

Site-Isolated Pt-SBA15 Materials from Tris(*tert*-butoxy)siloxy Complexes of Pt(II) and Pt(IV)

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Introduction

The stabilization of isolated catalytic sites is one approach to synthesize catalysts that exhibit improved activity and selectivity [1]. Earlier investigations have focused primarily on site-isolated early transition metal centers grafted to oxide supports, and their catalytic function have been determined for number of partial oxidation reactions [2]. Late transition metal site-isolated complexes of Rh [3] have been synthesized from Rh siloxy complexes via the thermolytic precursor method (TMP) introduced by Tilley et al. [4]. Recently, we synthesized single-site Pt(II) and Pt(IV) siloxy complexes and grafted them to mesoporous SBA15 silica via the TMP approach [5]. We demonstrate the Pt precursors remain intact after grafting to the silica surface and are site-isolated up to ~473 K. These materials are active for hydrogenation of simple cyclic aromatics in the liquid phase and ethylene in the gas phase.

Materials and Methods

The synthesis of the tris(*tert*-butoxy)siloxy Pt(II) and Pt(IV) complexes was conducted under a nitrogen atmosphere using standard Schlenk techniques. The Pt(II) and Pt(IV) were characterized by single-crystal X-ray analyses, [¹H, ¹³C, ²⁹Si and ¹⁹⁵Pt] NMR, and x-ray absorption spectroscopy. The Pt(II)/ and Pt(IV)/SBA15 was prepared under a nitrogen atmosphere to avoid the hydrolysis of the Pt precursors. SBA15 was suspended in pentane, and a pentane solution of the Pt siloxy precursor was added at room temperature and stirred for 16 h. The wt % Pt loading was determined by absorption methods. X-ray absorption measurements were made on the insertion device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory (USA). Measurements were made in transmission mode at the Pt L_{III} absorption edge. The coordination parameters were obtained by a least-squares fit in *k*- and *R*-space of the isolated multiple-shell, *k*²-weighted Fourier transform data. The catalytic hydrogenation of cyclohexene and styrene were conducted in NMR tubes at 323 K. The hydrogenation of ethylene was conducted in a plug flow reactor at sub-ambient temperatures.

Results and Discussion

The tris(*tert*-butoxy)siloxy platinum complexes were synthesized in high yield and structurally characterized via single crystal X-ray diffraction. These precursors served as excellent sources for introduction of uniform, site-isolated Pt(II) and Pt(IV) centers on the silica surface via a low-temperature protonolysis reaction with surface Si-OH groups. Due to the direct Pt-OSi linkages, they serve as spectroscopic models for the supported Pt sites. The free complexes decomposed at ~175°C as determined by thermogravimetric analysis (Figure 1A). The supported Pt(II) and Pt(IV) centers retain many structural similarities to the

molecular precursors as shown by the thermolytic behavior of the siloxy complexes and the grafted species (Figure 1B). Upon heating in He, noticeable changes in the EXAFS spectra were observed, suggesting structural changes (i.e. loss of ligands) in the Pt centers.

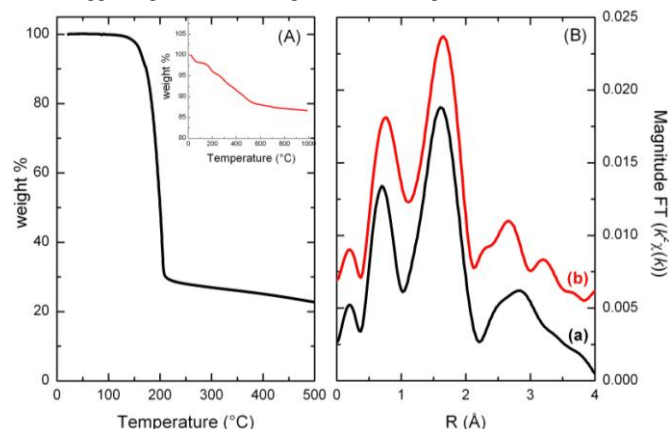


Figure 1. (A) TGA trace for Pt(II) complex in N₂. The inset is the TGA trace for the Pt(II) complex grafted to mesoporous SBA-15 silica. (B) X-ray absorption spectra of (a) Pt(II) and (b) Pt(II) complexes after grafting to SBA-15 at a weight loading of ~2% Pt.

Without ligand removal, the grafted materials had low activity for the liquid-phase hydrogenation of cyclohexene and styrene. After the removal of ligands under mild reducing conditions (~353 K), the grafted Pt(II) complex was active for the hydrogenation of ethylene at sub-ambient temperatures, while the grafted Pt(IV) complex required much higher temperatures for ligand removal, and subsequently had lower hydrogenation activity at 353 K compared with the Pt(IV) complex.

Significance

The ability to synthesize late-transition metal clusters with high stability has a number of fundamental and potential industrial significance. Site-isolated Pt centers should be identical and possess the same selectivity in a particular reaction leading to product streams containing high concentration of the desired product. From a fundamental prospective, structure-function (activity and selectivity) can be tested at the single site level for a number of reactions.

References

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