

Imaging Ir₆ Clusters in Zeolite NaY with Aberration-Corrected HAADF-STEM

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Supported metal catalysts are typically highly nonuniform materials, and consequently it is challenging to determine meaningful structure-activity relationships. The nonuniformity is associated both with the variations in size and shape of the supported metal clusters and with the nonuniformity of the support surface [1]. To gain fundamental understanding of these materials, it is essential to synthesize samples that have structural uniformity. Molecular organometallic precursors offer such synthesis routes, and crystalline aluminosilicates (zeolites) offer the supports with uniform arrays of surface sites [2]. One of the most powerful methods for characterizing supported metal clusters at the atomic level is high-angle annular dark-field aberration-corrected STEM [3, 4]. This method is especially well suited to characterization of clusters of heavy metals on supports consisting of light atoms, such as zeolites. HAADF-STEM images are easier to interpret than bright-field TEM images for supported mononuclear metal complexes or extremely small clusters because the contrast is approximately proportional to the square of the atomic number (e.g., high contrast between Ir, a heavy metal with $Z = 77$ and a zeolite, consisting of light elements in its framework: Al with $Z = 13$, Si with $Z = 14$, and O with $Z = 8$).

We prepared as a starting material zeolite-supported mononuclear iridium complexes containing 10 wt% Ir. They were synthesized by the reaction of Ir(CO)₂(acac) [acac is acetylacetonate, CH₃COCHCOCH₃] with zeolite NaY. To form clusters in the cages of the zeolite, a ship-in-a-bottle synthesis was carried out with the sample in a flow reactor treated with CO at 448 K for 16 h followed by a decarbonylation step as helium flowed through the sample at 573 K for 6 h [5]. Extended X-ray absorption fine structure (EXAFS) spectra of the resulting sample indicate the presence of clusters that are well approximated as octahedral Ir₆ in the zeolite supercages.

Imaging zeolite-supported metal clusters has been a challenge because of sample damage [6, 7]. There is a trade-off between the high resolution provided by a highly focused probe in STEM and sample deterioration resulting from the high-energy electron beam—which causes both destruction of the zeolite framework and migration of the metal—these processes occur within seconds under the influence of an electron beam. But recently low-dose imaging techniques in STEM have been used to image both Ir atoms in single-metal-atom complexes and iridium clusters containing only a few atoms each—within the zeolite framework [8]. However, with this technique there was substantial noise in the data, and extensive imaging processing was necessary. In our work, in contrast, Ir₆ clusters in the pores of the zeolite and on the outside surface of the zeolite crystallites have been imaged without compromising the signal to noise ratio in HAADF-STEM images. The images were obtained with a JEOL 2100F-AC electron microscope equipped with an FEG, operating at 200 kV with a CEOS hexapole probe (STEM) aberration corrector. The zeolite framework has been imaged in the (110) direction, in which all the pores are aligned with each other, yielding a simple pattern. A section of the STEM image shown in Fig. 1 clearly demonstrates the porous

structure of the NaY zeolite (a faujasite) in the (110) direction with very close similarity to the superimposed faujasite framework in (110) orientation. The circled bright features are Ir₆ clusters located in the zeolite pores. We emphasize the high degree of uniformity of the iridium clusters attained in our synthesis—notwithstanding the high metal loading (an order of magnitude higher than is typical of industrial supported metal catalysts).

References

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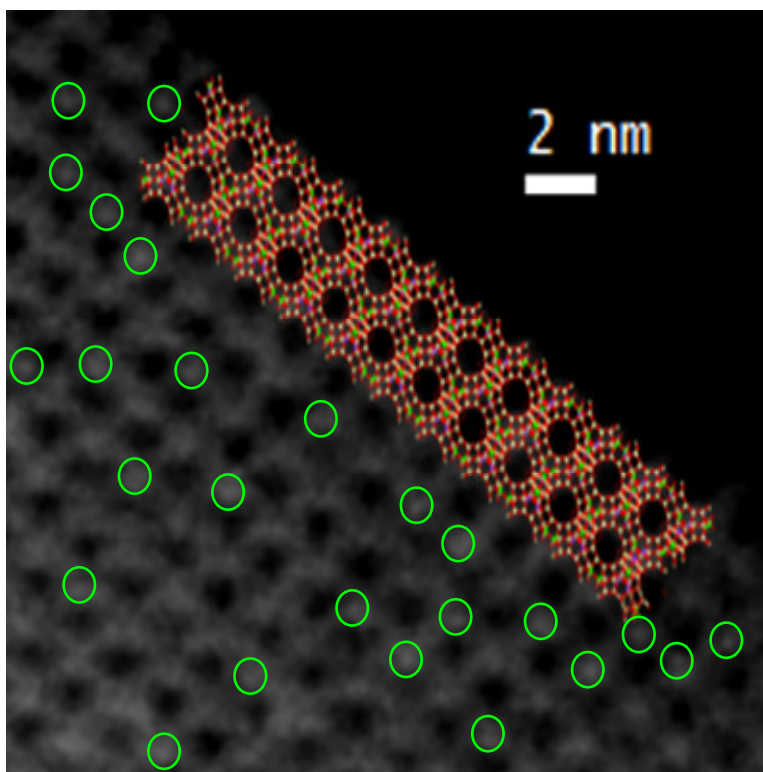


FIG. 1. A section of the STEM image showing few Ir₆ clusters highlighted in circles with superimposition of zeolite NaY crystal oriented in (110) direction