

Synthesis and Characterization of Zeolite-Supported Mononuclear Ruthenium Complex Catalyst

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Introduction

Supported metal complex catalysts with uniform structures offer the prospective advantages of molecular catalysts in solution and traditional solid catalysts: high selectivity associated with unique structures and easy separation from products. However, there are still only a few examples that clearly show structural uniformity of supported metal complexes. Now we report a ruthenium complex bonded to a crystalline support, a zeolite, formed from the precursor $\text{Ru}(\text{C}_2\text{H}_4)_2(\text{acac})_2$. We report structural characterization of the material with IR and EXAFS spectroscopies and evaluation of its performance in the catalytic conversion of ethylene and hydrogen.

Materials and Methods

$\text{Ru}(\text{C}_2\text{H}_4)_2(\text{acac})_2$ was synthesized as before¹ and chemisorbed on dealuminated zeolite Y (Si/Al = 30 [atomic], 1 wt% Ru). The sample was tested as a catalyst for dimerization of ethylene in a once-through flow reactor operated at atmospheric pressure. It was also characterized with IR and EXAFS (Ru K edge) spectroscopies in flow reactors that served as cells and were fed with gases of various compositions.

Results and Discussion

Fig. 1 shows the IR spectra of the precursor $\text{Ru}(\text{C}_2\text{H}_4)_2(\text{acac})_2$; the calcined zeolite; and the zeolite-supported Ru complex. The bands representing acidic silanol groups (3640 and 3550 cm^{-1}) in the calcined zeolite decreased significantly compared to the terminal silanol band (3750 cm^{-1}) upon chemisorption of the precursor, indicating that the Ru complex reacted with acidic silanol groups. EXAFS data characterizing the resultant zeolite-supported complex (Table 1) indicate approximately 4 Ru–O bonds per complex at a bonding distance of 2.1 Å and a Ru–Al contribution, consistent with the IR data in indicating bonding of the Ru complex at sites where the acidic silanol groups had been present. No detectable Ru–Ru contributions were evident in the EXAFS spectrum, within error, consistent with the presence of mononuclear Ru species and not clusters in the zeolite. The IR spectrum of the supported sample indicates that the ethylene ligands in the precursor were retained in the supported complex (bands at 3010 and 3060 cm^{-1}); the EXAFS data support this conclusion, showing a Ru–C contribution with a coordination number of nearly 4. Thus, we infer that the Ru complex was anchored tightly to the zeolite through Ru–O bonds and incorporated reactive ethylene ligands. Consistent with this conclusion, the IR spectrum includes bands indicating both acac dissociated from the ruthenium (1374 and 1537 cm^{-1}) and acac still bonded to it (1515 and 1576 cm^{-1}); the data thus suggest that only some of the acac ligands of the precursor were replaced with oxygen ligands from zeolite upon chemisorption. A coordination number of nearly 4 characterizing a Ru–O pair is accounted for by two oxygen atoms of the zeolite and

two per acac ligand. Therefore, we infer that the ruthenium was coordinated to two ethylenes and one acac ligand and anchored to the zeolite by Ru–O bonds.

Consistent with the presence of reactive ethylene ligands on the complex, it was found to be catalytically active for dimerization of ethylene, with 1-butene being the major product at room temperature, with TOF = 0.11 s^{-1} with ethylene and H_2 partial pressures 30 Torr each. The reaction is suggested to be initiated by activation of H_2 present in the feed and formation of hydride ligands on Ru. This requires the dissociation of either ethylene or acac ligands from the Ru center to start the catalytic cycle.

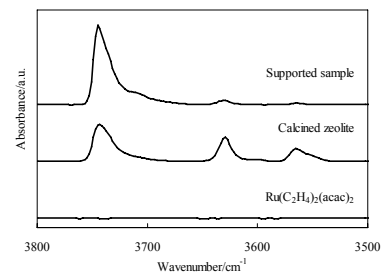


Figure 1. IR spectra of $\text{Ru}(\text{C}_2\text{H}_4)_2(\text{acac})_2$; calcined zeolite; and supported sample

Table 1. EXAFS parameters characterizing zeolite-supported Ru complex.

Shell	N	R [Å]	$\Delta\sigma^2 \cdot 10^3$ [Å ²]	E_0 [eV]
Ru - Ru	-	-	-	-
Ru - O	3.8	2.05	3.51	-1.94
Ru - C	4.1	2.21	4.14	-4.18
Ru - Al	0.9	3.11	0.62	-5.70

Notation: N , coordination number; R , inter-atomic distance; $\Delta\sigma^2$, Debye-Waller factor; ΔE_0 , inner potential correction. Errors: N , $\pm 20\%$; R , 0.02 Å; $\Delta\sigma^2$, $\pm 20\%$; ΔE_0 , $\pm 20\%$

Significance

Synthesis of supported catalysts with uniform, structurally defined catalytic sites is crucial to the advancement of fundamental understanding of supported metal complex catalysts—the data present here show substantial progress toward understanding of such a catalyst at a depth approaching that of the best-understood molecular catalysts in solution.

References

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