

Hydrogenation of Carbon Dioxide to Formate by Noble Metal Catalysts Supported on a Chemically Stable Lanthanum Rod-Metal–Organic Framework

Maureen Gumbo, Banothile C. E. Makhubela, Francoise M. Amombo Noa, Lars Öhrström, Bassem Al-Maythaly, and Gift Mehlana

Abstract

The conversion of carbon dioxide to formate is of great importance for hydrogen storage as well as being a step to access an array of olefins. Herein, we have prepared a JMS-5 metal–organic framework (MOF) using a bipyridyl dicarboxylate linker, with the molecular formula $[\text{La}_2(\text{bpdc})_3/2(\text{dmf})_2(\text{OAc})_3] \cdot \text{dmf}$. The MOF was functionalized by cyclometalation using Pd(II), Pt(II), Ru(II), Rh(III), and Ir(III) complexes. All metal catalysts supported on JMS-5 showed activity for CO₂ hydrogenation to formate, with Rh(III)@JMS-5a and Ir(III)@JMS-5a yielding 4319 and 5473 TON, respectively. X-ray photoelectron spectroscopy of the most active catalyst Ir(III)@JMS-5a revealed that the iridium binding energies shifted to lower values, consistent with formation of Ir–H active species during catalysis. The transmission electron microscopy images of the recovered catalysts of Ir(III)@JMS-5a and Rh(III)@JMS-5a did not show any nanoparticles. This suggests that the catalytic activity observed was due to Ir(III) and Rh(III). The high activity displayed by Ir(III)@JMS-5a and Rh(III)@JMS-5a compared to using the Ir(III) and Rh(III) complexes on their own is attributed to the stabilization of the Ir(III) and Rh(III) on the nitrogen and carbon atom of the MOF backbone.

Subjects

Catalysts, Ethanol, Functionalization, Metal organic frameworks, Metals