

A Well-Defined Rhodium Complex Catalyst Supported on Dealuminated Y Zeolite: Spectroscopic Characterization in the Working State

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Introduction

The characterization of most supported metal catalysts is hindered by their structural nonuniformity. Our broad goal was to use a well-defined (crystalline) support to prepare structurally uniform supported metal catalysts, characterize them, determine precise structure-catalytic property relationships, and establish details of catalytic cycles. We have already reported the synthesis and structural characterization of rhodium-ethylene complexes on dealuminated Y zeolite, demonstrating their dynamic uniformity by ¹³C NMR spectroscopy [1,2]. Here we report the activity of the catalyst for ethylene hydrogenation and its reactivity with ethylene and H₂ in dynamic experiments using IR and EXAFS spectroscopies.

Materials and Methods

The synthesis of the catalyst, reported elsewhere [2], and sample handling were done with exclusion of air and moisture. The sample was prepared by slurring the precursor Rh(C₂H₄)₂(acac) (acac is C₅H₇O₂) (Strem, 99%) in dried, deoxygenated *n*-pentane at 200 K with partially dehydroxylated zeolite Y (calcined at 723 K), followed by removal of the solvent by evacuation. The resultant powders contained 1 wt% Rh. Samples were brought in contact with various reactive gases in flow reactors and characterized by IR and EXAFS spectroscopies in transient experiments during the treatments. Ethylene hydrogenation catalysis was carried out under comparable conditions at steady state in a flow reactor, and spectra of the functioning catalysts were recorded.

Results and Discussion

The supported rhodium complex initially bonded to the zeolite has been characterized by IR, NMR, and EXAFS spectroscopies and density functional theory [1,2]. IR spectra of the supported sample indicate that the acac ligands were fragmented during absorption of Rh(C₂H₄)₂(acac) on the support and likely remained bonded to the support. A band observed at 3060 cm⁻¹ is indicative of ethylene ligands on the Rh, in excellent agreement with those observed for the precursor. Consequently, it is inferred that the ethylene ligands remained bonded to the Rh after anchoring of the complex. Within the error, the EXAFS data give no evidence of Rh–Rh contributions, consistent with the IR data in indicating the presence of mononuclear Rh complexes. The ¹³C NMR spectra of the sample, after exchange with ¹³C ethylene at various temperatures, demonstrate the dynamic uniformity of the supported complex.

The zeolite-supported Rh complex was found to be active for ethylene hydrogenation at 298 K. With a total flow rate of 100 mL/min and partial pressures of C₂H₄ and H₂ each being 30 Torr (in He) at 298 K and 1 bar, the initial turnover frequency (TOF) was 0.022 s⁻¹. The activity reached steady state after 18 h with a TOF of 0.0021 s⁻¹ and remained active for 23 h, until the experiment was stopped. With the reactive ethylene ligands remaining intact, the supported Rh complex was highly reactive, even with gas-phase ethylene, as indicated by IR bands in the C–H stretching region. After reaction with ethylene, the supported complex incorporated ethyl ligands, in addition to ethylene ligands, as shown by the IR spectra. These data indicate

that ethyl is a likely intermediate in the catalytic cycle for ethylene hydrogenation. Confirming this inference, IR spectra characterizing the catalyst in steady-state operation also included evidence of the ethyl ligands, without π-bonded ethylene. Thus, all the data point to ethyl groups as reaction intermediates. The supported rhodium complex as initially synthesized was found to be unreactive with N₂. However, when a stream of N₂ flowing over the sample in an IR cell was replaced with a mixture of 2% H₂ in N₂ at 298 K, a band appeared at 2214 cm⁻¹ (Figure 1), passing through a maximum as a function of time of flow of this mixture. Meanwhile, another band appeared at 2252 cm⁻¹, and its intensity increased at the expense of the band at 2214 cm⁻¹. According to Miessner [3], the band at 2214 cm⁻¹ is assigned to dinitrogen bonded to the Rh center and the band at 2252 cm⁻¹ to supported Rh(N₂)(CO). The assignments of these two bands were verified by results of experiments with ¹⁵N₂.

In summary, well-defined and uniform Rh complex supported on dealuminated zeolite Y is catalytically active for ethylene hydrogenation. With reactive ethylene ligands, the supported sample is highly reactive under mild condition in various reactive environments. The results show how detailed characterization of metal–ligand combinations related to catalysis can be determined for structurally nearly uniform samples.

Significance

These results demonstrate the opportunities for elucidation of reaction intermediates in complementary steady-state and transient IR and EXAFS experiments with well-defined metal complex catalysts on well-defined supports. With such samples, we expect to attain a depth of understanding of catalytic mechanisms rivaling that attainable in homogeneous catalysis.

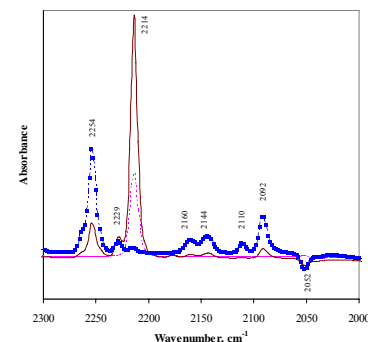


Figure 1. IR difference spectra in the carbonyl and dinitrogen stretching region of the DAY zeolite-supported rhodium complex obtained after a change the flowing gas from N₂ to 2% H₂ in N₂ at 298 K after 2 (pink dashed line), 10 (brown solid line), and 54 (blue dashed line) min. The spectrum of the sample in N₂ at 298 K was used as a reference.

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References

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