IN-SITU SPECTROSCOPIC STUDIES OF RHODIUM CATALYZED PRODUCTION OF HYDROGEN FROM DIMETHYLAMINE BORANE. HOMOGENEOUS OR HETEROGENEOUS CATALYSIS?

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Introduction
The US Department of Energy has recently issued a Grand Challenge in Hydrogen Storage. The ambitious goals for volumetric and gravimetric densities and the controlled release of H₂ from materials at temperatures below 80 °C contained within this Grand Challenge demand the discovery of new materials and catalysts. Our interests in discovery of novel materials for hydrogen storage have led us to examine the chemical and physical properties of amine borane complexes.

In previous work we have discovered that both the kinetics and thermodynamics for the dehydropolymerization of ammonia borane (NH₃BH₃) are perturbed when the material is coated into mesoporous silica. Recent work from the Manners group suggested that colloidal rhodium catalyzes the release of hydrogen via dimerization of dimethylaminoborane in solution at room temperature. However, whether the dehydrocoupling and release of hydrogen occurred by a heterogeneous catalytic or a homogeneous catalytic pathway was not conclusively identified. To help elucidate the mechanistic pathway we undertook an in-situ spectroscopy approach (XAFS/XANES) to help identify the active catalyst concurrent with ¹¹B NMR studies to follow the kinetics of the reaction. This study demonstrates the utility of in-situ XAFS and XANES to differentiate between heterogeneous and homogeneous reaction pathways.

Experimental
The catalyst precursor, [Rh(1,5-cod)(µ-Cl)]₂ (17mM) and Me₂NHBBH₃ (1.1M) were prepared in a solution of toluene in an Ar-purged glove box. The reaction solution was immediately transferred into sealed, 4-cm long glass EXAFS (extended x-ray absorption fine structure spectroscopy) sample holders having Kapton windows on both ends or into a 5 mm NMR tube. The reaction was conducted at 25°C for over 3 hrs. The in situ Rh K-edge (23222 eV) EXAFS spectra were collected on the bending magnet beamline (PNC-CAT; Sector 20) at the Advanced Photon Source, Argonne National Laboratory. Data were analyzed using AUTOBK and IFEFFIT routines. The kinetics of Me₂NHBBH₃ disappearance were followed using ¹¹B NMR spectroscopy run unlocked on a Varian VXR-300 NMR spectrometer operating at 96 MHz. Caution: The reactions described release a large amount of H₂ gas and can be exothermic and the gas release can be violent. Proper safety precautions including but not limited to pressure release devices and personal safety equipment should be used.

Results and Discussion
In-situ characterization of the active transition metal catalyst: EXAFS spectroscopy of Rhodium complex. In order to clarify the identity of the active Rh species, a series of in situ EXAFS spectra were collected as the solution was evolving hydrogen gas. Upon the initial mixing of the catalyst precursor with the dimethylamine borane solution the initial XAFS spectra shows that the Rh complex rapidly evolves during the first stages of the reactions, undergoing a complete conversion to a new Rh compound in about 20 min. Further, from the heights of the XAFS absorption edges we determine that, during the first 40 minutes of the reaction, the amount of soluble Rh species remains constant (during which 60% of the reaction has occurred). Thus we conclude that the complex at this point corresponds to the active rhodium complex. The spectrum for the active complex in Figure 1 was acquired after 30 minutes of reaction where all Rh was completely soluble in the toluene. Finally, we observe that as the reaction proceeds beyond 40 min, the amount of soluble Rh then steadily decreases until it reaches about 20% of the starting concentration after about 3 hrs of reaction time.

The EXAFS radial structure plot (RSP) for the active rhodium complex is shown in Figure 1, together with that for Rh(0) metal for comparison. The RSP is related to the probability of finding an atom at some radial distance from the central absorbing atom (Rh). The EXAFS backscattering amplitudes for high-Z atoms such as rhodium are uniquely different than those from the low-Z ligands around the rhodium. Hence we can uniquely identify the peak in Figure 1 at about 2.7 Å as belonging to Rh-Rh structures in the active rhodium complex.

As a first approximation, we know that the coordination number is proportional to the peak amplitude in the radial structure plot. The active complex has a Rh-Rh peak amplitude that is about 4 times smaller than that of bulk Rh(0) metal (12 first shell rhodiums). Furthermore, this peak for the active complex, is about 2 times smaller than that for a Rh(0)₆ metal cluster. Preliminary EXAFS peak fitting to theoretical standards shows that the active metal contains no more than 4-6 metal atoms in a core cluster surrounded by ligands. As shown in Figure 1 the Rh-Rh distance for the Rh(0)₆ metal cluster is the same as for the bulk metal, whereas the one for the active complex is significantly longer by about 0.06 Å. This is evidence that the strong ligand-rhodium interactions in the complex decrease the Rh-Rh interaction and thereby increase the Rh-Rh

![Figure 1](image-url)

**Figure 1.** The radial structure plot for the active Rh complex at t=30 min (solid), and for Rh metal (dashed), both without phase corrections. The phase-corrected Rh-Rh distances are listed next to their respective peaks. The (---) vertical line and the (+) symbol locates the distance and amplitude respectively for a Rh(0)₆ cluster (from Ref. 6).

distances. The same effect is observed for the Rh$_4$(CO)$_{16}$ complex.$^6$
This EXAFS study concludes that the active Rh complex for
[Rh(cod)Cl]$_2$ catalyzed Me$_2$NHBH$_3$ dehydrocoupling is most likely a
Rh (0) cluster with no more than 4-6 core Rh atoms with strongly-
bound external ligands. This cluster size is significantly smaller than
the 2 nm Rh(0) particles suggested in previous studies.$^4$

**Kinetics of hydrogen formation in the Rh catalyzed coupling of
dimethylamine borane.** Solution phase $^{11}$B NMR spectroscopy
was used to follow the reaction kinetics of the catalyzed
dehydrocoupling reaction of Me$_2$NHBH$_3$ in toluene to yield the
cyclic dimer and hydrogen. In the NMR experiment the solid
catalyst precursor and the solid amine borane complex were weighed
into the same vial and the mixture taken into the glove box. When
toluene was added to the [Rh(1,5-cod)(μ−Cl)]$_2$/amine borane mixture
the solution began to bubble immediately. As shown in Figure 2b the
$^{11}$B{[H]} NMR spectra at ca. 50% conversion shows the starting
material and the product are the predominate species. The reaction
does not appear to generate any significant amount of side products.

![Figure 2](image)

**Figure 2.** a) The $^{11}$B{[H]} toluene solution NMR spectra of
Me$_2$NHBH$_3$ (-14.2 ppm) b) at ca. 50% conversion, 30 minutes, c)
complete conversion, 200 minutes. The product [Me$_2$NBH$_2$]$_2$ (4.4
ppm) grows in over time.

For the kinetic analysis, the area under each peaks was
integrated at various times and provides the rates of disappearance of
the starting material Me$_2$NHBH$_3$ and the appearance of the product
dimer [Me$_2$NBH$_2$]$_2$. These results are shown in Figure 3.

![Figure 3](image)

**Figure 3.** Time evolution of Me$_2$NHBH$_3$ disappearance/[Me$_2$NBH$_2$]$_2$
appearance in toluene in the presence of rhodium at room
temperature as determined by $^{11}$B{[H]} NMR.

**Conclusions**

The *in-situ* EXAFS experiments permit the observation of the
transition metal species during the progression of the reaction. The
predominant species observed during H$_2$ evolution does not appear to
be colloidal but most likely is composed of 2 to 6 Rh atoms
surrounded by tightly bound external ligands. This result is in
contrast to previous conclusions that suggest the mechanism involves
a heterogeneous catalyst.

We believe the combination of *in-situ* EXAFS spectroscopy to
identify the active catalyst species and *in-situ* NMR spectroscopy to
monitor kinetics provides a unique approach to answering the elusive
question for many reported ambiguities, “Is it homogeneous or
heterogeneous catalysis?”

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