Supported Catalysts

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Evidence from NMR and EXAFS Studies of a Dynamically Uniform Mononuclear Single-Site Zeolite-Supported Rhodium Catalyst**

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The best transition-metal complex catalysts are characterized by both high activities and high selectivities, with the latter typically associated with the uniqueness of the catalytic species. Optimal use in technology also demands ease of separation of catalysts from products, and the goal of efficient separation has been a primary motivation for research with supported metal complexes, which offer the added benefit of being resistant to corrosion. General challenges in the synthesis of practical single-site catalysts on supports include the following: a) low catalytic activity associated with non-optimal ligands, which include the support and ligands remaining from the precursor metal complex that is adsorbed on the support; b) non-uniform distribution of metal sites as a consequence of the intrinsic heterogeneity of the surfaces of the inorganic support; and c) loss of structural integrity of the catalysts during operation, sometimes associated with reduction and sintering of the metal to form species of non-uniform (and often poorly characterized) metal nuclearity and often undesired oxidation states of the metal.

Several research groups have pursued the synthesis and testing of organometallic precursors suitable for the preparation of supported catalysts and meet the criteria stated above.[1,2] In particular, Basset and co-workers[1] have developed precursors that, when bonded to silica, closely mimic structures that may exist in catalytic cycles, with the expectation that these surface species will readily enter catalytic cycles once presented with suitable reagents (point (a), above).[1]

We have been drawn to zeolites as potential supports because their well-defined, highly uniform adsorption sites seem to address point (b) above.[3,4] As shown below and elsewhere, EXAFS (extended X-ray absorption fine structure) spectroscopy, used in concert with IR and NMR spectroscopic techniques, provides the means to test directly the efficacy of synthetic procedures intended to provide specific mononuclear (or polynuclear) metal sites.[5]

Herein, we report the synthesis of the first supported mononuclear Rh^+ species with exchangeable ethylene ligands; the support is dealuminated zeolite Y. The isotopically unmodified ethylene ligands (natural abundance) introduced in the synthesis of the catalyst are easily and completely exchanged by either ^2H- or ^{13}C-labeled ethylene, as verified by IR and NMR spectroscopy, respectively. Furthermore, the as-synthesized or ^{13}C-exchanged ethylene ligands readily undergo reduction with autogenous hydrogen (i.e., reverse spillover), as expected for an active catalyst.

Central to this report, by using variable-temperature ^{13}C CP-MAS (cross-polarization magic-angle spinning) NMR spectroscopy we observed that all of the [$^{13}C_2$]ethylene ligands on the zeolite-supported catalyst undergo anisotropic rotation at the same frequency at a given temperature which is characteristic of the precursor compound either in solution or as a crystalline compound.[6] Given the extreme sensitivity of dynamical barriers to electronic and steric effects, we consider this observation to be a convincing demonstration of the structural uniformity or our supported metal sites.[7]

The active site of the zeolite-supported rhodium catalyst (Figure 1) is represented as a structure optimized at the B3LYP level using appropriate basis sets and a cluster model of a zeolite anion site. Table 1 provides a summary of the structural parameters that were optimized on the basis of EXAFS data which characterize the supported metal complex. These data compare favorably with the coordination numbers and distances indicated in Figure 1 and, where appropriate, with the crystal structure of the precursor complex, acetylacetonatobis(ethylene)rhodium ([Rh(acac)(C_2H_4)$_2$]).[8] We emphasize the lack of a Rh–Rh contribution in the EXAFS data, consistent with the presence of exclusively mononuclear rhodium within the catalyst. The experimental Rh–O coordination number is 2.2 ± 0.4, representing the coordination of Rh to the zeolite framework. The Rh–O

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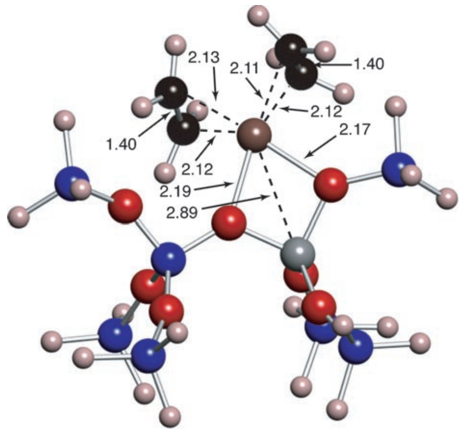

Figure 1. Geometry of $\{Rh(C_2H_4)_2\}$ bonded to a zeolite anion cluster, optimized at the B3LYP level. Rh brown, C black, Al gray, O red, Si blue, H beige.

Table 1: Fit parameters for EXAFS data and bond lengths/distances from density functional calculations (B3LYP level) for the DAY-zeolite-supported rhodium complex.[a]

Shell	Distance [Å][b]	R [Å]	N	$\Delta\sigma^2$ [Å^2]	ΔE_0 [eV]
Rh–Rh	–	–	–	–	–
Rh–O$_s$[c]	2.18	2.19	2.2	0.00673	−3.05
Rh–C	2.12	2.09	3.9	0.00345	3.24
Rh–O$_l$[d]	3.58	3.41	0.7	−0.00371	6.55
Rh–Al	2.89	2.92	0.4	0.00221	0.68

[a] Scanned at 77 K and $<10^{-5}$ Torr. Notation: N = coordination number; R = absorber–backscatter distance; $\Delta\sigma^2$ = Debye–Waller factor; ΔE_0 = inner potential correction. The approximate experimental uncertainties of the contributions other than for Rh–Al are as follows: N ±20%; R ±1%; the errors representative of the Rh–Al contribution are greater than these and are not well characterized. [b] Average bond lengths/distances determined at the B3LYP level. [c] s = short. [d] l = long.

bond distance is 2.19 Å, consistent with previously reported distances for rhodium complexes bonded to oxide supports.[9]

The Rh–C coordination number was determined to be approximately 3.9, as would be expected for ethylene that is π-bonded to Rh. The structure is also in line with the expectation of two ethylene units ligated to each Rh atom, although the data do not definitively confirm this. The Rh−C bond length, determined from the EXAFS data to be 2.09 Å, is close to the value determined by X-ray crystallography for the precursor $[Rh(acac)(C_2H_4)_2]$ (2.13, 2.14 Å).[10] The Rh–Al coordination number was determined to be 0.4, but this contribution could be determined only tentatively, as the error bound is high. The Rh–Al distance determined by EXAFS spectroscopy was 2.92 Å (compare with the calculated value of 2.89 Å, Figure 1).

The ^{13}C CP-MAS NMR spectra in Figure 2a decisively demonstrate that the supported rhodium complex has intact π-bonded ethylene ligands and that no other carbonaceous species were introduced during the [$^{13}C_2$]ethylene-exchange procedure. The single resonance at $\delta = 60$ ppm is in excellent agreement with the values reported for the precursor complex in solution ($\delta = 59.54$ ppm) and for the crystalline solid ($\delta = 59.4$ and 60.3 ppm).[6]

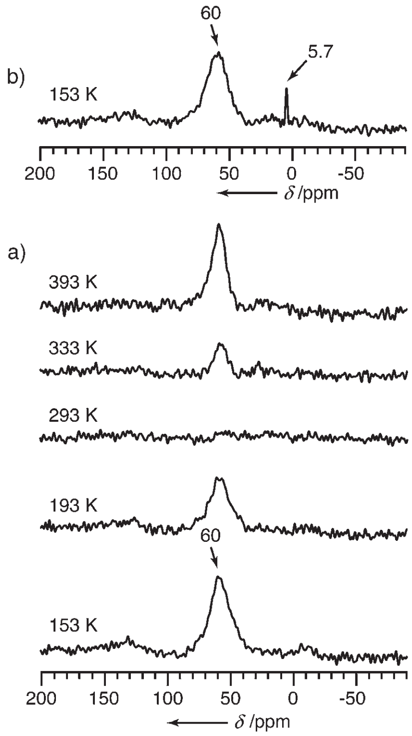

Figure 2. ^{13}C CP-MAS spectra (75.4 MHz) of the sample formed from $[Rh(acac)(C_2H_4)_2]$ and dealuminated zeolite Y and then exchanged with ^{13}C-labeled ethylene. a) Variable-temperature spectra showing the temperature dependence of the signal intensity. b) Spectrum obtained at low temperature after heating and subsequent cooling of the sample which demonstrates the results of a reverse-spillover reaction. The signal at $\delta = 5.7$ ppm corresponds to ethane.

Most important, by acquiring ^{13}C CP-MAS NMR spectra of the supported complex over a range of temperatures (Figure 2a) we observed a temperature dependence of the line width, similar to that reported by others for a crystalline sample of the precursor complex.[6] As was determined in earlier work, the ^{13}C resonance of the π-bonded ethylene ligands is broadened as a result of a conflict of ^{1}H–^{13}C dipolar decoupling and random anisotropic reorientation of the ^{1}H–^{13}C bond vector. When these two dynamical processes occur on the same timescale for *all* spin-pairs in the sample, the carbon resonance is broadened in its entirety and, correspondingly, no signal was observed for our sample at temperatures near room temperature with a 27-kHz proton dipolar decoupling field. If the metal sites of our zeolite-supported rhodium catalyst were structurally diverse, this diversity would map into a distribution of rotational barriers for the ethylene ligands and some of the sites would yield sharp ^{13}C components at each temperature investigated, as we have verified by using other less-uniform support materials (data not shown).[11] The rotational barrier for ethylene ligands in our supported complex will be sensitive to both electronic and steric interactions. The result that all ethylene ligands in our catalyst have a common rotational barrier is powerful evidence that we have synthesized a supported rhodium complex that has a degree of structural—and hence dynamical—uniformity, characteristic of crystalline complexes and solution species. Thus, we propose that this sample is a true supported molecular catalyst.

Our justification for referring to the sample as a catalyst includes the result shown in Figure 2b: upon first heating the NMR probe in the rotor and then by acquiring the ^{13}C NMR spectrum at lower temperatures, we observed a sharp resonance at $\delta = 5.7$ ppm, assigned to gas-phase and/or physisorbed [$^{13}C_2$]ethane. Autogenous reduction reactions of this sort are known to be the result of reverse-spillover, in which hydrogen associated with the support material, for example, as OH groups, migrates to the metal site to provide H_2 equivalents.[12]

The absence of a Rh–Rh contribution (and thus mononuclear rhodium), as indicated by the EXAFS data (Table 1), combined with the Rh–O coordination number of approximately 2 (representing the coordination of Rh to two oxygen atoms of the zeolite framework, with a Rh−O distance of 2.19 Å) are consistent with bonding of Rh to the support[9] after dissociation from the acac ligands of the precursor.

Experimental Section

Highly dealuminated HY zeolite (DAY zeolite; Zeolyst International; atomic ratio of Si/Al $\approx$ 30) was calcined in O_2 at 773 K for 4 h and evacuated for 16 h at 773 K, isolated, and stored in a glovebox until used in the preparation of the supported rhodium complex. *n*-Pentane solvent (Fisher, 99%) was dried and purified by refluxing over sodium benzophenone ketyl and deoxygenated by purging with N_2. The precursor metal complex $[Rh(C_2H_4)_2(C_5H_7O_2)]$ (Strem, 99%) was brought into contact with the treated zeolite in a slurry in dried, deoxygenated *n*-pentane at 200 K. The Rh content of the resultant powders was 1 wt%.

EXAFS spectra of the supported catalyst were measured at Beamline X-18B at the National Synchrotron Light Source at Brookhaven National Laboratory at a temperature near 77 K, with cells and methods as previously reported.[13] EXAFS data were analyzed using standard software. IR spectra were measured as reported previously and showed loss of the acac ligand.[14]

The ethylene ligands of the as-synthesized catalyst were exchanged with [$^{13}C_2$]ethylene using multiple contacts with pressures of [$^{13}C_2$]ethylene of less than 1.5 Torr and exposure times of less than 1 min. GC-MS analysis of gas fractions drawn from the vacuum line was used to validate the exchange procedure. Variable-temperature in situ ^{13}C CP-MAS NMR measurements were performed with a sealed rotor and standard methods, as described elsewhere.[15,16] The ^{1}H decoupling power level was 27 kHz.

Computational modeling of the structure was carried out at the B3LYP level by using the Stuttgart rsc basis functions with relativistic effective core potentials on Rh and Ahlrich's triple-zeta polarization basis sets on all other atoms.[17]

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