

## Molecular Heterogeneous Catalysis: A single-site Zeolite-Supported Rhodium Complex for Acetylene Cyclotrimerization

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### Introduction

Attempts to anchor metal complexes to supports to obtain highly uniform catalytic sites have often been hindered by the non-uniformity of the support. Here we report the behavior of a catalyst with highly uniform active sites synthesized from  $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{CH}_3\text{COCHCOCH}_3)$  and a crystalline support, dealuminated Y zeolite. The supported catalyst consists of framework-bound bis-ethylene Rh sites. Treatment of this supported metal complex catalyst with acetylene initiates the catalytic acetylene cyclotrimerization to benzene. We report characterization of the catalyst by NMR and EXAFS spectroscopies complemented by density functional theory (DFT), having determined structures of the observable supported complexes and elucidated the catalytic cycle theoretically, including transition states.

### Materials and Methods

The zeolite-supported Rh catalyst was prepared from a slurry of  $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{acac})$  and highly dealuminated HY zeolite (DAY). The ethylene ligands were exchanged on a vacuum line with ethylene- $^{13}\text{C}_2$ , and acetylene- $^{13}\text{C}_2$  was added to the sample, which was characterized by  $^{13}\text{C}$  MAS NMR during the ensuing cyclotrimerization reaction. Once the NMR analysis was complete, EXAFS spectra were collected at beamline X-18B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Spectra were collected in transmission mode at the Rh K edge with the sample at liquid nitrogen temperature. Catalytic reaction experiments characterizing both acetylene cyclotrimerization and ethylene and propylene hydrogenation were carried out with a once-through quartz flow reactor; products were monitored by online GC-FID and GC-MS.[1]

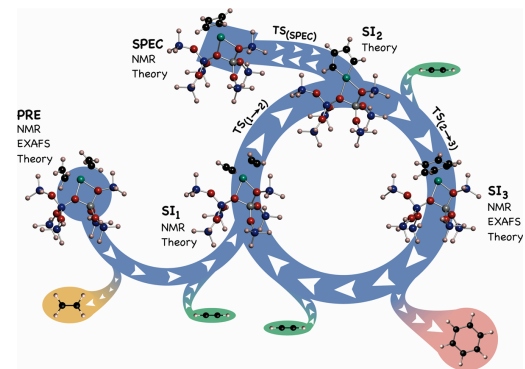
### Results and Discussion

Variable temperature  $^{13}\text{C}$  MAS NMR spectra show that the ethylene signals exhibit uniform rotation at the same frequency at a given temperature, consistent with the behavior of the ethylene ligands in the precursor in the liquid or crystalline state. The EXAFS data give no evidence of Rh–Rh contributions, consistent with absence of rhodium clusters and the presence of the rhodium exclusively in mononuclear site-isolated complexes.[2] The  $^{13}\text{C}$  NMR spectra characterizing the acetylene-treated catalyst indicate four distinct signals identified with species associated with the cyclotrimerization reaction. Comparison of this spectrum with the spectrum of the benzene- $^{13}\text{C}_6$ -treated catalyst shows the presence of gas-phase benzene and a

Rh-bound benzene complex. Determination of the species responsible for the two remaining signals in the spectrum was aided by theoretical modeling. Thus, candidate complexes were investigated, and their calculated chemical shifts were compared with experiment. The presence of bis-acetylene and cyclobutadiene complexes was established and further verified by comparison of the chemical shifts with those of analogous solution-state compounds. DFT was also used to construct the potential energy surface for the acetylene cyclotrimerization reaction on an  $\text{Al}(\text{OH})_4^-$  zeolite cluster model. Characterization of the catalyst following the cyclotrimerization reaction by EXAFS spectroscopy demonstrated that the monomolecular nature of the Rh species was retained, and the structure data agree with the DFT calculation.

### Significance

We report the first site-isolated supported metal species with essentially a uniform, molecular character and reactive ligands, as well as a catalytic cycle involving it. The work is based on characterization of the catalyst by  $^{13}\text{C}$  NMR and EXAFS spectroscopies complemented by DFT calculations.



**Figure 1.** Catalytic cycle for cyclotrimerization of acetylene catalyzed by a single-site  $\text{Rh}^+$  center bonded to a zeolite support by two Rh–O bonds.

### References

- Marcus, D. M.; McLachlan, K. A.; Wildman, M. A.; Ehresmann, J. O.; Kletnieks, P. W.; Haw, J. F. *Angew. Chem. Int. Ed.* **2006**, *45*, 3133-3136.
- Ehresmann, J. O.; Kletnieks, P. W.; Liang, A.; Bhirud, V. A.; Bagatchenko, O. P.; Lee, E. J.; Klaric, M.; Gates, B. C.; Haw, J. F., *Angew. Chem. Int. Ed.* **2006**, *45*, 574-576.

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