

Probing the electron-donor proprieties and bonding sites of Zr₆ based Metal-organic frameworks with anchored iridium complexes

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MOFs with Zr₆ nodes, exemplified by UiO-66 and NU-1000, are characterized by relatively good thermal stability and are potentially valuable for catalytic applications. The proton topologies of these Zr₆ nodes are quite different, as shown by X-ray diffraction and by infrared spectroscopy combined with DFT calculations indicating [Zr₆(μ₃-O)₄(μ₃-OH)₄]¹²⁻ and [Zr₆(μ₃-O)₄(μ₃-OH)₄(OH)₄(OH₂)₄]⁸⁻ for UiO-66 and NU-1000, respectively. The OH and/or OH₂ groups on these Zr₆ nodes provide bonding sites for single-site metal complexes and potentially for a large new class of catalysts. However, the reactivities of these different Zr₆ node with organometallic compounds as probe molecules—and catalyst precursors—has barely been investigated.

We used Ir(C₂H₄)₂(acac) and Ir(CO)₂(acac) (acac is acetylacetonate) as probes, reacting each with the OH groups on the Zr₆ nodes of UiO-66, making samples with iridium loadings of 1 wt%; the supported species that formed were identified by infrared spectroscopy to be mononuclear Ir(C₂H₄)₂ or Ir(CO)₂ complexes, respectively. Information about the nodes as electron-donor ligands has been determined by infrared spectroscopy. The ν_{CO} values characterizing the supported species identify them as iridium gem-dicarbonyls, and the data provide a measure of the electron-donor properties of the support relative to those of conventional metal oxide supports. The electron donor strength decreases in the order MgO > ZrO₂ > γ-Al₂O₃ > UiO-66 >> zeolite HY. The MOF-supported iridium complexes (initially in the form of the iridium diethylene complexes) were tested as catalysts with the simple probe reaction ethylene hydrogenation as well as one of our target reactions, ethylene dimerization. The results show that the electron-donor properties of the supports strongly influence the catalytic activity for each reaction; the activities increase with decreasing electron-donor strength of the support.

When the iridium loading was increased to 10 wt%, infrared spectra demonstrated that the supported species were still mononuclear iridium. Two different Ir(CO)₂ species were detected by IR spectroscopy, suggesting two different type of sites on the Zr₆ node of UiO-66, but only one type of site on the node of NU-1000. We infer that one of the bonding sites on UiO-66 consists of two terminal OH groups (site 1) and the other consists of one terminal OH group and one terminal OH₂ group (site 2), whereas the bonding site on NU-1000 is site 2. The results characterizing Ir(CO)₂ complexes present at lower loadings (e.g., 1 wt%) on the nodes of UiO-66 indicate only one kind of bonding site, that is, site 1, which we infer is more reactive with our precursor than site 2. EXAFS spectra confirm the bonding of iridium on the Zr₆ node (the data are being analyzed now).

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