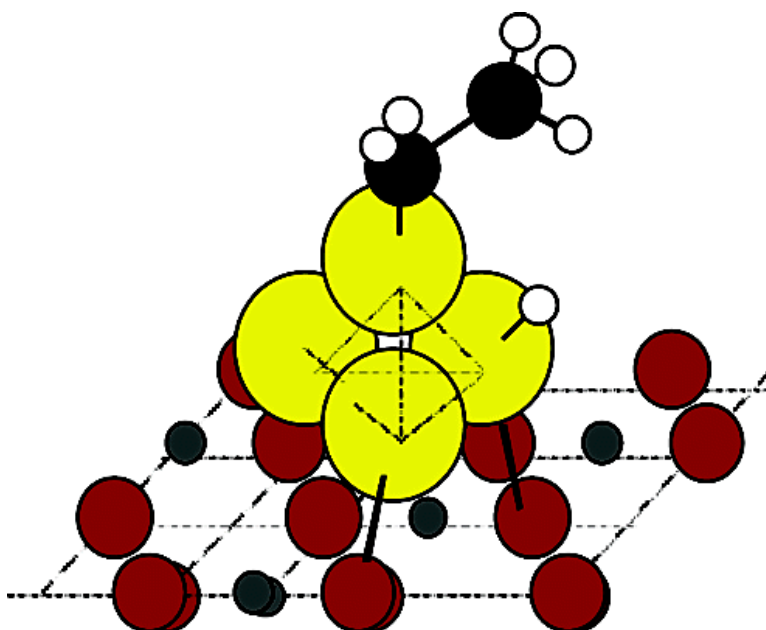


Role of Cluster Size in Catalysis: Spectroscopic Investigation of η -AlO-Supported Ir and Ir during Ethene Hydrogenation

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Role of Cluster Size in Catalysis: Spectroscopic Investigation of γ -Al₂O₃-Supported Ir₄ and Ir₆ during Ethene Hydrogenation

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Abstract: γ -Al₂O₃-supported Ir₄ and Ir₆ were prepared by decarbonylation of tetra- and hexanuclear iridium carbonyls, respectively, and compared as catalysts for ethene hydrogenation at atmospheric pressure and temperatures in the range 273–300 K. Rates of the reaction were determined along with extended X-ray absorption fine structure (EXAFS) and IR spectra characterizing the clusters in the working catalysts. EXAFS data show that the Ir₄ and Ir₆ cluster frames remained intact during catalysis. Di- σ -bonded ethene and π -bonded ethene on the clusters were identified by IR spectroscopy and found to compete as the principal reaction intermediates, with the former predominating at ethene partial pressures less than about 200 Torr and the latter at higher ethene partial pressures. Hydrogen on the clusters is inferred to form by dissociative adsorption of H₂; alternatively, it is provided by OH groups of the support. The rate of ethene hydrogenation on Ir₄ is typically several times greater than that on Ir₆.

Introduction

When metal clusters are small enough, their sizes and interactions with supports markedly influence their catalytic properties, setting them apart from larger metal particles and extended metal surfaces, as illustrated by results characterizing oxide- and zeolite-supported 4- and 6-atom clusters of iridium catalyzing arene and alkene hydrogenation¹ and clusters of Pt² and Au³ catalyzing CO oxidation. Our goal was to investigate the performance of small, nearly uniform supported metal cluster catalysts and to characterize the cluster structures, cluster–support interactions, and reactant-derived ligands on the clusters. We report rates of catalytic hydrogenation of ethene and extended X-ray absorption fine structure (EXAFS) and IR spectra of the catalysts recorded as the catalysts functioned. The catalysts were γ -Al₂O₃-supported Ir₄ (Ir₄/ γ -Al₂O₃) and Ir₆ (Ir₆/ γ -Al₂O₃). Ethene hydrogenation was chosen because (a) it takes place under mild conditions, leaving the clusters intact, (b) it is one of the best-investigated test reactions and provides a basis for comparison of supported metal clusters with conventional metal catalysts, and (c) the reactant-derived ligands on the clusters are identifiable by IR spectroscopy.

Experimental Section

Materials, Sample Preparation, and Handling. The supported metal cluster catalysts were synthesized as follows: (a) Ir₄/ γ -Al₂O₃ by adsorption of Ir₄(CO)₁₂ on γ -Al₂O₃ followed by decarbonylation in He;^{1b,4} (b) Ir₆/ γ -Al₂O₃ by adsorption of [Ir(CO)₂(acac)] (acac is

acetylacetonato) on γ -Al₂O₃ followed by reductive carbonylation to give [Ir₆(CO)₁₅]²⁻/ γ -Al₂O₃, which was decarbonylated in He;^{1b,5} and (c) larger, nonuniform clusters of iridium on γ -Al₂O₃ (Ir_{agg}/ γ -Al₂O₃) by aggregation of clusters formed from Ir₄(CO)₁₂/ γ -Al₂O₃ by treatment in H₂.⁶ Syntheses were carried out on a vacuum line or in a drybox (Vacuum Atmospheres HE-63-P) purged with N₂ that was recirculated through O₂- and moisture-scavenging traps containing particles of supported Cu and zeolite 4A, respectively. The drybox was equipped with O₂ and moisture detectors, indicating concentrations < 2 ppm. Reagent-grade *n*-hexane solvent (Aldrich) was dried over sodium benzophenone ketyl. He (Matheson, 99.999%) and ethene (Matheson, 99.5%) were purified by passage through traps to remove traces of O₂ and moisture. H₂ was supplied by Matheson (99.999%) or generated by electrolysis of water in a Balston generator (99.99%) and purified by traps. CO (Matheson, CP grade) was further purified by passage through a trap containing activated particles of γ -Al₂O₃ and zeolite 4A, respectively, to remove traces of metal carbonyls from the high-pressure gas cylinder and water. Ir(CO)₂(acac) (Strem, 99%) and Ir₄(CO)₁₂ (Strem, 98%) were used as received. γ -Al₂O₃ powder (Aluminum Oxide C, Degussa) was made into a paste by adding deionized water, followed by drying overnight at 393 K. It was then ground and stored in a drybox. The BET surface area of the γ -Al₂O₃ calcined at 673 K was about 100 m² g⁻¹.⁴ Each catalyst contained 1.0 wt % Ir.

Ethene Hydrogenation Catalysis in a Plug-Flow Reactor. Ethene hydrogenation catalysis was carried out in a once-through tubular flow reactor at atmospheric pressure and temperatures ranging from 273 to 300 K. The reactor was loaded in the drybox as particles of inert α -Al₂O₃ were mixed with catalyst powder (typically, 8–30 mg) in a 100:1 ratio by mass.⁷ The catalyst bed was held in the middle of the reactor by glass wool plugs. The loaded reactor was isolated, removed from the drybox, and installed in a flow system without contacting the catalyst with air. An on-line gas chromatograph (Hewlett-Packard, HP-

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(7) Dilution of the catalyst particles with inert α -Al₂O₃ particles minimized preferential channeling of reactants through the catalyst bed and heat and mass transfer limitations.

5890 Series II), equipped with a 30-m \times 0.53-mm DB-624 (J&W Scientific) capillary column (with N₂ as the carrier gas, 2.5 mL (NTP) min⁻¹) and a flame-ionization detector, was used to analyze the reaction products. Conversions of ethene to ethane were < 5% and shown to be differential, determining reaction rates directly.

The total feed flow rate (He + H₂ + ethene) was typically 100 mL (NTP) min⁻¹. Under these conditions, the reactor was well approximated as an isothermal plug-flow reactor. Typical reaction experiments were done with an ethene partial pressure of 40 Torr and a H₂ partial pressure of 100 Torr at 294 \pm 1 K. In kinetics experiments carried out at 273 K, the ethene and H₂ partial pressures were varied in the range 40 to 300 Torr, respectively. Steady-state reaction rates were determined from differential conversions with an accuracy of about \pm 10%.⁸

EXAFS Spectroscopy of Functioning Catalysts. X-ray absorption spectra characterizing the supported metal cluster catalysts were recorded at beamline X-11A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, Upton, NY, and at beamline 2-3 of the Stanford Synchrotron Radiation Laboratory (SSRL) at the Stanford Linear Accelerator Center, Stanford, CA. The storage ring electron energy was 2.5 GeV at NSLS and 3 GeV at SSRL; the beam current ranged from 140 to 240 mA at NSLS and from 50 to 100 mA at SSRL. Higher harmonics in the X-ray beam were minimized by detuning the Si(111) double-crystal monochromator at NSLS or the Si(220) monochromator at SSRL by 20–25% at the Ir L_{III} edge (11215 eV). Samples for the transmission EXAFS experiments were prepared in dryboxes and loaded into the EXAFS cell at the synchrotrons.

The cell⁹ consisted of a temperature-controlled stainless steel body (approximated as a plug-flow reactor) sealed with Mylar windows. Catalysts were characterized in the presence of flowing He and also in the presence of flowing ethene + H₂ as hydrogenation catalysis took place. The powder catalyst was held in the middle of the reaction zone by glass wool plugs. A gas chromatograph (GOW-MAC, Series 600), equipped with a 30 m \times 0.53 mm Supel-Q plot column (with N₂ as the carrier gas; 3.0 mL (NTP) min⁻¹) and a flame-ionization detector was installed at the beamline for analysis of the product gas to quantify the catalytic activity, with the reported data for reaction occurring at steady state. The catalyst powder (0.40 g) was loaded into the cell in the drybox; the cell was sealed and isolated for installation into the flow system at the beamline so that the catalyst did not come in contact with air.

The EXAFS cell/flow reactor operated at atmospheric pressure and temperatures of 253–298 K with feed partial pressures in the range of 131–397 Torr of H₂ and 203–244 Torr of ethene (the balance being He). The conversions in the cell were greater than differential because the use of catalyst masses small enough to give differential conversions led to X-ray absorbances that were too weak to provide useful data. Consequently, concentration gradients across the characterized portion of the catalyst bed were not insignificant, and the conversions attained in the cell are not quite quantitatively comparable to those attained in the plug-flow reactor; details of the comparison are given elsewhere.¹⁰

IR Spectroscopy of Functioning Catalysts. Transmission IR spectra were recorded with a Bruker IFS-66v spectrometer with a spectral resolution of 4 cm⁻¹. Catalyst samples were pressed into self-supporting wafers and loaded into the cell in the drybox. The cell was also a flow reactor (In-situ Research Instruments, Granger, IN), allowing measurement of transmission spectra while treatment gases (or catalytically reacting ethene + H₂) flowed over and through the wafer at temperatures ranging from 273 to 573 K. Each sample was scanned 128–512 times, and the signal was averaged. Difference spectra were calculated by subtracting the spectrum of the sample in the presence of He from that of the sample in the treatment gas. When the absorption

Table 1. EXAFS Parameters Characterizing γ -Al₂O₃-Supported Iridium Clusters Scanned in Flowing Helium at 760 Torr^a

backscatterer	cluster/temperature, K							
	Ir ₄ /253				Ir ₆ /298			
	<i>N</i>	<i>R</i> [Å]	$\Delta\sigma^2 \times 10^3$ [Å ²]	ΔE_0 [eV]	<i>N</i>	<i>R</i> [Å]	$\Delta\sigma^2 \times 10^3$ [Å ²]	ΔE_0 [eV]
Ir	3.2	2.62	5.7	4.4	3.7	2.63	6.4	-0.4
					1.3	3.73	8.5	2.0
Al					0.2	1.83	1.8	-18.1
	0.4	3.48	-1.2	13.0	0.4	2.43	2.1	-7.2
O	0.8	2.01	1.6	5.9	0.7	2.07	-1.0	4.7
	1.1	2.61	-2.6	1.5	0.4	3.29	-5.6	0.2

^a Notation: *N*, coordination number; *R*, absorber–backscatterer distance; $\Delta\sigma^2$, Debye–Waller factor; and ΔE_0 , inner potential correction. The approximate experimental uncertainties are as follows: *N* (\pm 10%); *r* (\pm 0.02 Å); $\Delta\sigma^2$ (\pm 20%); and ΔE_0 (\pm 20%).¹⁷

by the treatment gas was significant, the spectrum of the treatment gas was also subtracted from that of the sample in the reactant/product gas. The conversions attained in the IR cell/flow reactor quantitatively matched those attained in the plug-flow reactor.¹⁰

Spectra of high quality were obtained for the nearly uniform supported clusters Ir₄ and Ir₆, but the less uniform sample formed by aggregation of these clusters on the support did not yield satisfactory IR spectra.

EXAFS Data Analysis

EXAFS data were analyzed with experimentally and theoretically determined reference files, the former obtained from EXAFS data characterizing materials of known structure and the latter estimated with the software FEFF 5.0 and 7.0 (Supporting Information, Table 1).^{11–17} Preparation of the EXAFS reference files is described separately,^{18–21} as are details of the analysis procedures.^{21–23}

Results

EXAFS Evidence of Structure of Initially Prepared Catalysts. EXAFS parameters characterizing the sample formed by adsorption of Ir₄(CO)₁₂ on γ -Al₂O₃ (calcined at 673 K) followed by decarbonylation in flowing He at 598 K for 2 h, specifically including an Ir–Ir first-shell coordination number of about 3 (Table 1), are consistent with the expected⁴ site-isolated tetrahedral Ir₄ clusters and the maintenance of the cluster frame on decarbonylation of the precursor Ir₄(CO)₁₂. There are many data reported for similar samples indicating that the tetrahedral metal frame of the precursor Ir₄(CO)₁₂ is essentially maintained when the supported cluster is decarbonylated under mild conditions.^{1b,4} The data also indicate Ir–O and Ir–Al

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Table 2. EXAFS Parameters Characterizing γ -Al₂O₃-Supported Ir₄ Clusters Scanned during Ethene Hydrogenation Catalysis at 298 K and 760 Torr^a

P_{H_2} [Torr]	$P_{C_2H_4}$ [Torr]	$X^{b,c}$	absorber–backscatterer pair															
			Ir–Ir				Ir–O				Ir–C				Ir–Al			
			N	R [Å]	$\Delta\sigma^2 \times 10^3$ [Å ²]	ΔE_0 [eV]	N	R [Å]	$\Delta\sigma^2 \times 10^3$ [Å ²]	ΔE_0 [eV]	N	R [Å]	$\Delta\sigma^2 \times 10^3$ [Å ²]	ΔE_0 [eV]	N	R [Å]	$\Delta\sigma^2 \times 10^3$ [Å ²]	ΔE_0 [eV]
131	209	0.65	3.3	2.65	5.6	1.9												
							1.4	2.63	0.2	−1.3					0.5	2.01	−1.6	7.2
															0.2	1.86	0.0	−18.8
															0.2	3.23	−2.0	4.5
191	205	0.77	3.3	2.66	5.5	−0.1	0.2	2.03	−0.6	7.3	0.4	1.86	−5.0	18.6	0.2	1.59	−0.7	15.6
							1.1	2.65	−1.7	−2.5								
228	203	0.95	3.3	2.67	5.4	−2.0	0.6	2.04	9.5	1.1	0.2	1.92	−1.9	−0.5	0.2	3.24	0.3	4.5
							0.9	2.67	−4.4	−4.8								
292	203	0.98	3.3	2.68	5.4	−4.2	0.4	2.23	2.9	−13.8	0.3	1.93	−1.0	−1.0	0.2	3.22	−3.0	8.8
							0.8	2.68	−4.5	−5.4								

^a Notation as in Table 1. ^b X is conversion of ethene. ^c Total gas flow rate, 28 ± 2 mL min^{−1}.

contributions (the latter being small and determined with less confidence than the former; the Ir–Al contribution is identified only tentatively), which characterize the cluster–support interface. The Ir–O contribution, at a distance of about 2.0 Å, indicates bonding of the clusters to the γ -Al₂O₃, as expected.^{24–28}

EXAFS parameters characterizing the sample formed by adsorption of Ir(CO)₂(acac) on γ -Al₂O₃ (evacuated at 298 K for 2 h) followed by reductive carbonylation in flowing CO at 373 K for 12 h (to give a high yield of [Ir₆(CO)₁₅]^{2−}/ γ -Al₂O₃)⁵ and then decarbonylation in flowing He at 598 K for 2 h, specifically including Ir–Ir first- and second-shell coordination numbers of about 4 and 1, respectively (Table 1), are consistent with the expected^{1b,5} site-isolated octahedral Ir₆ clusters and the maintenance of the cluster frame of [Ir₆(CO)₁₅]^{2−} upon decarbonylation. The data also indicate Ir–O and Ir–Al contributions (the latter only tentatively identified) and the bonding of the clusters to the support, as in Ir₄/ γ -Al₂O₃. An Ir–C contribution (too small to determine quantitatively; not shown) indicates some residual carbon on the clusters from decomposition of CO during the decarbonylation step, as had been observed for Ir₄ supported on TiO₂.²⁶

The sample formed by treatment of Ir₄(CO)₁₂/ γ -Al₂O₃ in flowing H₂ at a higher temperature, 673 K, and 760 Torr for 2 h is reported⁶ to have undergone migration and aggregation of the iridium. EXAFS spectra of the sample confirm the report, as shown by an Ir–Ir first-shell coordination number of 7.1 and higher Ir–Ir shells,⁶ consistent with the formation of iridium aggregates with an average diameter of about 13 Å; details concerning the sample are given elsewhere.⁶ This sample is referred to as Ir_{agg}/ γ -Al₂O₃ and is representative of highly dispersed, nonuniform catalysts prepared conventionally.

Kinetics of Ethene Hydrogenation. After brief transient induction periods (0.5–2.0 h), each supported iridium cluster catalyst was found to have stable activity for ethene hydrogenation. To facilitate a quantitative comparison of the activities of the three catalysts, each was tested in the plug-flow reactor at differential conversions²⁹ at 294 K, 100 Torr of H₂, 40 Torr of C₂H₄, and 620 Torr of He, with a total flow rate of 100 mL (NTP) min^{−1}. The respective catalytic activities of Ir₄/ γ -Al₂O₃, Ir₆/ γ -Al₂O₃, and Ir_{agg}/ γ -Al₂O₃ were found to be 0.23, 0.055, and 0.34 molecules (total Ir atom \times s)^{−1}.³⁰

At 273 K, each catalyst was characterized by a reaction order in H₂ in the range 0.5 to 1.0, which is typical of conventional supported transition metal catalysts (Supporting Information,

Figure 1A–C).^{31–34} The reaction orders in ethene were also found to be in the range typical of such catalysts; the reaction order in ethene was slightly negative at low ethene partial pressures ($P_{C_2H_4} < 200$ Torr) and zero to slightly positive at higher values of $P_{C_2H_4}$ (Supporting Information, Figure 2A–C).^{31–34} The value of $P_{C_2H_4}$ at which the reaction order in ethene changed sign was found to depend on P_{H_2} . These results point to saturation kinetics, but the kinetics were too complex to be represented well by simple Langmuir–Hinshelwood or Eley–Rideal equations; details of the fits obtained with such equations are given in a thesis.¹⁰

EXAFS Evidence of Structure of γ -Al₂O₃-Supported Clusters during Ethene Hydrogenation Catalysis. The EXAFS parameters characterizing Ir₄/ γ -Al₂O₃ during ethene hydrogenation catalysis at 298 K (Table 2) show that the Ir₄ tetrahedra were maintained, as evidenced by the essentially unchanged Ir–Ir first-shell coordination number of nearly 3 and the lack of higher-shell Ir–Ir contributions. This result and the observation that the support was catalytically inactive bolster the inference that these clusters were the catalytically active species. The small Ir–C contributions (Table 2) are consistent with the presence of hydrocarbon reaction intermediates on the clusters, but the EXAFS data are not sufficient to identify such intermediates or distinguish between candidate intermediates.

Similarly, the EXAFS parameters characterizing Ir₆/ γ -Al₂O₃ during catalysis at 298 K (Table 3) show that the Ir₆ octahedra were maintained, as shown by the essentially unchanged Ir–Ir first- and second-shell coordination numbers of about 4 and 1,

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Table 3. EXAFS Parameters Characterizing γ -Al₂O₃-Supported Ir₆ Clusters Scanned during Ethene Hydrogenation Catalysis at 298 K and 760 Torr^a

P_{H_2} [Torr]	$P_{C_2H_4}$ [Torr]	X^{bc}	absorber-backscatterer pair											
			Ir–Ir				Ir–O				Ir–Al			
			N	R [Å]	$\Delta\sigma^2 \times 10^3$ [Å ²]	ΔE_0 [eV]	N	R [Å]	$\Delta\sigma^2 \times 10^3$ [Å ²]	ΔE_0 [eV]	N	R [Å]	$\Delta\sigma^2 \times 10^3$ [Å ²]	ΔE_0 [eV]
139	244	0.32	3.7	2.64	6.7	−1.0	0.8	2.04	2.7	6.8	0.2	1.79	4.0	−17.3
219	224	0.51	0.4	3.81	4.2	−8.9	0.4	3.30	−6.7	1.6	0.7	2.46	5.2	−12.7
			1.0	3.82	8.7	−12.6	0.5	3.29	−6.1	1.6	0.7	2.48	5.9	−14.6
397	213	0.86	3.9	2.66	6.0	−4.4	0.3	2.18	2.3	−9.4	0.2	1.82	5.0	−18.2
			1.1	3.82	7.9	−11.5	0.4	3.29	−7.1	7.4	0.7	2.54	8.1	−19.5

^a Notation as in Tables 2 and 3. ^b X is conversion of ethene. ^c Total gas flow rate, 31 ± 2 mL min^{−1}.

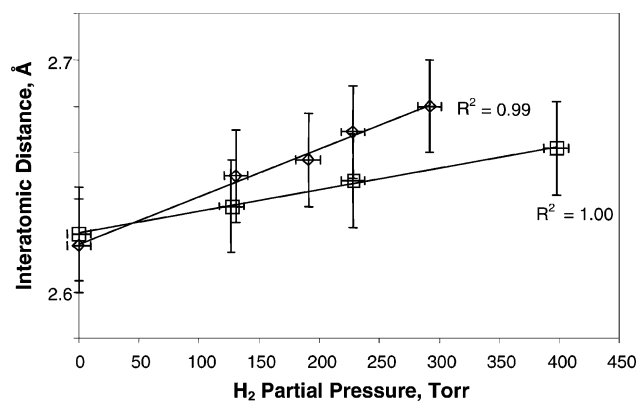


Figure 1. Dependence of Ir–Ir distance in supported cluster catalysts (upper curve, Ir₄ and lower curve, Ir₆) on the partial pressure of H₂ during ethene hydrogenation catalyzed by the γ -Al₂O₃-supported metal clusters at 298 K and 760 Torr (131–397 Torr H₂ and 203–244 Torr C₂H₄, with the balance He).

respectively, and the lack of other Ir–Ir shells. Because the Ir₆ octahedra were maintained during catalysis and the support was catalytically inactive, we infer that these clusters were the catalytically active species. No Ir–C contributions were evident in the EXAFS spectra, suggesting that carbon remaining from the CO ligands present on the precursor had been removed, but the EXAFS data are not sufficient to support any conclusions about candidate reaction intermediates.

Although the metal cluster frames were maintained during catalysis, the structural parameters determined by EXAFS spectroscopy were altered slightly, indicating adsorbates (ligands) on the clusters. At nearly constant $P_{C_2H_4}$ and constant temperature, the Ir–Ir bonding distances in Ir₄/ γ -Al₂O₃ and Ir₆/ γ -Al₂O₃ increased approximately in proportion to P_{H_2} (Figure 1); similarly, the catalytic activity increased approximately in proportion to P_{H_2} (Supporting Information, Figure 1A). We recently communicated³⁵ results demonstrating that the presence of reactive intermediates (alkyl, di- σ -bonded alkene, π -bonded alkene, and/or hydride) on the clusters modified the structure of Ir₄/ γ -Al₂O₃ during ethene or propene hydrogenation catalysis (other data show that propylidyne inhibits propene hydrogenation catalysis³⁶). The full set of data characterizing Ir₄/ γ -Al₂O₃, reported here, with new data characterizing Ir₆/ γ -Al₂O₃ (Tables 2 and 3) provide a basis for comparison of the two clusters as catalysts.

IR Evidence of Adsorbates on Ir₄ and on Ir₆ during Ethene Hydrogenation Catalysis at Low $P_{C_2H_4}$. The IR spectra

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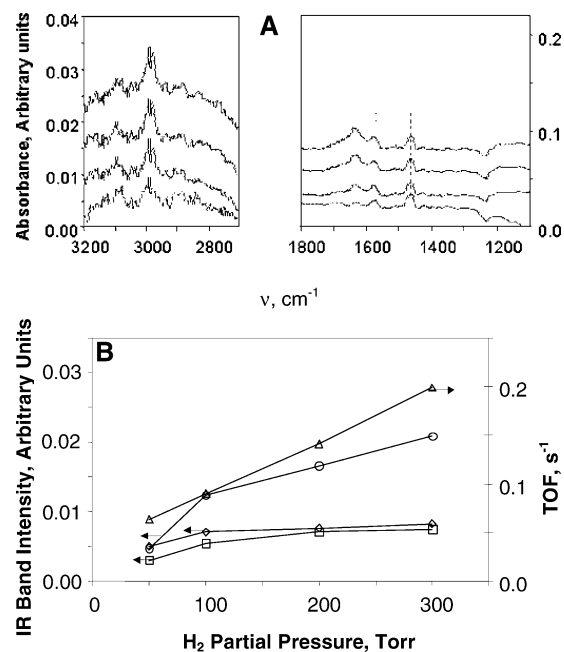


Figure 2. (A) IR spectra of the adsorbates on Ir₄/ γ -Al₂O₃ during steady-state catalysis of ethene hydrogenation catalysis at 288 K and 760 Torr (40 Torr C₂H₄, 50–300 Torr H₂, and the balance He). The total flow feed flow rate was 100 mL min^{−1}. The upper spectrum represents the sample at an H₂ partial pressure of 300 Torr; the next ones, in decreasing order, represent the sample at H₂ partial pressures of 200, 100, and 50 Torr, respectively. (B) Dependence of IR band intensities on H₂ partial pressure during ethene hydrogenation catalyzed by Ir₄/ γ -Al₂O₃ at 288 K and 760 Torr (40 Torr C₂H₄, 50–300 Torr H₂, and the balance He). The bands at 2990 (\diamond) and 2981 cm^{−1} (\square) were chosen to represent di- σ -bonded ethene, and that at 1635 cm^{−1} (\circ) was chosen to represent water on the γ -Al₂O₃ support. These IR bands were chosen as the best ones to minimize error caused by overlap with other bands. The triangles (Δ) represent the reaction rate expressed as a turnover frequency (TOF), the rate of reaction in units of molecules of ethene converted per Ir atom per second.

of the adsorbates on Ir₄/ γ -Al₂O₃ during ethene hydrogenation catalysis at 288 K and 760 Torr and low $P_{C_2H_4}$ (40 Torr C₂H₄, 50–300 Torr H₂, the balance He) indicate two weak bands in the C–H stretching range (at 2990 and 2979 cm^{−1}) (Figure 2A). The dependence of the band intensities on P_{H_2} is shown in Figure 2B. The bands are assigned to di- σ -bonded ethene (Table 4), as the frequencies almost match those of a vibrational band of di- σ -bonded ethene on Pt(111) (3000 and 2920 cm^{−1})^{37,38} and on Fe(100) (2985 cm^{−1}).³⁹ We infer that the lower-frequency (symmetric C–H stretching) band expected for di- σ -bonded

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Table 4. IR Bands Characterizing Adsorbates on Ir₄ and Ir₆ Supported on γ -Al₂O₃ during Ethene Hydrogenation Catalysis^a and Vibrational Spectra of Reference Materials^b

sample	band locations, cm ⁻¹	adsorbate assignment	reference
Ir ₄ / γ -Al ₂ O ₃ ^a	2990, 2979	di- σ -bonded ethene	this work
Ir ₆ / γ -Al ₂ O ₃ ^a	2980, 2895	di- σ -bonded ethene	this work
Pt(111)	3000, 2920	di- σ -bonded ethene	37,38
Fe(100)	2985	di- σ -bonded ethene	39
Ir ₄ / γ -Al ₂ O ₃ ^a	2930, 2877	ethyl	this work
CH ₃ CH ₂ Cl	2967, 2947, 2881	ethyl	45
Pt(111)	2918	ethyl	38

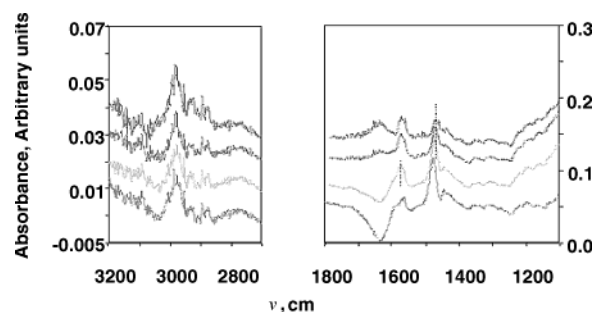
^a Conditions of ethene hydrogenation catalysis in flow system: 288 K, 760 Torr total pressure (50–300 Torr of H₂, 40 Torr of C₂H₄, and the balance He), and total gas flow rate of 100 mL min⁻¹. ^b Data obtained at relatively low ethene partial pressures.

ethene was likely too low in intensity to distinguish from the noise. The low intensities of the bands indicate low concentrations (and perhaps short residence times) of di- σ -bonded ethene on the clusters during catalysis. The splitting of the band indicating di- σ -bonded ethene is suggested to be an indication of di- σ -bonded ethene on clusters with different ligand environments (e.g., caused by the presence of different adsorbates on some of the clusters).⁴⁰

In addition to bands corresponding to hydrocarbon species on Ir₄ during catalysis, bands were observed at 1635, 1571, 1463, and 1232 cm⁻¹; the freshly decarbonylated sample was characterized by bands at 1577, 1465, 1231, and 1155 cm⁻¹ (data not shown), indicative of support modes (e.g., Al–O), and thus the bands at 1571, 1463, and 1231 cm⁻¹ in the difference spectra of the working catalyst are inferred to result from small changes in the support induced by the presence of ligands formed during catalysis.

The band at 1635 cm⁻¹ is associated with water on the γ -Al₂O₃ surface,⁴¹ formed by dissociative adsorption of H₂ on the clusters and spillover onto the support,⁴² whereby hydrogen reacts with surface hydroxyl groups of the support to give water.⁴³ This process was previously characterized by IR spectroscopy⁴⁴ when H₂ (alone) was brought in contact with Ir₄/ γ -Al₂O₃ at 298 K and 760 Torr. The intensity of the surface water band at 1635 cm⁻¹ during ethene hydrogenation catalysis increased with increasing P_{H_2} (Figure 2B), indicating that increasing amounts of hydrogen were spilled over onto the support at increasing values of P_{H_2} . We emphasize that the increased amount of hydrogen spilled over onto the support at higher P_{H_2} was not a transient phenomenon, as the spectra represent steady states under each set of catalytic reaction conditions.

The spectra of the adsorbates on Ir₆/ γ -Al₂O₃ during catalysis under the conditions stated previously (low $P_{\text{C}_2\text{H}_4}$) include peaks at 2980, 2954, 2930, 2895, and 2877 cm⁻¹ (Figure 3). Those at 2980 and 2895 cm⁻¹ are assigned to di- σ -bonded ethene (Table 5), as previously, and those at 2954, 2930 and 2877 cm⁻¹, to ethyl (Table 4), as they occur at frequencies similar to those of ethyl chloride (2967, 2947, and 2881 cm⁻¹).⁴⁵ The di- σ -bonded

**Figure 3.** IR spectra of the adsorbates on Ir₆/ γ -Al₂O₃ during catalysis of ethene hydrogenation at 288 K and 760 Torr (40 Torr C₂H₄, 50–300 Torr H₂, and the balance He). The total flow rate was 100 mL min⁻¹. The upper spectrum represents the sample at an H₂ partial pressure of 300 Torr; the next ones, in decreasing order, represent the sample at H₂ partial pressures of 200, 100, and 50 Torr, respectively.**Table 5.** IR Bands of Adsorbates on Ir₄ and Ir₆ Supported on γ -Al₂O₃ during Ethene Hydrogenation Catalysis^{a,b} and Vibrational Spectra of Reference Materials^c

sample	adsorbate	bands, cm ⁻¹	reference
Ir ₄ / γ -Al ₂ O ₃ ^a	di- σ -bonded ethene	2988, 2975, 2897, 2884	this work
Ir ₆ / γ -Al ₂ O ₃ ^a	di- σ -bonded ethene	2988, 2894	this work
Ir ₄ / γ -Al ₂ O ₃ ^b	di- σ -bonded ethene	2992, 2987, 2896, 2887	this work
Ir ₆ / γ -Al ₂ O ₃ ^b	di- σ -bonded ethene	3003, 2988, 2906, 2890	this work
Pt(111)	di- σ -bonded ethene	3000, 2920	37,38
Fe(100)	di- σ -bonded ethene	2985	39
Ir ₄ / γ -Al ₂ O ₃ ^a	ethyl	2956, 2933	this work
Ir ₆ / γ -Al ₂ O ₃ ^a	ethyl	2952, 2873	this work
Ir ₄ / γ -Al ₂ O ₃ ^b	ethyl	2957, 2929, 2863	this work
Ir ₆ / γ -Al ₂ O ₃ ^b	ethyl	2952, 2927, 2868	this work
CH ₃ CH ₂ Cl	ethyl	2967, 2947, 2881	45
Pt(111)	ethyl	2918	38
Ir ₄ / γ -Al ₂ O ₃ ^b	π -bonded ethene	3060, 3026	this work
Ir ₆ / γ -Al ₂ O ₃ ^b	π -bonded ethene	3050, 3023	this work
Rh(111)	π -bonded ethene	3060, 3000	46
Pt(111)	π -bonded ethene	3060	48
Pt(111)	π -bonded ethene	3015	47
Ir ₄ / γ -Al ₂ O ₃ ^b	ethylidyne	2947, 2896	this work
Ir/Al ₂ O ₃	ethylidyne	2947, 2896	50
Ir(111)	ethylidyne	2950	49
Pt/ γ -Al ₂ O ₃	ethylidyne	2940, 2887	51

^a Conditions of ethene hydrogenation in flow system: 288 K, 760 Torr total pressure (300 Torr of H₂, 40–200 Torr of C₂H₄, and the balance He), and total gas flow rate of 100 mL min⁻¹. ^b Conditions of ethene hydrogenation in flow system: 288 K, 760 Torr total pressure (300 Torr of H₂, 200–293 Torr of C₂H₄, and the balance He), and total gas flow rate of 100 mL min⁻¹. ^c Data obtained at relatively high ethene partial pressures.

ethene and ethyl band intensities remained approximately constant over the range of H₂ partial pressures investigated (Figure 4).

In addition to the bands corresponding to hydrocarbon ligands on Ir₆, bands were observed at 1635, 1562, and 1470 cm⁻¹ (Figure 3). Again, those at 1562 and 1470 cm⁻¹ are associated with small changes in the support caused by ligands formed during catalysis. The intensity of the surface water band at 1635 cm⁻¹ increased approximately in proportion to P_{H_2} , consistent with the pattern stated previously for Ir₄. However, at low values of P_{H_2} , the apparent intensity of this band was less than zero. This result arises from the measurement of the difference spectrum; subtraction of the spectrum of the catalyst in He from that of the catalyst in reacting ethene + H₂ resulted in a negative peak indicating that the concentration of water on the sample during steady-state catalysis was less than that in the presence of He (prior to catalysis). As both spectra were recorded with the sample at only 288 K, the negative water peak is attributed

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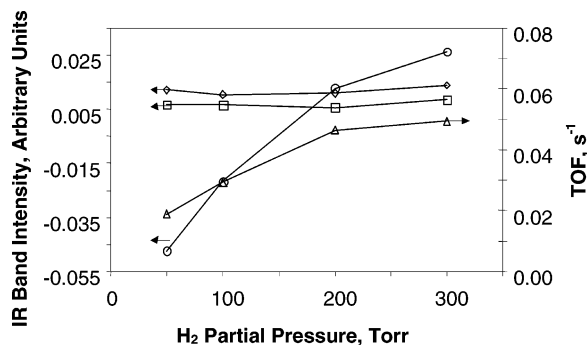


Figure 4. Dependence of IR band intensities on H_2 partial pressure during ethene hydrogenation catalyzed by $Ir_6/\gamma-Al_2O_3$ at 288 K and 760 Torr (40 Torr C_2H_4 , 50–300 Torr H_2 , and the balance He). The bands at 2980 and 2895 cm^{-1} were chosen to represent di- σ -bonded ethene (\diamond); those at 2954, 2930, and 2877 cm^{-1} , to represent ethyl (\square); and that at 1635 cm^{-1} was chosen to represent water on the $\gamma-Al_2O_3$ support (\circ). Other information as in caption of Figure 2.

not to thermal desorption of surface water but rather to changes induced by catalysis. This point is discussed in the following.

IR Evidence of Adsorbates on Ir_4 and Ir_6 during Ethene Hydrogenation Catalysis at High $P_{C_2H_4}$. In contrast to ethene hydrogenation on supported Ir_4 or Ir_6 at low ethene partial pressures (when principally di- σ -bonded ethene was observed as the adsorbate), ethene hydrogenation at $P_{C_2H_4} > 200$ Torr resulted in complex spectra, indicating multiple adsorbates.

The spectra of the adsorbates on $Ir_4/\gamma-Al_2O_3$ during catalysis at 288 K, 300 Torr of H_2 , and $P_{C_2H_4}$ values < 200 Torr include peaks at 2988, 2975, 2956, 2933, 2897, and 2884 cm^{-1} (Figure 5A). The peaks at 2988, 2975, 2897, and 2884 cm^{-1} are assigned to di- σ -bonded ethene (the band splitting is discussed previously), and those at 2956 and 2933 cm^{-1} , to ethyl (Table 5), as previously.

When $P_{C_2H_4}$ exceeded 200 Torr, the spectra of the adsorbates on $Ir_4/\gamma-Al_2O_3$ during catalysis included peaks at 3060, 3026, 2992, 2988, 2957, 2947, 2929, 2896, 2887, and 2863 cm^{-1} (Figure 5A). Those at 3060 and 3023 cm^{-1} are assigned to π -bonded ethene (Table 5), nearly matching those of π -bonded ethene on Rh(111) (3060, 3000 cm^{-1})⁴⁶ or Pt(111) (3060, 3015 cm^{-1}).^{47,48} The bands at 2947 and 2896 cm^{-1} are assigned to ethylidyne (Table 5) (cf. the spectra of ethylidyne on Ir(111) (2950 cm^{-1})⁴⁹ or $\gamma-Al_2O_3$ -supported iridium particles (2947 and 2896 cm^{-1})^{50,51}). The bands at 2992, 2988, 2896, and 2887 cm^{-1} are assigned to di- σ -bonded ethene, and those at 2957, 2929, and 2863 cm^{-1} , to ethyl, as previously.

The intensities of the π -bonded ethene changed with $P_{C_2H_4}$ (Figure 5B); because the bands assigned to ethyl, ethylidyne, and di- σ -bonded ethene overlapped significantly, the correlations with $P_{C_2H_4}$ are relatively unreliable.

The intensity of the surface water band (Figure 5B) was positive for $P_{C_2H_4} < 200$ Torr and negative for $P_{C_2H_4} > 200$ Torr, the latter result indicating a lower steady-state concentration of water on the support during catalysis than prior to catalysis (when the sample was in flowing He). Thus, we infer

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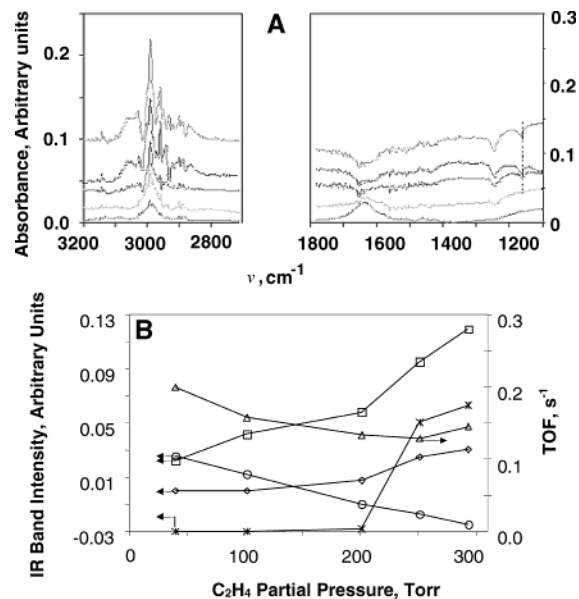


Figure 5. (A) IR spectra of the adsorbates on $Ir_4/\gamma-Al_2O_3$ during catalysis of ethene hydrogenation at 288 K and 760 Torr (40–293 Torr C_2H_4 , 300 Torr H_2 , and the balance He) (total flow of 100 mL min^{-1}). The upper spectrum represents the sample at a C_2H_4 partial pressure of 293 Torr; the next ones, in decreasing order, represent the sample at C_2H_4 partial pressures of 251, 201, 102, and 40 Torr, respectively. (B) Dependence of IR band intensities on ethene partial pressure during ethene hydrogenation catalyzed by $Ir_4/\gamma-Al_2O_3$ at 288 K and 760 Torr (40–293 Torr C_2H_4 , 300 Torr H_2 , and the balance He). The bands at 3060 and 3028 cm^{-1} were chosen to represent π -bonded ethene (\diamond); that at 2988 was chosen to represent di- σ -bonded ethene (\square); that at 2877 cm^{-1} was chosen to represent ethyl ($*$); and that at 1635 cm^{-1} was chosen to represent water on the $\gamma-Al_2O_3$ support (\circ). The catalytic activity (Δ) is expressed as the turnover frequency, defined in the caption of Figure 2.

that (a) hydrogen from the support participates in ethene hydrogenation on Ir_4 (indicated by the decrease in surface water content during catalysis at high $P_{C_2H_4}$), moving to the clusters by reverse spillover, and (b) there is a driving force for hydrogen transport from the support at higher $P_{C_2H_4}$ because of hydrogen depletion from the clusters in the hydrogenation reaction.⁵²

The spectra of the adsorbates on $Ir_6/\gamma-Al_2O_3$ during catalysis at 288 K, $P_{H_2} = 300$ Torr, and $P_{C_2H_4} < 200$ Torr include bands at 2988, 2952, 2927, 2894, and 2873 cm^{-1} (Supporting Information, Figure 3). The bands at 2988 and 2894 cm^{-1} are assigned to di- σ -bonded ethene, and those at 2952, 2927, and 2873 cm^{-1} , to ethyl, as previously (Table 5). (The dependence of the intensities of di- σ -bonded ethene bands and ethyl on $P_{C_2H_4}$ (for $P_{C_2H_4} < 200$ Torr) is shown in the Supporting Information, Figure 3B.)

When $P_{C_2H_4}$ was > 200 Torr, peaks were observed at 3050, 3023, 3003, 2988, 2952, 2927, 2906, 2890, and 2868 cm^{-1} (Supporting Information, Figure 3A). The peaks at 3050 and 3023 cm^{-1} are assigned to π -bonded ethene; those at 3003, 2988, 2906, and 2890 cm^{-1} are assigned to di- σ -bonded ethene; and those at 2952, 2927, and 2868 cm^{-1} are assigned to ethyl (Table 5). (The intensities of the π -bonded ethene and ethyl

- (52) A transient experiment involving monitoring the support water concentration during catalysis following a step change in conditions was done to characterize the hydrogen spillover/reverse spillover in catalysis. The experiment was carried out as the reaction occurred in the EXAFS cell: following steady-state ethene hydrogenation catalysis on $Ir_4/\gamma-Al_2O_3$ or $Ir_6/\gamma-Al_2O_3$, the flow of H_2 to the reactor was stopped, but the flow of ethene continued. For 1–2 h following the step change, ethane was observed in the product stream in amounts that decreased with time; evidently the hydrogen was supplied from the support during this period.

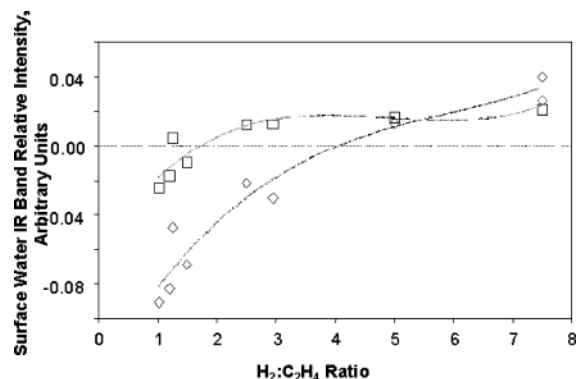


Figure 6. Dependence of intensity of IR band of water on the γ -Al₂O₃ support on reactant composition (H₂:C₂H₄ molar ratio) during ethene hydrogenation on Ir₄/ γ -Al₂O₃ (□) and on Ir₆/ γ -Al₂O₃ (◇) at 288 K and 760 Torr (50–300 Torr H₂ and 40–293 Torr C₂H₄, with the balance He).

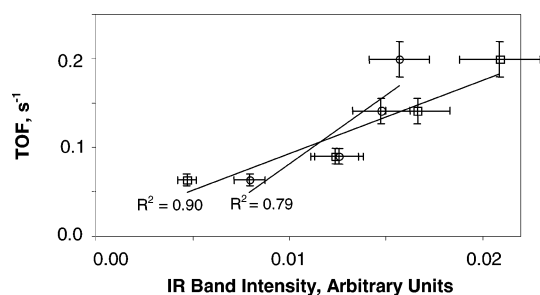


Figure 7. Dependence of catalytic activity measured by TOF on intensities of IR bands of di- σ -bonded ethene (□) and water on the γ -Al₂O₃ support (○) during ethene hydrogenation on Ir₄/ γ -Al₂O₃ at 288 K and 760 Torr. Details as in Figure 2.

peaks are shown as a function of $P_{C_2H_4}$ in the Supporting Information, Figure 3B.)

The support water band at 1635 cm⁻¹ decreased in intensity with increasing $P_{C_2H_4}$ (Figure 6). The intensity of the surface water band was positive for $P_{C_2H_4} < 100$ Torr and negative for higher $P_{C_2H_4}$ values. As previously, we infer that hydrogen from the support participated in ethene hydrogenation on Ir₆.

Discussion

Reaction Mechanism. Only di- σ -bonded ethene and ethyl were observed on the supported clusters, either Ir₄ or Ir₆,⁵³ during ethene hydrogenation catalysis at low ethene partial pressures (<200 Torr). On Ir₄, the concentration of di- σ -bonded ethene (inferred from the IR band intensity) increased with increasing catalytic activity (Figure 7). The results provide evidence that di- σ -bonded ethene is a reactive intermediate in the hydrogenation of ethene on Ir₄ at low $P_{C_2H_4}$.

In contrast, a plot of the catalytic reaction rate as a function of the IR band intensities of these adsorbates shows that the parameters are not correlated (Figure 8). The result suggests either that the adsorbates are spectators in the catalysis on Ir₆

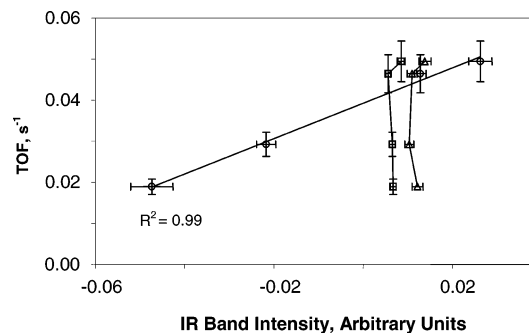


Figure 8. Dependence of catalytic activity measured by TOF on intensities of IR bands of di- σ -bonded ethene (Δ) and ethyl (\square) on clusters and water on the γ -Al₂O₃ support (○) during ethene hydrogenation on Ir₆/ γ -Al₂O₃ at 288 K and 760 Torr. Details as in Figure 4.

at low $P_{C_2H_4}$ or that these adsorbates are involved in virtually equilibrated steps of the catalytic reaction.

Neurock and van Santen⁵⁴ showed theoretically that di- σ -bonded ethene and ethyl are reactive intermediates in ethene hydrogenation on Pd(111) at low ethene coverages, and others^{55–57} showed experimentally that ethyl is a reactive intermediate on Pt(111). Our interpretation of the catalysis on Ir₆ is similar, as we infer that di- σ -bonded ethene and ethyl are reactive intermediates involved in virtually equilibrated steps during the hydrogenation of ethene at low $P_{C_2H_4}$.

At higher $P_{C_2H_4}$ values (> 200 Torr), π -bonded ethene, in addition to di- σ -bonded ethene and ethyl, was observed on each of our catalysts; the concentration of π -bonded ethene increased with $P_{C_2H_4}$. As $P_{C_2H_4}$ was raised to approximately 200–250 Torr, the reaction rate observed with each catalyst began to increase with increasing $P_{C_2H_4}$ (whereas, at ethene partial pressures less than about 200 Torr, the rate decreased with increasing $P_{C_2H_4}$). The results suggest that π -bonded ethene is a reactive intermediate on each catalyst at the relatively high $P_{C_2H_4}$.

These results observed at the higher values of $P_{C_2H_4}$ (and presumably at higher coverages of the clusters with hydrocarbon ligands) are consistent with results characterizing ethene hydrogenation on extended metal surfaces. Cremer et al.^{56,57} showed experimentally that π -bonded ethene is the principal reactive intermediate (forming ethyl) in the hydrogenation of ethene on Pt(111). Neurock and van Santen⁵⁴ showed theoretically that, at high ethene coverages, hydrogenation of ethene on Pd(111) also proceeds predominantly via π -bonded ethene; they showed that repulsive adsorbate–adsorbate interactions, appreciable at higher surface coverages, lead to a lowering of the energy barrier for hydrogenation via π -bonded ethene, whereas, at low surface coverages, hydrogenation is energetically favored to proceed through di- σ -bonded ethene.

Thus, in broad terms, the hydrogenation of ethene on γ -Al₂O₃-supported clusters of Ir₄ and of Ir₆ proceeds similarly to that on Pd(111), on which, at low $P_{C_2H_4}$, catalysis proceeds predominantly through di- σ -bonded ethene, and on which, at high $P_{C_2H_4}$, it proceeds predominantly through π -bonded ethene. When $P_{C_2H_4}$ was increased to 150–250 Torr, the predominant reaction pathway on the clusters evidently changed, as indicated by the

(53) These adsorbates are inferred to have been bonded principally to the clusters and not the support, because their vibrational spectra are similar to those of the corresponding adsorbates on extended metal surfaces and because separate adsorption experiments showed that adsorption on the γ -Al₂O₃ support itself was not appreciable under our conditions. However, we do not rule out the possibility that some hydrocarbon was present on the support or perhaps bridging the cluster–support interface, and it is also possible that adsorption of ethene on the support could have affected the (reverse) spillover of hydrogen. The whole question of the possibly distinct role of the Ir atoms at the interface with the support remains open and warrants attention.

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IR and kinetics data. We suggest that, at these values of $P_{C_2H_4}$, the coverage of the clusters with ligands may become sufficient to enable ligand–ligand interactions to shift the predominant reaction mechanism.

Spilled-Over Hydrogen. The data indicate a role of spilled-over hydrogen in the catalysis. H_2 adsorbs dissociatively on the clusters, presumably forming hydrides⁵⁸ that spill over onto the support and react with surface hydroxyl groups to form water. On either cluster, at $P_{C_2H_4} = 40$ Torr, an increasing amount of hydrogen was observed to spill over as P_{H_2} increased, and simultaneously, the catalytic reaction rate increased (Figures 7 and 8). The IR data show that at $P_{H_2} = 300$ Torr decreasing amounts of hydrogen were spilled over onto the support with increasing $P_{C_2H_4}$ (Figure 5B and Supporting Information Figure 3B). At $P_{C_2H_4}$ greater than about 150 Torr when the catalyst was $Ir_4/\gamma-Al_2O_3$, and greater than about 70 Torr when the catalyst was $Ir_6/\gamma-Al_2O_3$, the concentrations of water on the surface were less than on the catalyst in He. The observation of negative intensities of surface water bands at the lower $P_{C_2H_4}$: P_{H_2} ratios during catalysis suggests that hydrocarbons adsorbed preferentially, resulting in less than the stoichiometric amounts of hydrogen required for catalysis on the clusters. Plots of catalytic activity against the IR band intensity of surface water (Figures 7 and 8 for $Ir_4/\gamma-Al_2O_3$ and $Ir_6/\gamma-Al_2O_3$, respectively) showing that the two variables are positively correlated imply that the reactive form of adsorbed hydrogen (presumably hydride⁵⁹) tends to equilibrate with water on the $\gamma-Al_2O_3$ support via hydrogen spillover/reverse spillover.⁴² The steady-state concentration during catalysis is determined by a balance between the rates of dissociative H_2 adsorption, hydrogen spillover/reverse spillover onto/from the support, and hydrogen consumption in catalysis. This last point indicates an indirect role of the support in catalysis, particularly important for supported metal clusters in which the metal–support interface is maximized, as in our samples.

Figure 6 depicts the relationship between the IR band intensity indicating the surface water concentration (relative to that of the catalyst in flowing He) and the P_{H_2} : $P_{C_2H_4}$ ratio. At a P_{H_2} : $P_{C_2H_4}$ ratio of about 2, no net hydrogen was spilled over onto the support during ethene hydrogenation on supported Ir_4 . The equivalent statement pertains to supported Ir_6 at a P_{H_2} : $P_{C_2H_4}$ ratio of about 4 or 5. The results indicate that hydrogen competes with ethene for bonding sites on the clusters and are consistent with the reaction orders in H_2 , which range from 0.5 to 1.0.^{32–34}

Recent theoretical work⁶⁰ provides insights into the hydrogen spillover/reverse spillover phenomena: Calculations done at the density functional level representing Rh_6 clusters supported on a faujasite zeolite show that the cluster decorated with three hydrogen atoms is markedly more stable than the bare cluster on the zeolite containing hydroxyl groups bonded near the cluster (and more stable than the cluster decorated with C atoms); the calculations indicate that reverse spillover of hydrogen to form the hydrogen-decorated clusters leads to oxidation of the clusters, with the Rh atoms near the cluster–support interface becoming positively charged; the Rh–O

distances correspond to those between rhodium and oxygen ligands in Rh(I) complexes, and these distances nearly match the Ir–O distances observed by EXAFS spectroscopy in this work. The presence of cationic and polarized clusters on the support leads to the suggestion that a difference between the Ir_4 and Ir_6 clusters with regard to how they bond to the support and perhaps a contrast between the role in catalysis of the Ir atoms bonded to the support and those farther from the support; thus, the theoretical results might be a start toward explaining the difference in catalytic behavior between the clusters of the two sizes. More work is needed to test both this suggestion and the suggestion that differing strengths of ligand–ligand interactions may distinguish the Ir_4 and Ir_6 clusters.

Similarities between Ethene Hydrogenation on $\gamma-Al_2O_3$ -Supported Iridium Clusters and That on Other Metal Catalysts. Our results show that ethene hydrogenation on $\gamma-Al_2O_3$ -supported Ir_4 or Ir_6 is similar to that on extended metal surfaces in terms of reaction kinetics (indicated by reaction orders) and mechanism (indicated by the reaction intermediates). Several groups^{1–3} have observed results comparable to ours in showing that the rate of catalytic hydrogenation of alkenes (or arenes) depends on the structure or size of a supported metal catalyst, particularly for the smallest metal structures. For example, Masson *et al.*¹² reported a size dependence of the activity for ethene hydrogenation on platinum clusters supported on planar alumina films (supported on Si(111)) for average cluster diameters < 17 Å (with a maximum activity observed for clusters estimated to be 6 Å in diameter). Others⁶¹ showed that rates of butadiene hydrogenation depend on the roughness of the platinum single-crystal plane ($Pt(111) < Pt(100) < Pt(110)$) and that hydrogen dissociation is favored on the rougher faces. When taken together, these results illustrate connections between catalysis on metal clusters and catalysis on extended metal surfaces and provide some justification for the use of single crystals as model catalysts. Nonetheless, extended metal surfaces differ substantially from supported metal clusters, lacking supports and structures that would account for cluster size effects, as summarized in the following.

Contrasts between Ir_4 and Ir_6 as Ethene Hydrogenation Catalysts. The two $\gamma-Al_2O_3$ -supported clusters, Ir_4 and Ir_6 , differ severalfold in their catalytic activities for ethene hydrogenation. Furthermore, the reaction orders in H_2 differ from one catalyst to the other. When the ethene partial pressure was 40 Torr, the reaction orders in H_2 were 0.68 ± 0.04 and 0.60 ± 0.05 for Ir_4 and Ir_6 , respectively, and when the ethene partial pressure was 250 Torr, the reaction orders in H_2 were 0.81 ± 0.01 and 0.71 ± 0.04 for Ir_4 and Ir_6 , respectively. The results suggest that H_2 adsorption on Ir_4 occurred more competitively (with ethene) than on Ir_6 ,^{32,33} presumably because Ir_6 was more nearly saturated with hydrocarbon adsorbates that hindered the adsorption of hydrogen.

The IR data demonstrate that depletion of support water via reverse spillover of hydrogen to the clusters⁴² during catalysis was more appreciable on Ir_6 than on Ir_4 . The result is consistent with the suggestion that ethene-derived adsorbates were more prevalent on Ir_6 than on Ir_4 and that these adsorbates blocked sites on the clusters and hindered hydrogen uptake directly from the gas phase, shifting the hydrogen spillover/reverse spillover balance toward reverse spillover. Furthermore, at high P_{H_2} : $P_{C_2H_4}$

(58) IR and 1H NMR spectroscopies indicate hydride ligands on Rh_6 supported on La_2O_3 during ethene hydrogenation catalysis. The concentration of hydride was shown to correlate well with the catalytic activity.¹⁰

(59) During ethene hydrogenation on Rh_6/La_2O_3 at 298 and 760 K (348 Torr H_2 , 75 Torr C_2H_4 , and 337 Torr He), we observed (with IR and 1H NMR) terminally bonded hydride on the clusters.¹⁰

(60) Vyssilov, G. N.; Gates, B. C.; Rösch, N. *Angew. Chem.* **2003**, *42*, 1391.

(61) Pradier, C.-M.; Berthier, Y. *J. Catal.* **1991**, *129*, 356.

ratios, when neither cluster would be saturated with hydrocarbon adsorbates, the amount of hydrogen spilled over onto the support from the clusters was about the same for Ir₄/ γ -Al₂O₃ and Ir₆/ γ -Al₂O₃ (Figure 6).

The spectroscopic data also indicate contrasts between catalysis on Ir₄ and Ir₆. At low $P_{\text{C}_2\text{H}_4}$, the band intensities of di- σ -bonded ethene on Ir₄ correlate well with catalytic activity, but the statement does not pertain to Ir₆. The results suggest that the adsorbates are more reactive on Ir₄ than on Ir₆, even to the extent that ethyl is not apparent on the former clusters. If the suggestion of greater ligand-ligand interactions on the smaller clusters, Ir₄, has some validity, it would suggest that the limited size of this cluster forces the adsorbed species closer to one another than on Ir₆, increasing the repulsive adsorbate–adsorbate interactions and the catalytic activity. Consistent with this hypothesis, the C–H stretching frequency of π -bonded ethene on Ir₄ (3060 cm⁻¹) indicates that it was less rehybridized on Ir₄ than on Ir₆ (3050 cm⁻¹)⁵⁵ during ethene hydrogenation under the same conditions. However, we emphasize that other explanations are not excluded, such as a cluster size effect related to the degree of polarization of the metal at the metal-support interface and even the charge on the cluster.⁶⁰

Conclusions

γ -Al₂O₃-supported Ir₄ is several times more active than Ir₆ as a catalyst for ethene hydrogenation under our conditions. EXAFS spectra of the functioning catalysts show that the tetrahedral and octahedral cluster frames of Ir₄ and Ir₆ were maintained, indicating that Ir₄ and Ir₆ were the active species in the respective catalysts. IR spectra identify reaction intermediates on the clusters (which match those reported for extended metal surfaces), di- σ -bonded ethene, π -bonded ethene,

and ethyl, the abundances of which depend on the cluster size and the composition of the reactant gas, with di- σ -bonded ethene predominating at ethene partial pressures less than 200 Torr and π -bonded ethene more important at higher ethene partial pressures. The data indicate both similarities and differences in the comparison of supported metal clusters and extended metal surfaces as catalysts, and they illustrate the role of hydrogen spilled up from the support in the catalysis and suggest a role of increased adsorbate–adsorbate interactions on the smaller (Ir₄) clusters favoring the catalytic activity of Ir₄ over Ir₆.

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Supporting Information Available: Figures showing data referred to by number in the preceding text are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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