Ir/KLTL Zeolites: Structural Characterization and Catalysis of *n*-Hexane Reforming

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Ir/KLTL zeolite catalysts were prepared by incipient wetness impregnation of LTL zeolites with [Ir(NH₃)₅Cl]Cl₂. The catalysts were characterized by extended X-ray absorption fine structure (EX-AFS) spectroscopy, infrared spectroscopy, and H₂ chemisorption. EXAFS data show that the average Ir cluster size (after treatment at 300°C in H₂) increased from about 7 to 20 Å as the zeolite K : Al atomic ratio increased from 0.34 to 1.56. Infrared spectra of adsorbed CO show that the electron donation to the Ir increased as the K: Al ratio increased. In contrast to the performance reported for Pt/KLTL zeolites with metal clusters as small as those observed in the present experiments, the Ir/KLTL catalyst has a low selectivity for dehydrocyclization of *n*-hexane at 440–480°C and 1 atm with a H₂: n-hexane feed molar ratio of 6. Instead, the catalysts are selective for hydrogenolysis. The selectivity is insensitive to the K: Al ratio, but the activity for dehydrocyclization is a maximum at a K: Al atomic ratio of about 1. The results show that even the smallest Ir clusters to which electron donation is significant still behave essentially like metallic Ir in the catalytic reactions. © 1996 Academic Press, Inc.

INTRODUCTION

An important reaction in catalytic reforming of naphtha is dehydrocyclization of C₆ and C₇ paraffins. These reactions are catalyzed selectively when the catalyst consists of Pt clusters supported in zeolite LTL containing K⁺ or K⁺ and Ba²⁺ exchange ions (1–3). The zeolite LTL catalysts are nonacidic, and evidently the Pt clusters alone are the catalytically active species. LTL zeolite is evidently the best support for selective Pt-catalyzed dehydrocyclization reactions; this zeolite incorporates straight parallel pores that incorporate cages that are approximately ellipsoidal in shape with approximate dimensions of $4.8 \times 12.4 \times 10.7$ Å; the apertures are 12-membered oxygen rings with diameters of about 7.5 Å.

Notwithstanding many data in the literature (4–10), there is still no consensus about why Pt-containing LTL zeolites

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are so selective for dehydrocyclization. The various suggestions for why the catalysts are so selective are summarized elsewhere (11); in short, high dehydrocyclization selectivites are attributed to some combination of the effects of Pt cluster size (8), the constraints imposed by the zeolite pores, and electronic effects associated with the basicity of the support.

Ir/KLTL catalysts have been prepared with clusters of about five to six atoms each, which are about the same size as those in well-prepared Pt/KLTL zeolites (11). In contrast to Pt, Ir is quite resistant to sintering on a number of metal oxide and zeolite supports in the presence of H₂ at relatively high temperatures (12–17). Ir on various supports (MgO, Al₂O₃, NaY zeolite, and NaX zeolite) is both a hydrogenolysis and a dehydrogenation catalyst (18–20). Because Ir is highly active for hydrogenolysis (18–20), it is not applied as a hydrocarbon-reforming catalyst. However, it has been used with Pt in bimetallic-reforming catalysts, in which it seems to minimize deactivation of the catalyst resulting from coke formation (18, 21, 22).

The goal of the research summarized here was to prepare and characterize a family of KLTL zeolite-supported Ir catalysts with various K : Al ratios and to determine how the Ir cluster size and the support properties influence the catalytic properties for *n*-hexane conversion. Ir was chosen because well-defined Ir clusters, including Ir_4 and Ir_6 , have been prepared on metal oxide and zeolite supports, and one of the goals was to prepare and investigate such small clusters on supports similar to those used for Pt clusters, namely, zeolite LTL. The catalysts were characterized by extended X-ray absorption fine structure (EXAFS) spectroscopy and infrared spectroscopy and used for dehydrocyclization and hydrogenolysis of *n*-hexane.

EXPERIMENTAL

Sample Preparation

KLTL zeolites (Union Carbide) were prepared with various K : Al ratios. They were converted into the NH_4^+ form by aqueous ion exchange or simply washed with water to lower the K^+ content; alternatively, some samples were impregnated with KNO₃ to increase the K^+ content. The several procedures were as follows:

(A) KLTL zeolite (130 g) was ion exchanged with 1 liter of $1.5 M \text{ NH}_4\text{NO}_3$ at 60°C for 2 h. The zeolite was filtered, washed, and calcined at 540°C for 3 h.

(B) KLTL zeolite (50 g) was washed six times with 500 ml of hot water (pH 8.0); the resultant sample was calcined at 400° C for 3 h.

(C) KLTL zeolite (100 g) was washed three times with 500 ml of hot water (pH 9.0) and calcined at 400° C for 3 h.

(D) KLTL zeolite (15 g) was added to a solution of 0.78 g KNO₃ in 11 ml of water, dried, and calcined at 400° C for 3 h.

(E) KNO₃ (1.5 g) was dissolved in 11 ml of water and added to KLTL zeolite (15 g), which was then dried and calcined at 400° C for 3 h.

(F) KNO₃ (2.5 g) was dissolved in 11 ml of water and added to 15 g of zeolite, which was dried and calcined at 400° C for 3 h.

Each of these samples was dried, crushed into a fine powder, and brought in contact with $[Ir(NH_3)_5Cl]Cl_2$ (Johnson Matthey) in water by the incipient wetness method. For example, 2.0 g of $[Ir(NH_3)_5Cl]Cl_2$ dissolved in 40 ml of water at 70°C was added to 50.0 g of zeolite. After the addition of a few drops of HNO₃, the pH of the $[Ir(NH_3)_5Cl]Cl_2$ solution was adjusted to 7 by addition of NH₄OH. The solution was filtered and added dropwise to the zeolite. The resultant slurry was allowed to stand at room temperature for 3 h, and the sample was dried at 120°C overnight. The crystallites of zeolite were held together without a binder.

Elemental Analysis

The zeolites were analyzed for Ir by Schwartzkopf Microanalytical Laboratories, Woodside, NY, and for Al and K by the analytical division of Amoco Oil Co. by inductively coupled plasma analysis.

Extended X-Ray Absorption Fine Structure Spectroscopy

In preparation for EXAFS spectroscopy, the catalysts were treated for 1 h at 300°C in flowing H₂ (99.999 + %, formed by electrolysis of water in a Balston generator). Traps containing Cu₂O and 4A zeolite were used to remove traces of oxygen and water, respectively. The catalysts were pressed into self-supporting wafers and loaded into a cell in the absence of air. EXAFS measurements were done at Beamline X-11A at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY. The synchrotron energy was maintained at 2.5 GeV, and the ring current was at least 110 mA. Two scans were done for each sample at the Ir $L_{\rm III}$ edge (11215 eV), with the sample at near liquid nitrogen temperature, and the scans were aver-

aged. A Si(111) double-crystal monochromator was used, with a resolution of $\Delta E/E = 2 \times 10^{-4}$. Higher harmonics were rejected by detuning the monochromator by 20%.

EXAFS Data Analysis (11)

Phase shift and backscattering amplitude data were obtained from EXAFS spectra of suitable reference compounds. Pt foil was used as a reference for Ir-Ir absorber-backscatterer pairs. Na₂Pt(OH)₆ was used for Ir-O absorber-backscatterer pairs. The crystallographic data and details of the preparation of the reference files are summarized elsewhere (11). The transferability of phase shifts and backscattering amplitudes has been shown theoretically (23, 24) and experimentally (12, 25-27). Standard procedures (27) were used to extract the EXAFS (chi) function from the raw data. Normalization of the EXAFS data was performed by dividing the absorption intensity by the height of the background absorption at 50 eV beyond the absorption edge. The main EXAFS contributions were isolated by Fourier filtering of the final EXAFS function (extracted EXAFS data), with k^3 weighting (k is the wave vector) and phase and amplitude correction by using the Pt foil reference (Table 1). Data analysis was performed on the filtered data. Best-fit parameters were obtained by fitting with the Koningsberger difference file technique (28). Low-Zand high-Z contributions were fitted on both r space (r is the radial distance from absorbing atom to backscattering atom) and k space, with both k^1 and k^3 weighting so as not to overemphasize either the low-Z or high-Z backscatterers. Details of the fitting procedures are given elsewhere (27).

Chemisorption Measurements

 H_2 chemisorption was carried out with an RXM-100 catalyst testing and characterization apparatus (Advanced Scientific Design, Inc.). The Ir/KLTL zeolites were reduced at either 300 or 500°C for 1 h and then evacuated at pressures $<10^{-6}$ Torr for 2 h at the reduction temperature. The

TABLE 1

Parameters Used for Isolation of Main EXAFS Data in Fourier Filtering^a

K : Al atomic ratio in zeolite	$\Delta k ({ m \AA}^{-1})$	Δr (Å)	р
0.34	3.59–14.55	1.74–3.47	13
0.95	3.48–13.96	1.42–3.52	15
1.34	3.62-13.60	1.70-3.38	12
1.56	3.70-13.60	1.67-3.40	12

^{*a*} Notation: Δk , range used for forward Fourier transform; Δr , range used for isolation of main data; *p*, number of free parameters from Nyquist theorem, $p = (2\Delta k\Delta r)/\pi + 1$. Spectral isolation was carried out on k^3 -weighted Fourier transform, with phase and amplitude correction using Pt foil reference.

catalysts were cooled to room temperature under vacuum before the chemisorption experiments were carried out.

Infrared Spectroscopy of Chemisorbed CO

Catalysts reduced at either 300 or 500° C were loaded into a gas-tight infrared cell and treated with flowing CO for 30 min at room temperature and then evacuated at pressures $<10^{-3}$ Torr to remove any gas-phase or physisorbed CO. Infrared spectra were recorded in the transmission mode with a Nicolet 510 M FTIR or a Bruker IFS-66 v FTIR instrument.

Catalytic Reaction Experiments

Details of the apparatus used for catalytic reforming of n-hexane are given elsewhere (11). Catalysts were reduced at 500°C for 1 h and then cooled under flowing H₂ to the operating temperature of 400, 440, or 480°C prior to the start of reactant flow. n-Hexane, fed at rates of 1.33 to 2.7 ml/h, was vaporized before mixing with H₂ and He. The H₂, He, and n-hexane flow rates were chosen so that the n-hexane partial pressure was 76 Torr and the molar H₂:n-hexane ratio 6. The mass of catalyst varied from 15 to 600 mg. Products were analyzed by on-line gas chromatography.

RESULTS

Catalyst Compositions

The catalyst compositions are summarized in Table 2. In what follows, the KLTL zeolites are referred to by the K : Al atomic ratio.

EXAFS Data

The data show oscillations in the raw EXAFS up to $k = 14 \text{ Å}^{-1}$ or greater. Typical data are shown in Fig. 1. The largest contribution in each EXAFS spectrum, attributed



FIG. 1. Raw EXAFS data characterizing the sample with K : Al = 0.34 after treatment in H₂ at 300°C.

to Ir–Ir interactions, was first estimated for k > 8 Å⁻¹, because this part of the spectrum is dominated by Ir–Ir contributions. The EXAFS function representing the best-fit parameters was then subtracted from the filtered data over the entire k range. The residual spectrum was fitted with two Ir–O contributions. The EXAFS function representing these two contributions was subtracted from the full data to give a better estimate of the Ir–Ir contribution. The fitting of the Ir–Ir contribution and the Ir–O contributions was then continued iteratively. Figures 2 and 3 show the difference files representing the sample with K : Al = 0.34; these data are typical. The best-fit parameters from all three contributions were added and compared with the filtered data, both in r space and in k space, until the fit was satisfactory.

The fits obtained for each sample are very good. The EXAFS parameters are summarized in Table 3. The Ir–Ir first-shell coordination number increased from 3.7 to 7.9 as the K: Al ratio increased from 0.34 to 1.34. However,

TABLE 2

Elemental Analysis Results for Ir in KLTL Zeolites with Different K : Al Ratios and Results of H₂ Chemisorption Experiments

K : Al atomic ratio in zeolite	Ir (wt%)	H/Ir ratio after treatment at 300°C	H/Ir ratio after treatment at 500°C	N _{Ir-Ir} ^a	Estimated particle size (Å) ^b	Reference
0.34	1.16	0.30	0.63	3.7	7	
0.95	1.87	0.25	0.70	6.3	11	
0.99	0.95	1.24	1.44			
1.08	1.03			3.2	6	(11)
1.08	1.03			4.2^{c}	8	(11)
1.14	1.66	1.69	1.99			
1.34	1.29	0.80	1.04	7.9	18	
1.56	1.56	0.49	0.73	7.8	18	

 a N_{Ir-Ir}: Ir-Ir first shell coordination number from EXAFS analysis, after treatment in H₂ at 300°C, except where noted.

^b Particle size estimated for spherical particle [Ref. (13)].

^c After treatment in H₂ at 500°C.

TABLE 3

K : Al atomic ratio in zeolite	Shell	Ν	<i>R</i> (Å)	$\Delta\sigma^2$ (Å ²)	$\Delta E_0 ({ m eV})$	Reference
0.34	Ir–Ir	3.7	2.71	0.00119	-2.72	This work
	Ir–O	0.9	2.04	0.00560	2.82	This work
	Ir–O	0.9	2.54	-0.00518	9.81	This work
0.95	Ir–Ir	6.3	2.70	0.00209	-1.20	This work
	Ir–O	1.6	2.02	0.00990	6.34	This work
	Ir–O	0.6	2.53	-0.00428	7.15	This work
1.08^{b}	Ir–Ir	3.2	2.70	0.0017	-0.45	(11)
	Ir–O	1.2	2.18	0.0034	-4.68	(11)
	Ir–O	2.5	2.60	0.0088	-0.47	(11)
1.08^{c}	Ir–Ir	4.2	2.70	0.0022	0.68	(11)
	Ir–O	0.7	2.09	0.0085	7.05	(11)
	Ir–O	1.2	2.67	0.0085	-6.50	(11)
1.34	Ir–Ir	7.9	2.71	0.00169	-0.81	This work
	Ir–O	0.9	2.01	0.00990	2.03	This work
	Ir–O	0.5	2.50	-0.00424	0.03	This work
1.56	Ir–Ir	7.8	2.71	0.00161	-1.69	This work
	Ir–O	1.2	2.03	0.00990	1.69	This work
	Ir–O	0.3	2.48	-0.00597	2.12	This work

Best-Fit EXAFS Parameters for Samples after Treatment in H₂ at 300°C for 1 h^a

^{*a*} Notation: *N*, coordination number for absorber–backscatterer pair; *R*, radial distance from absorber to backscatterer; $\Delta\sigma^2$, Debye-Waller factor; ΔE_0 , inner potential correction. Estimated errors: *N* (Ir–Ir), ±15%; *N* (Ir–O), ±20%; *R*, ±1%, $\Delta\sigma^2$, ±10%, ΔE_0 , ±10%.

^b Sample reduced at 300°C.

^c Sample reduced at 500°C.

there was no significant change in the Ir–Ir coordination number as the K : Al ratio increased further to 1.56. The Ir–Ir distance in each sample was the same within experimental error, 2.70-2.71 Å.

Two Ir–O contributions were needed to fit the data satisfactorily (Table 3). Similar metal–oxygen contributions have been reported for highly dispersed Ir and other metals on metal oxide supports (9, 10, 13–15, 28–34). The shorter Ir–O distances, 2.02 ± 0.02 Å, which are bonding distances (35), are slightly less than those observed for other supported Ir samples (12, 33, 34, 36). The longer Ir–O distances, 2.48–2.54 Å, are about the same as Pt–O (36) and Ir–O (37) distances reported for supported metals, but a value of about 2.7 Å is more typical of metal oxide-supported Pt and Ir (12, 28, 30, 33–35), perhaps being associated with hydrogen at the metal–support interface, such as in Pt–H–



FIG. 2. EXAFS data characterizing the sample with K : AI = 0.34: k^{1} -weighted Fourier transform of the filtered EXAFS data minus the calculated Ir–Ir contribution (solid line) and the best-fit Ir–O contributions (dashed line), phase corrected using Na₂Pt(OH)₆ reference file.



FIG. 3. EXAFS data characterizing the sample with K : AI = 0.34; k^3 -weighted Fourier transform of the filtered EXAFS data minus the sum of the calculated Ir–O contributions (solid line) and best-fit Ir–Ir contribution (dashed line), phase and amplitude corrected using Pt foil reference file.

O moieties (38). The longer Ir–O distance decreased by about 0.05 Å with increasing K: Al ratio, but no trend was observed for the short Ir–O distance.

No Ir-K contribution was detected in any of the samples.

Chemisorption on Unused Catalysts

Results of H_2 chemisorption experiments are given in Table 2 for samples treated in H_2 at 300 and at 500°C.

Infrared Spectra of Chemisorbed CO

The infrared spectra of CO chemisorbed on Ir/KLTL zeolites reduced at 300°C are shown in Fig. 4. Similar results (not shown) were obtained for the sample reduced at 500°C. The intensity of the v_{CO} bands decreased as the K : Al ratio increased; the amount of CO adsorbed was not quantified. As the K : Al ratio in the zeolite changed from 0.34 to 1.56, the bands in the range of about 1950–2150 cm⁻¹ (indicating terminal CO ligands bonded to Ir) decreased drastically in intensity and shifted markedly (about 100 cm⁻¹), and the band at about 1650 cm⁻¹ increased markedly in intensity.

Catalyst Performance

At 400 and at 480°C, *n*-hexane was not converted in the absence of a catalyst. *n*-Hexane reacted with H₂ in the presence of each of the catalysts to form the following products: benzene, methylcyclopentane, 3-methylpentane, 2-methylpentane, 1-hexene, 2-hexene, 3-hexene, cyclohexane, cyclohexene, and C₁–C₅ hydrocarbons. All the catalysts were found to be unselective, having low selectivities for benzene and high selectivities for the hydrogenolysis products (C₁–C₅ hydrocarbons).



FIG. 4. Infrared spectra of CO chemisorbed on Ir/KLTL catalysts after treatment in H_2 at 300°C: (a) K:Al = 0.34; (b) K:Al = 0.95; (c) K:Al = 1.34; (d) K:Al = 1.56.

Most runs were carried out with *n*-hexane conversions <10%. When conversions were higher (22–48%), the product distributions observed for each catalyst were similar to those observed at 10% conversion; however, small amounts of toluene were observed as well. Selectivity for benzene formation is defined as the fraction of nhexane converted that formed benzene. Since the products, which include methylcyclopentane, 2-methylpentane, 3-methylpentane, C₆ olefins, cyclohexane, and cyclohexane, can also react to form benzene, a second definition of benzene selectivity, referred to as the ultimate benzene selectivity, is also used to account for the loss of C₆ hydrocarbons by hydrogenolysis. The ultimate benzene selectivity is the mass ratio of *n*-hexane converted to benzene divided by the sum of *n*-hexane converted to benzene and that converted to light (C_1-C_5) hydrocarbons (38). The selectivity of the methylcyclopentane ring opening reaction is defined as the ratio of 2-methylpentane to 3-methylpentane.

Plots of conversion vs inverse space velocity (not shown) were nearly linear at the low conversions (<10%), showing that the reactions were differential and determined reaction rates. The rates are reported per total Ir atom in the catalyst; these approximate turnover frequencies, as discussed below. The catalysts are compared on the basis of their performance after 10 h on stream.

Table 4 is a summary of the selectivities of the various catalysts at 480°C and at low conversions (with all the conversions being approximately the same). The ratio of 2-methylpentane to 3-methylpentane observed with the KLTL zeolite having the lowest K : Al ratio was 0.1, whereas no 2-methylpentane was detected in the products when the other catalysts were used. Table 5 is a summary of the benzene selectivities of the catalysts at 440°C and low conversions. The trends evident in Table 4 hold for these data as well. The exceptions are that at 440°C 2-methylpentane was

TABLE 4

K : Al atomic ratio in zeolite	<i>n</i> -Hexane conversion (%)	Benzene selectivity ^b	Ultimate benzene selectivity ^c	2MP/3MP ^d
0.95	8.43	0.13	0.21	0.1
0.99	7.94	0.16	0.42	~ 0
1.14	8.66	0.15	0.25	~ 0
1.34	10.1	0.12	0.15	~ 0
1.56	8.35	0.14	0.21	~ 0

^{*a*} The *n*-hexane flow rate was 1.33 ml/h for each run.

^b Benzene selectivity is defined as the fraction of *n*-hexane converted that formed benzene.

 c Ultimate benzene selectivity is defined as the mass ratio of *n*-hexane converted to benzene divided by the sum of *n*-hexane converted to benzene and that converted to light (C₁₋₅) hydrocarbons.

^d Ratio of 2-methylpentane to 3-methylpentane in product stream.

K : Al atomic ratio in zeolite	<i>n</i> -Hexane conversion (%)	Benzene selectivity	Ultimate benzene selectivity	2MP/3MP
0.34	4.42	0.04	0.05	0.42
0.95	8.09	0.12	0.22	0.38
0.99	6.24	0.13	0.28	0.26
1.14	8.54	0.12	0.18	0.22
1.34	6.52	0.11	0.17	0.10
1.56	5.17	0.12	0.27	0.12

^{*a*} Notation and *n*-hexane flow rate as in Table 4.

detected, and the 2-methylpentane to 3-methylpentane ratio decreased as the K : Al ratio of the catalysts increased. Table 6 summarizes the benzene selectivities of the catalysts at 480°C and relatively high conversions (ranging from 23 to 48%). The data show that the benzene selectivity and ultimate benzene selectivity are not strongly sensitive to the K : Al ratio. However, in contrast to the performance of well-prepared Pt/KLTL or Pt/BaKLTL catalysts (1–3, 39), selectivity to benzene remained essentially unchanged or decreased as conversion increased. The zeolite with a K : Al ratio of 1.14 is characterized by a benzene selectivity of 0.18 and an ultimate benzene selectivity of 0.20; these values are slightly higher than the respective values characterizing the other Ir-containing catalysts.

At the intermediate conversions, small amounts of toluene were observed for Ir/KLTL zeolites with K : Al ratios of 0.34, 0.95, and 0.99. The toluene formation is attributed to acidic sites in the zeolite. However, when enough K was present to neutralize the acidic sites, the selectivity to any of the product groups was found to be insensitive to the K : Al ratio.

Approximate benzene formation rates for *n*-hexane conversion at 480° C are summarized in Table 7. The activity of the zeolite, approximated from low conversion data at 480° C, increased and then decreased as the K:Al ra-

TABLE 6

Catalyst Selectivities at 480°C and Conversions of 22.6–48.0%^a

K : Al atomic ratio in zeolite	<i>n</i> -Hexane conversion (%)	Benzene selectivity	Ultimate benzene selectivity	2MP/3MP
0.34	26.3	0.02	0.02	0.61
0.95	34.5	0.12	0.13	0.19
0.99	48.0	0.14	0.15	0.15
1.14	29.8	0.18	0.20	~ 0
1.34	22.6	0.14	0.16	0.16

^{*a*} Notation and *n*-hexane flow rate as in Table 4.

TABLE 7

K : Al atomic ratio in zeolite	$10^2 \times \text{rate at}$ 480°C , mol hexane converted/(mol Ir · s)	Apparent activation energy (kcal/mol)
0.95	10 ± 2	28
0.99	28 ± 6	23
1.14	22 ± 2	39
1.34	4 ± 1	38

tio increased. The apparent activation energies estimated from the temperature dependence of the reaction rates decreased and then increased as the K : Al ratio increased.

DISCUSSION

Ir Dispersions Estimated from EXAFS Results

The Ir–Ir first-shell coordination numbers determined by EXAFS spectroscopy provide evidence of the average sizes of the clusters or particles in the zeolite-supported catalysts. The data reported here, and elsewhere (11) for similar samples (Table 3), indicate how three variables affect the average cluster or particle size: (1) the temperature of reduction (11), (2) the Ir loading, and (3) the K : Al ratio. Changing the temperature of reduction in H₂ from 300 to 500°C had a small effect on the cluster size (11) (Table 2). Increasing the Ir loading from 1.03 to 1.87 wt% with only a small change in the K : Al ratio generally led to an increase of the Ir–Ir coordination number from 3.2 to 6.3 (Table 2). Increasing the K : Al ratio generally led to an increase in the EXAFS Ir–Ir first-shell coordination number; this was the most significant effect (Table 3).

The Ir–Ir coordination numbers estimated from the EXAFS spectra represent a range in cluster diameter from about 6 to about 20 Å on average, assuming spherical clusters (13). The smallest clusters easily fit in the cages of the LTL zeolite. The average cluster diameter observed for the sample with K : AI = 0.95 (about 11 Å) is just small enough to allow the clusters to fit in the cages. The samples with Ir–Ir coordination numbers of about 8 contain particles that are too large to fit in the cages.

Although the comparison of the Ir–Ir coordination numbers for the two catalysts with approximately equal K : Al ratios (0.95 and 1.08) but different Ir contents (1.87 and 1.03 wt%, respectively) indicates that higher Ir loadings give larger clusters (Table 2), a comparison of the two catalysts with the highest K : Al ratios suggests that a change in the Ir loading does not affect the average particle size. However, some unknown fraction of the Ir in these samples was present in particles too large to fit in the cages, and there is too little information to allow a comparison of the sizes of the clusters residing inside the cages.

The smallest Ir clusters in these samples, characterized by Ir–Ir coordination numbers of 3.2 and 3.7, are about the same size as the Pt clusters in LTL zeolite observed by Vaarkamp *et al.* (9, 10); these are characterized by Pt–Pt coordination numbers of 3.7 [in BaKLTL zeolite (9)], 4.1 [in HLTL zeolite reduced in H₂ at 300°C (10)], and 4.0 [in KLTL zeolite reduced in H₂ at 300°C (10)]. The Vaarkamp catalysts contained about 1 wt% Pt. The close agreement in average cluster sizes among the family of LTL zeolitesupported Pt and Ir clusters suggests that, with some generality, the preparation method gives extremely small noble metal clusters from salt precursors in LTL zeolite when the metal loading is low, provided that there is not a substantial excess of cation such as K⁺ over the ion-exchange capacity.

The Ir–O contributions to the EXAFS (Table 3) give evidence of metal–support interactions, and the shorter Ir–O distances of 2.1 ± 0.1 Å suggest a bonding interaction. The EXAFS data give no evidence of Ir–K interactions. The results thus suggest that any electron transfer to the Ir from the support (or vice versa) would occur through the oxygen ions of the support. The Ir–O coordination numbers indicated by the EXAFS data do not indicate any clear trends, and we suggest that the experimental uncertainties in these values are too large to allow any conclusions about how the metal–support interface structure depends on the preparation conditions for these samples.

Comparison of EXAFS and Chemisorption Results

The estimates of average Ir cluster or particle size determined from EXAFS data agree well with the estimates based on the chemisorption data assuming a H:Ir stoichiometry of 1 for the largest cluster or particle size determined by EXAFS spectroscopy, i.e., for the samples with K : A1 = 1.34 and 1.56 (Table 2). Consistent with these results, McVicker *et al.* (40) observed a 1:1 H: Ir ratio for 10–30 Å Ir clusters on γ -Al₂O₃ characterized by transmission electron microscopy.

However, H: Ir stoichiometries >1 have been reported for Ir supported on metal oxides when the dispersion was approximately 1, as determined by electron microscopy or EXAFS spectroscopy (11, 13, 40). Consistent with these observations, we observed H: Ir ratios >1 for samples with K: Al = 0.99 and 1.14 (Table 2); however, no EXAFS data are available for these samples.

In contrast, the hydrogen chemisorption results characterizing the smallest supported clusters, those consisting of only about four or five atoms each, on average, indicate that the chemisorption on them is markedly less than that on metallic Ir (Table 2). The H: Ir values are as low as 0.3 after treatment of the samples at 300°C. Similar low values of H: Ir ratios have been observed for extremely small Ir clusters, modeled as Ir_4 and formed by decarbonylation of $[HIr_4(CO)_{11}]^-$ supported on MgO (41). Consistent with this pattern, values of H:Pt of less than 0.04 have been observed for extremely small zeolite-supported Pt clusters (42).

The H: Ir ratio observed for each sample increased after treatment at 500° C (Table 2). The increase observed for the smaller clusters may be the result of a slight increase in cluster size, resulting from aggregation. The reason for the increase in the H: Ir ratio for the other samples is unexplained, but the increases were small.

Infrared Spectra of Adsorbed CO

The infrared spectra of CO chemisorbed on the family of Ir/LTL zeolite catalysts (Fig. 4) are qualitatively similar to infrared spectra of CO adsorbed on a similar family of Pd/LTL zeolite catalysts (43). Terminal and bridging CO ligands are evident from the spectra of both families. The striking result is how much the spectra change with changes in the K: Al ratio. Like Mojet et al. (43), we interpret the changes in the spectra with K: Al ratio as evidence of increasing electron density on the Ir clusters with increasing K: Al ratio. The v_{CO} frequency is indicative of the backbonding between the metal centers and the π^* orbitals of CO. A decrease in the v_{CO} frequency indicates an increase in backbonding associated with an increase in electron density on the metal. Furthermore, the bridging ligands are favored when the metal is capable of donating more electrons into the $2\pi^*$ orbital of CO (44), consistent with the pattern of increasing electron donation to the Ir clusters with increasing K: Al ratio. We discount the possible importance of dipole-dipole interactions because the effects are so large and because the Ir surfaces were virtually saturated with CO in all the infrared experiments.

Electron donation from potassium could lead to increased electron density on the Ir. Because no direct Ir–K interaction was indicated by the EXAFS data, we suggest that this donation takes place through the oxygen of the support. Similar electron donation from alkali cations to metal in LTL zeolite-supported Pt has been reported by Han *et al.* (45) and Larsen and Haller (46).

The infrared results characterizing samples with equal K: Al ratios reduced at different temperatures are similar, indicating that the reduction temperature did not influence the electronic environments of the Ir significantly. Thus we infer that any changes in electronic properties of the metal associated with changes in cluster or particle size are small in comparison with the effects in the K : Al ratio.

Catalyst Performance

Approximate reaction rates at 480° C are shown in Table 7 for *n*-hexane conversion to benzene. The rates approximate the turnover frequencies for the catalyst having K : Al = 0.95, which has an EXAFS first-shell Ir–Ir coordination number of 6.3. The Ir dispersions of the catalysts

with K: Al = 1.14 and 1.34 are inferred from the EXAFS and H_2 chemisorption data to be slightly less than unity; hence the turnover frequencies are inferred to be greater than the rates shown in Table 7. Furthermore, the Ir particles in these latter catalysts are large enough to suggest the possibility of pore blocking by the Ir as a cause of the reduction in rate with increasing K: Al ratio in this range (Table 7).

The selectivity data for benzene, summarized in Tables 4-6 and consistent with reported data (11), are much different from those characterizing LTL zeolite-supported Pt catalysts. The latter have high selectivities for dehydrocyclization of n-hexane, whereas the LTL zeolite-supported Ir catalysts, even those with structures similar to those of the supported Pt catalysts, are unselective for dehydrocyclization. In addition, there is little or no increase in benzene selectivity with increasing conversion, in contrast to the observations for Pt in LTL zeolite, for which the dependence is strong (2, 3, 8, 39). This difference between the two classes of catalyst is explained by the high hydrogenolysis activity of Ir. A significant difference between Pt clusters in LTL zeolite and Ir clusters in LTL zeolite may be that the former catalyze the back reaction of 2-methylpentane and of 3-methylpentane to give benzene, whereas the latter, having a high hydrogenolysis activity, rapidly catalyze the conversion of these compounds to light products instead of the back reactions leading to benzene. The Ir-containing zeolite with K: Al = 0.34 has acidic sites, and these are expected to catalyze additional hydrocracking of hydrocarbons, leading to the relatively low value of benzene selectivity for this catalyst.

Thus the major reaction catalyzed by all the Ir/KLTL catalysts is hydrogenolysis, consistent with the known activity of Ir (47). One possible reason why Pt-Ir catalysts have been used for reforming is that Ir helps to maintain the activity of Pt-Ir catalysts by catalyzing hydrogenolysis of coke precursors (18, 21, 22). One of the questions addressed in the present research was whether it would be possible to curb the hydrogenolysis activity of Ir without minimizing its dehydrocyclization activity by using extremely small clusters and by varying the K: Al ratio of the support. This possibility might seem reasonable because of the evidence (mentioned in the Introduction) that very small clusters of Pt in zeolite LTL are selective for benzene formation. However, the data show that extremely small Ir clusters in the zeolite are not selective for benzene formation, even though the infrared spectra of CO indicate substantial electron transfer to the Ir in some of the catalysts.

Thus the major conclusions are the following: Although changes in the K : Al ratio of the zeolite affect the Ir cluster size and electronic environment significantly, the essential catalytic nature of the Ir remains unchanged, even when it is present in virtually the smallest clusters that can be made and is subject to significant electron donation. Ir in all the forms observed here is an active hydrogenolysis catalyst. Although the activity of the catalyst can be modified by addition or removal of potassium, Ir with a range of electronic environments and a range of average cluster and particle sizes from about 6 to 20 Å is generally not a good dehydrocyclization catalyst. The contrast with Pt/LTL catalysts that are very similar in structure, and which are highly selective for dehydrocyclization, shows that the selectivity depends critically on the metal. Thus, although the effects of the support here perhaps been nearly maximized by the smallness of the clusters and the strength of the electron donation, they are still not great enough to alter the fundamental catalytic character of Ir, which does not become sufficiently electron rich to act catalytically like Pt.

Nonetheless, the data give evidence of support effects. By comparison with other Ir catalysts, the Ir/KLTL zeolite catalysts show unusual selectivity for formation of 3-methylpentane, with almost no 2-methylpentane being produced. Foger and Anderson (48) reported the hydrogenolysis of methylcyclopentane at intermediate temperatures (200-300°C), observing a 2-methylpentane:3methylpentane ratio close to 2. At 480°C and low conversions, almost no 2-methylpentane was observed with the catalysts reported here. At intermediate conversions, a greater 2-methylpentane: 3-methylpentane ratio was observed for all the catalysts except the one with K:Al =1.14. The catalyst with K: Al = 0.34 was characterized by the highest 2-methylpentane : 3-methylpentane ratio, 0.61. The high selectivity to 3-methylpentane could possibly result from an orientation of the methylcyclopentane intermediates by the pores (49).

The Ir clusters in the zeolite with K: Al = 0.34 are characterized by a very low benzene selectivity and ultimate benzene selectivity, because this zeolite incorporated acidic sites that were involved in catalytic hydrocracking of hydrocrabons, i.e., in bifunctional catalysis.

CONCLUSIONS

The EXAFS data show that the Ir clusters and particles formed on the KLTL zeolite support increased in average diameter from about 6 Å to about 20 Å as the K : Al ratio increased from 0.34 to 1.56. Infrared spectra of adsorbed CO indicate that potassium donates electron density to Ir clusters, but the EXAFS data give no indication of Ir–K contributions. These results suggest that electron donation was through the oxygen ions from the support. The selectivities of the Ir/KLTL zeolites for *n*-hexane conversion were found to be insensitive to the K : Al ratio, except for the catalyst with the lowest K : Al ratio, whereas the reaction rate for benzene formation was highest at a K : Al ratio of about 1.0 and decreased with increasing K : Al ratios exceeding this value. All the supported Ir catalysts were selective for hydrogenolysis; the smallest Ir clusters still behave catalytically like metallic Ir. Thus, although the effects of the support are significant, leading to various sizes of Ir clusters in the preparations and to various degrees of electron donation to the clusters, the support effects are not great enough to alter the fundamental catalytic character of Ir, which does not become sufficiently electron rich to act catalytically like Pt.

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