



Rhodium pair-sites on magnesium oxide: Synthesis, characterization, and catalysis of ethylene hydrogenation



Dong Yang^a, Pinghong Xu^a, Erjia Guan^a, Nigel D. Browning^b, Bruce C. Gates^{a,*}

^aDepartment of Chemical Engineering & Materials Science, University of California, Davis, CA 95616, United States

^bFundamental and Computational Sciences, Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99352, United States

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ABSTRACT

Supported rhodium acetate dimers were prepared by the reaction of $\text{Rh}_2(\text{OAc})_4$ (OAc is acetate) with highly dehydroxylated MgO powder and characterized by extended X-ray absorption fine structure and infrared (IR) spectra, which show that the supported species were well represented as $\text{Rh}_2(\text{OAc})_3$, with each Rh atom on average bonded to one oxygen atom of the MgO surface. Aberration-corrected scanning transmission electron microscopy gave images of Rh atoms in pairs on the MgO. The supported rhodium dimers were probed with a pulse of CO, and the IR spectra indicate a Rh(II) species with weakly bonded carbonyl ligands; the sharpness of the ν_{CO} band indicates highly uniform surface species. Further treatment in CO led to breakup of the rhodium dimers into mononuclear species; such fragmentation took place in other treatment gases as well, with the degree of fragmentation decreasing in the order $\text{CO} > \text{C}_2\text{H}_4 > \text{helium}$. The fragmentation is inferred on the basis of IR spectra to have proceeded through intermediate Rh_2 species without acetate ligands. In contrast, rhodium dimers were reduced and not fragmented in the presence of H_2 at 353 K, but at higher temperatures the rhodium aggregated to give larger clusters. The supported species catalyzed ethylene hydrogenation at 298 K and 1 bar at a H_2 :ethylene molar ratio of 4; after 27 h of catalysis in a once-through flow reactor, acetate ligands were removed from the dimers, and some of them fragmented, as shown by IR spectroscopy. The intermediate dirhodium species without acetate ligands are two or three orders of magnitude more active as catalysts than the supported mononuclear rhodium species or those present predominantly as $\text{Rh}_2(\text{OAc})_3$, respectively.

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1. Introduction

Single-site catalysts consisting of isolated metal atoms on solid surfaces have emerged as a class of materials with surprising new properties; the discovery of these supported metal complex catalysts has been facilitated by atomic-resolution images of the isolated metal atoms, obtained by aberration-corrected scanning transmission electron microscopy (STEM) [1–5]. Single-metal-atom complex catalysts are most commonly used in solution, and the discovery of better ones typically results from investigations of new metal–ligand combinations; however, the metal nuclearity is also important, because metal centers neighboring each other may have reactivities different from those of isolated metal centers [1,6]. Metal complexes with pairs of metal atoms require stabilization by ligands—and solid surfaces in prospect can serve as such ligands. MgO has been found to stabilize dimeric rhodium species (having Rh–Rh bonds) that catalyze hydrogenation of olefins—

with major differences between isolated and paired rhodium centers as catalysts for hydrogenation of the bifunctional molecule 1,3-butadiene indicating a unique role of the neighboring rhodium centers [7,8]. Rhodium catalysts with controlled nuclearities are especially appealing in prospect because of the versatility of rhodium as a catalyst, in forms ranging from mononuclear complexes [9–12] to clusters [13–16] to metallic particles [17–19].

We now report an extension of this class of catalyst, consisting of pairs of Rh centers on a support. The catalyst was synthesized from MgO-supported dinuclear rhodium species formed by adsorption of the rhodium acetate dimers $\text{Rh}_2(\text{OAc})_4$ (OAc is acetate). The supported species were characterized by infrared (IR) and X-ray absorption spectra complemented by STEM images that provide the first direct evidence of supported rhodium pair sites. High-area MgO powder was chosen as the support because it consists of light atoms—for a strong contrast with Rh atoms in STEM—and because it is highly crystalline, facilitating the imaging of the support surfaces. Processes involving the fragmentation of supported dinuclear rhodium species to give mononuclear Rh sites were monitored spectroscopically with the samples in various gas

* Corresponding author.

E-mail address: bcgates@ucdavis.edu (B.C. Gates).

atmospheres, some leading to the aggregation of the rhodium into small clusters. The catalytic properties of the paired Rh centers were compared with those of single-site rhodium species and rhodium dimers without acetate ligands, on the same support. Ethylene hydrogenation was chosen as a test reaction because it takes place under such mild conditions that aggregation of the rhodium during catalysis is limited and because ethylene forms ligands on the rhodium that are identifiable by IR spectroscopy. The results demonstrate that the dirhodium species without acetate ligands are much more active catalytically than either the supported dirhodium species with acetate ligands or supported mononuclear rhodium species.

2. Experimental methods

2.1. Sample synthesis

Sample synthesis and handling were performed with the exclusion of moisture and air by use of standard Schlenk line techniques and inert-atmosphere glove boxes.

The precursor $\text{Rh}_2(\text{OAc})_4$ (99%) was purchased from Strem. The MgO support (Matheson Coleman & Bell) was calcined in flowing O_2 at 973 K for 4 h and then evacuated for 16 h at 973 K, giving a material with a BET surface area of $70 \text{ m}^2/\text{g}$. H_2 was supplied by Airgas (99.995%) or generated by electrolysis of water in a Balston generator (99.99%) and purified by passage through traps containing reduced $\text{Cu}/\text{Al}_2\text{O}_3$ and activated zeolite 4A to remove traces of O_2 and moisture, respectively. Helium (Airgas, 99.999%), ethylene (Airgas, 99.99%), and CO (10% in helium) were purified by passage through similar traps.

To prepare the supported catalyst containing 1.0 wt% Rh, the precursor $\text{Rh}_2(\text{OAc})_4$ (21.5 mg) and calcined MgO (1.0 g) were slurried in dried and deoxygenated *n*-pentane (Fisher, 99%) at room temperature. The slurry was kept at this temperature with mixing for a day, and thereafter the solvent was removed by evacuation for a day, leaving all the rhodium on the support; thus, the rhodium loadings were determined from the masses of rhodium and support present initially. The slurry was initially green in color (the color of the $\text{Rh}_2(\text{OAc})_4$ precursor), but the powder changed to light blue in color after one day of reaction, and the solution become clear and colorless, consistent with the complete uptake of the rhodium precursor by the support even before the solvent was removed by evacuation. The resultant supported catalyst was stored in an argon-filled glove box (<1 ppm O_2).

2.2. Infrared spectroscopy

A Bruker IFS 66v/S spectrometer with a spectral resolution of 2 cm^{-1} was used to collect transmission IR spectra of the supported samples. In an argon-filled glove box, each supported sample (typically, 40 mg) was pressed into a thin wafer; when the sample was the $\text{Rh}_2(\text{OAc})_4$ precursor, 5 mg of that solid was mixed with 50 mg of KBr, and the mixture was pressed into a wafer. Each of these samples was mounted in a cell (In-situ Research Institute, South Bend, IN) for transmission spectroscopy. The cell was connected to a vacuum system with a base pressure of 10^{-4} bar, which allowed recording of spectra with gases (helium, H_2 , ethylene, or CO) flowing through the cell at temperatures in the range of 298–393 K and atmospheric pressure. Each spectrum is the average of a number of scans ranging from 8 to 128.

2.3. X-ray absorption spectroscopy

X-ray absorption spectra were recorded at X-ray beamline 4-1 at the Stanford Synchrotron Radiation Lightsource (SSRL). The storage ring electron energy and ring current were 3.0 GeV and

300 mA, respectively. A double-crystal Si(220) monochromator was detuned by 15–20% at the Rh K edge to minimize the effects of higher harmonics in the X-ray beam. The experimental methods are essentially the same as those described elsewhere [8].

2.4. STEM imaging

Samples for imaging by STEM were prepared by dipping a 200-mesh lacey-carbon-coated copper grid (Ted-Pella) into the initially prepared catalyst powder in the glove box. Samples were transported to the microscope and mounted onto a sample holder in an argon-filled glovebag and then transferred under an argon blanket to the microscope with a maximum period of air exposure of 3 s. Samples were imaged with an aberration-corrected FEI Titan 80/300S operating at 300 keV. The convergence angle was 35.6 mrad ; the HAADF collection inner angle was $\sim 75 \text{ mrad}$. To minimize artifacts in the images caused by beam damage, the microscope was first aligned for one region of the sample, and then the beam was shifted to a nearby region for image acquisition.

2.5. Catalytic activity testing

Ethylene hydrogenation catalysis was carried out in a conventional laboratory once-through tubular plug-flow reactor at 298 K and 1 bar. The catalyst (10–50 mg per sample) was diluted with 10 g of inert, nonporous $\alpha\text{-Al}_2\text{O}_3$ powder (Sigma-Aldrich, 100–200 mesh, $\geq 99\%$) and loaded into the reactor in the glove box. The feed partial pressures were 100 mbar of ethylene, 400 mbar of H_2 , and 500 mbar of helium, with a total flow rate of 100 mL(NTP)/min . Products were analyzed with an on-line Agilent 6890 gas chromatograph. The ethylene conversions were <5% and shown to be well approximated as differential, determining reaction rates directly. Rates are expressed as turnover frequencies (TOF), defined as the number of mols of ethylene converted per total Rh atom per second; the TOF data are based on conversions to the product ethane.

3. Results

3.1. Characterization of MgO-supported species formed from $\text{Rh}_2(\text{OAc})_4$

IR spectroscopy was used to characterize the adsorption of $\text{Rh}_2(\text{OAc})_4$ on MgO that had been calcined at 973 K to give a high degree of surface dehydroxylation [6]. Spectra in the ν_{OH} region (Fig. S1, Supporting Information) give evidence of only one peak, at 3747 cm^{-1} , which is assigned to terminal OH groups on MgO [23,24]. This band decreased markedly in intensity upon adsorption of $\text{Rh}_2(\text{OAc})_4$, indicating the involvement of the support surface OH groups in the adsorption.

IR spectra characterizing the $\text{Rh}_2(\text{OAc})_4$ precursor and the sample prepared by its adsorption on the MgO powder from a solution of *n*-pentane (Fig. 1, Table 1) include bands in the ν_{CH} region ($3200\text{--}2650 \text{ cm}^{-1}$) and the ν_{CO} region representative of the acetate groups ($1750\text{--}1200 \text{ cm}^{-1}$). Bands characterizing the supported species at 1599, 1578, 1520, 1444, 1409, and 1349 cm^{-1} nearly match those of $\text{Rh}_2(\text{OAc})_4$ itself (Fig. 1, Table 1), indicating that the rhodium retained most of its acetate ligands after adsorption; however, a band at 1666 cm^{-1} disappeared after the adsorption.

Xu et al. [21] investigated the IR spectra of CH_3COOH adsorbed on MgO. Two bands arose upon adsorption, at 1701 and 1653 cm^{-1} , which have been assigned to $\nu_{\text{C=O}}$ vibrations of OAc^- in dimeric or oligomeric forms. These chain structures are formed by hydrogen bonding involving CH_3 and COO^- groups. Ma et al. [22] reported a band at 1710 cm^{-1} when they performed a similar

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