	non-Schulz–Flory	structure not identi- fied	27, 28

^a Each sample was heated in flowing CO + H₂ prior to catalysis experiments.

^b Molar ratios.

lytic CO hydrogenation at 250°C and 21 atm with an equimolar CO + H₂ feed. In contrast, iridium carbonyls supported on γ-Al₂O₃ were converted into metallic particles under these conditions. [Ir₆(CO)₁₅]²⁻ clusters on MgO may be catalytically active themselves or may be precursors of catalytically active species; however, the catalyst incorporating this cluster anion is relatively inactive, although it is selective for olefin formation.

ACKNOWLEDGMENT

This research was supported by the National Science Foundation.

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