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Cluster Formation

Real-Time Characterization of Formation and Breakup of Iridium Clusters in Highly Dealuminated Zeolite Y**

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The initial steps of formation of metal clusters and the chemistry of cluster deconstruction are not well understood, because the structures are typically complex, complicated by the presence of solvents in the metal ligand spheres.[1] When such chemistry occurs on a solid support in the absence of solvents,[2–4] however, spectroscopic methods allow elucidation of details of the chemistry—provided that the structures are nearly uniform.

We now show how clusters well approximated as Ir_4 form from well-defined iridium complexes anchored to dealuminated zeolite Y. The precursor $[Ir(C_2H_4)_2(acac)]$[5] (acac = $CH_3COCHCOCH_3$) reacted with the zeolite to form $[Ir(C_2H_4)_2]$ complexes incorporating π-bonded ethylene ligands that are bonded to the zeolite through two Ir–O bonds (Figure 1).[6]

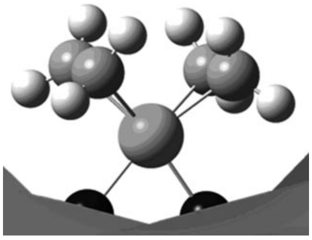

Figure 1. Bonding of $[Ir(C_2H_4)_2]$ to zeolite through Ir–O bonds.

IR spectra showed that the reaction of $[Ir(C_2H_4)_2(acac)]$ with the zeolite led to partial removal of zeolite OH groups, dissociation of acac ligands from the precursor, and retention of π-bonded C_2H_4 ligands on the Ir center. Extended X-ray absorption fine structure (EXAFS) data indicate site-isolated mononuclear iridium complexes on the zeolite, confirmed by the lack of detectable contributions for Ir–Ir, whereby each Ir atom is bonded (on average) to four C atoms (two ethylene ligands) (at a distance of 2.10 Å) and two zeolite O atoms (2.15 Å).[6]

When this iridium complex was treated in flowing H_2 at 298 K, the ligand environment changed; IR spectra (see the Supporting Information) taken after 2 h show that some ethylene ligands (peaks at 3082 and 3021 cm^{-1})[6] reacted with H_2 to form ethyl groups (2961, 2933, 2875, 2855 cm^{-1}).[7,8] The ethyl bands decreased in intensity during the treatment, and ethane was observed in the effluent by mass spectrometry. Concomitantly, new bands grew; after 2 h, a weak new band at 2949 cm^{-1} indicated methyl groups,[8] and a very weak band at 2984 cm^{-1} indicated di-σ-bonded ethylene,[9,10] which requires neighboring metal sites, indicating the onset of iridium cluster formation. EXAFS data recorded during this treatment (see the Supporting Information) gave no evidence of Ir–Ir—the clusters were too few to be detected with this method.

The EXAFS data also indicate 1) that each zeolite-supported iridium complex remained bonded, on average, to two zeolite O atoms during the treatment; 2) that the π-bonded ethylene ligands were partially converted; and 3) that new hydrocarbon ligands formed, indicated by a new Ir–C contribution with a coordination number (C.N.) of 2.8 at a distance of 3.12 Å, which is consistent with the ethyl ligands indicated by IR spectroscopy.

When the temperature was raised to 353 K at 1 K min^{-1} as the sample was treated in flowing H_2 at 1 bar, X-ray absorption near edge (XANES) spectra at the Ir L_{III} edge (Figure 2a) show that the intensity of the white line increased during the first 20 min and then decreased. The isosbestic points indicate the transformation of one species to another (Figure 2a). A comparison of the XANES spectrum of the resultant species with those of Ir powder and the initial supported mononuclear complex (Figure 2a) indicates that the resultant species were different from both.

EXAFS data (Figure 3a) measured simultaneously with XANES during the temperature ramp demonstrate the appearance of an Ir–Ir contribution and decreases in the coordination numbers of the metal low-Z scatterer contributions (Ir–O and Ir–C) (Figure 3a). Thus, the data demonstrate cluster formation and show how it took place: The first evident change was the breaking of Ir–C bonds, indicated by reduction of the Ir–C C.N.; after approximately 15 min of rapid decline in this value, an Ir–Ir contribution became detectable, at a (bonding) distance of 2.67 Å.[11] As the Ir–C C.N. decreased further, the Ir–Ir C.N. continued to increase, approaching a value of 3. Shortly before the Ir–C C.N. reached the minimum value of 1 (within error), the Ir–O C.N.

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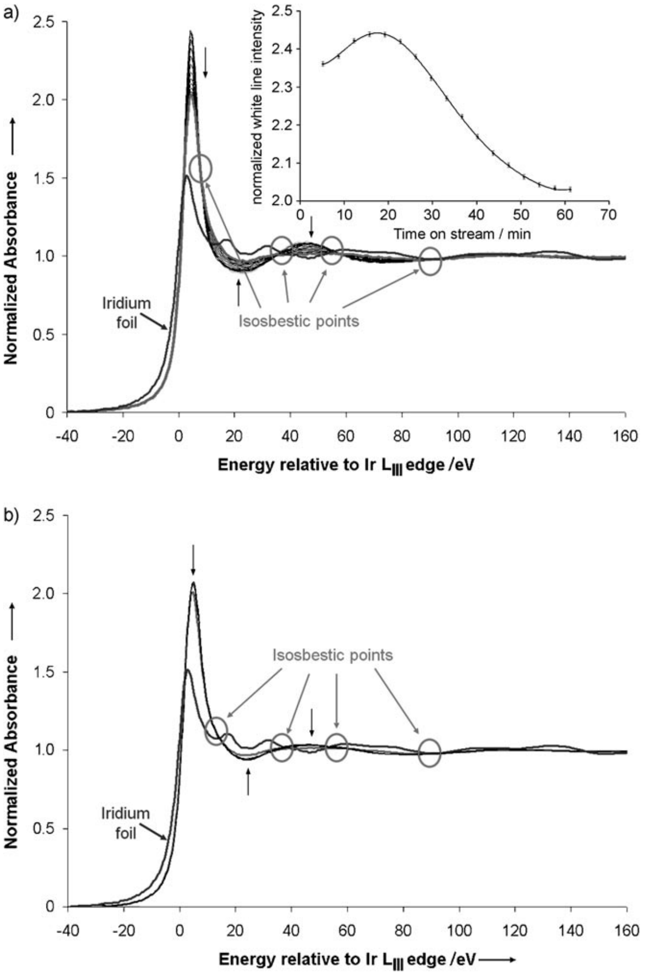

Figure 2. Normalized XANES spectra at the Ir L_{III} edge of the sample formed from $[Ir(C_2H_4)_2(acac)]$ and dealuminated zeolite Y: a) during the cluster formation as the temperature was ramped from 298 to 353 K (at 1 K min^{-1}) in H_2 flow at 1 bar (the inset shows the change in white line intensity with respect to time on stream); b) during C_2H_4 flow at 1 bar and 353 K during cluster breakup following the temperature ramp in H_2 flow.

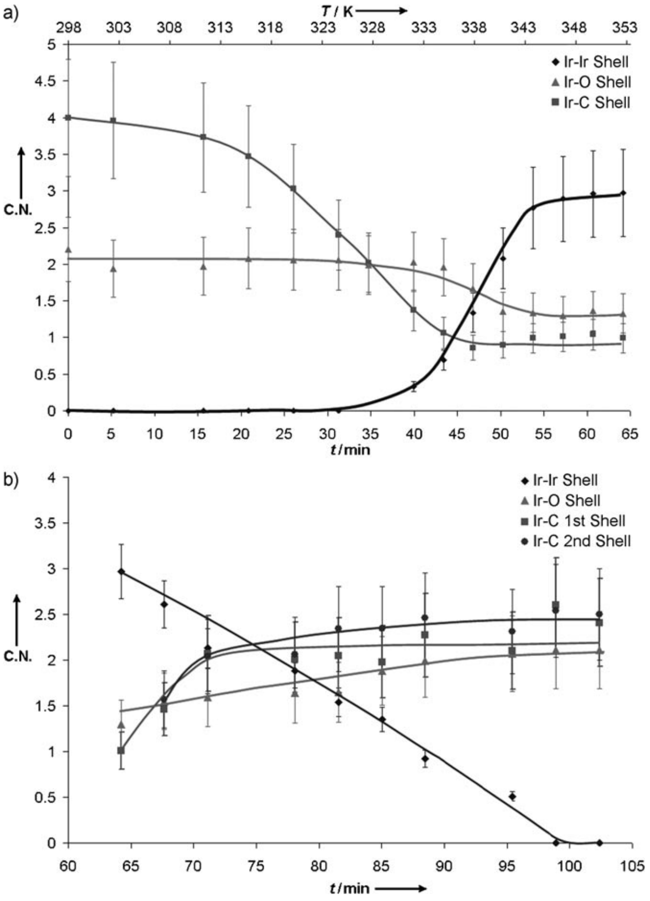

Figure 3. EXAFS analysis characterizing the change in the coordination numbers of the sample formed from $[Ir(C_2H_4)_2(acac)]$ and dealuminated zeolite Y: a) as the temperature increased from 298 to 353 K (at 1 K min^{-1}; H_2 partial pressure, 1 bar); b) during C_2H_4 flow at 1 bar and 353 K following the temperature ramp in H_2 flow.

began to decrease (from approximately 2.0 to approximately 1.4; Figure 3 a).

Thus, the data show that the breaking of Ir–C bonds generated coordinative unsaturation that led to Ir–Ir bond making, which required breaking of Ir–O bonds and migration of iridium atoms on the zeolite surface (and between cages).

The final Ir–Ir C.N. of approximately 3, on average, corresponds to tetrahedral Ir_4 clusters; the tetrahedral frame is stable in numerous compounds (e.g. $[Ir_4(CO)_{12}]$[12]). We emphasize that EXAFS spectroscopy provides only average information; thus, the results do not provide a foundation for identifying the intermediate structures in the cluster formation or determination of kinetics to help elucidate the chemistry of the cluster formation.

Difference IR spectra (Figure 4 and the Supporting Information) confirm the EXAFS data; the ethyl bands at 2964, 2936, 2876, and 2854 cm^{-1} appeared just as the Ir–C C.N. began to decrease noticeably. Simultaneously, a band

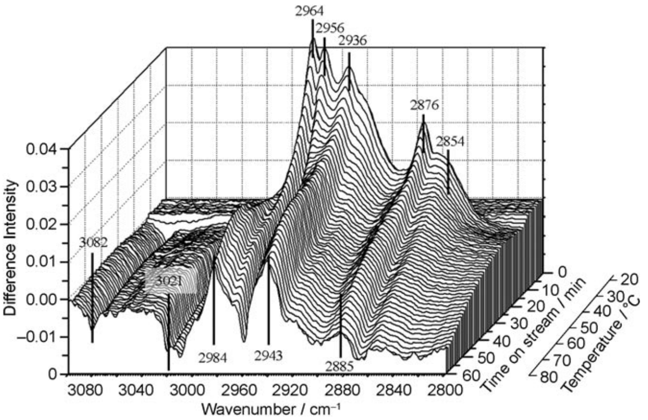

Figure 4. Difference IR spectra calculated by subtraction of the spectrum characterizing the fresh sample formed from $[Ir(C_2H_4)_2(acac)]$ and dealuminated zeolite Y from those of the sample recorded at 1 min intervals during H_2 flow as the temperature increased from 298 to 353 K at 1 K min^{-1}. The negative bands at 3021 and 3082 cm^{-1} indicate removal of π-bonded ethylene bands.

appeared at 2956 cm^{-1} indicating gas-phase ethane and demonstrating complete hydrogenation of some of the ligands.[13,14]

As the Ir–Ir bonds formed and the Ir–C C.N. reached the minimum value of 1.0, the ethyl bands in the IR spectra disappeared, and new bands arose at 2984, 2943, and 2885 cm^{-1} (Figure 4 and the Supporting Information). The latter two bands are assigned to ethylidyne[9,15] and that at 2984 cm^{-1} to di-σ-bonded ethylene, confirming cluster formation.

For clarity, a schematic summary of the cluster formation mechanism based on the EXAFS, XANES, and IR results is shown in Figure 5. We caution that it includes simplified structures and intermediates for which there is no direct evidence; nonetheless, there is indirect evidence of dimeric species, as iridium carbonyl dimers were observed in the formation of small iridium carbonyl clusters in the cages of zeolite NaY.[16]

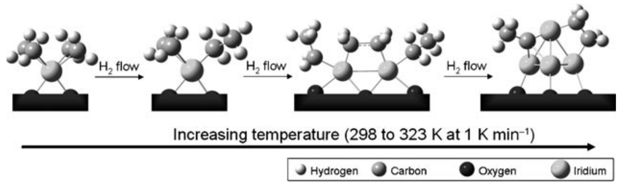

Figure 5. Schematic model of cluster formation in H_2 as the temperature increased from 298 to 353 K at 1 K min^{-1}. These structures were constructed on the basis of EXAFS, XANES, and IR results and are simplified; there is no direct evidence of the dinuclear intermediate species.

When the gas stream was switched from H_2 to C_2H_4 at 353 K, the cluster formation was reversed. The white line intensity increased during the treatment, and isosbestic points indicate the conversion from essentially one species to another (Figure 2b).

EXAFS results (Figure 3b) recorded during the C_2H_4 treatment demonstrate the cluster breakup, indicated by the decreasing Ir–Ir C.N.; this was accompanied by the formation of metal low-Z scatterer contributions, indicating bonding of ligands to Ir.

The Ir–Ir C.N. decreased to an undetectably small value after 35 min, indicating the removal of the clusters. Simultaneously, the Ir–O and Ir–C contributions characterizing the metal–support and metal–ligand interactions, respectively, underwent the following changes: The Ir–O C.N. increased to a value of 2.0 (Figure 3b and the Supporting Information), showing that the resultant mononuclear iridium complex was bonded, on average, to two zeolite O atoms, as in the initial supported complex.[6]

Similarly, the Ir–C C.N. (at 1.97 Å) increased from 1.0 to approximately 2 within 10 min, and a second Ir–C contribution (at 2.78 Å) became detectable within 4 min; the C.N. increased to 2.5 within 6 min. These two Ir–C contributions then remained approximately constant until the Ir–Ir C.N. decreased to essentially zero.

The hydrocarbon ligands are identified by the IR spectra (see the Supporting Information). Bands at 2964, 2936, 2877, and 2856 cm^{-1} indicate ethyl groups. A weak shoulder at 2984 cm^{-1} indicates a small amount of di-σ-bonded ethylene (thus, cluster fragmentation was not quite complete, although no clusters could be detected by EXAFS spectroscopy and no ethylidyne bands were evident in the IR spectra).

Mass spectra of the effluent indicated ethane after 13 min of treatment in ethylene, and traces of butene after 25 min (see the Supporting Information). We suggest that iridium hydride species that formed in the H_2 treatment reacted with ethylene to form ethane, and, when the hydride was consumed, ethylene dimerization ensued to give butene.

Both mononuclear supported iridium complexes (on the zeolite[6]) and tetrairidium clusters (on oxides[11]) catalyze ethylene hydrogenation under conditions close to those we used. The data presented herein show that the dynamic balance between these catalytically active species can be controlled by the temperature and C_2H_4:H_2 ratio.

The breakup (oxidative fragmentation) of supported metal clusters (including iridium[17]) by reaction with CO is well known,[18,19] but ours is the first evidence that C_2H_4 causes cluster disintegration. Our data are also the first that provide detailed evidence of changes in the ligands on the metal and the metal–support interface during cluster formation and breakup.

Experimental Section

Highly dealuminated HY zeolite (Zeolyst International; Si/Al = 30 (atomic)) was calcined in O_2 at 773 K for 4 h and evacuated at 773 K for 16 h, isolated, and stored in a glove box. $[Ir(C_2H_4)_2(acac)]$[5] reacted with the treated zeolite in a slurry in dried, deoxygenated *n*-pentane at 273 K. The Ir content of the resultant powder was 1 wt%. Details are reported elsewhere.[6]

Time-resolved X-ray absorption spectra were recorded at X-ray beam line MR-CAT at the Advanced Photon Source at Argonne National Laboratory. The storage ring electron energy and ring currents were 7.0 GeV and 105 mA, respectively. The cryogenic double-crystal Si(111) monochromator was detuned by 20–25% at the Ir L_{III} edge to minimize the effects of higher harmonics in the X-ray beam. X-ray absorption spectra were recorded at 1 bar and temperatures between 298 and 353 K. In an argon-filled glove box, powder samples were loaded into a flow-through cell,[20] which was sealed in the inert atmosphere. The mass of each sample (approximately 0.25 g) was chosen for optimal absorption measurements at the Ir L_{III} edge (11 215 eV) (giving an X-ray absorbance of approximately 2.0 calculated at an energy 50 eV greater than the absorption edge). Spectra were collected in transmission mode. Data were recorded for 3.5 min to determine each spectrum; this time represents a compromise between data quality and frequency of data collection. In the data analysis, an average of two consecutive spectra was used; thus, for example, the first two spectra were averaged to determine the first set of results; then, the second and third spectra were averaged to determine the second set of results, and so on. This procedure gave data of higher quality than those obtained from single scans.

Other methods are described in the Supporting Information and references cited therein.

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