

# New Fe/SiO<sub>2</sub> materials prepared using diiron molecular precursors: Synthesis, characterization and catalysis

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Received 21 April 2005; revised 1 July 2005; accepted 7 July 2005

Available online 25 August 2005

## Abstract

Several well-defined diiron siloxide complexes have been synthesized, isolated, characterized, and used as molecular precursors for the grafting of well-defined isolated iron species on the surface of mesoporous silica SBA-15. The precursors have bridging siloxide ligands, a diamine linker, or a  $\mu$ -oxo diiron core, and their binuclear structures have been confirmed by elemental analysis, solution molecular weight measurements, and nuclear magnetic resonance spectroscopy. All precursors react with SBA-15 to immobilize the iron centers and produce silanol; the various stoichiometries and structural implications of these grafting reactions are discussed. Calcination of the grafted iron complexes yields materials largely devoid of organic components, and these calcined catalysts are active in the oxidation of hydrocarbons by hydrogen peroxide. The catalytic activities and selectivities of these materials are compared with each other and with those of other Fe/SiO<sub>2</sub> catalysts. Issues including iron-loading dependence and grafting conditions are discussed. Characterization of the catalysts by diffuse-reflectance ultraviolet–visible, X-band electron paramagnetic resonance, Mössbauer, and extended X-ray absorption fine structure spectroscopies indicates that although the diiron structures of the precursors are usually maintained during the initial grafting process, calcination results in their conversion to monoiron centers on the support. This theory is also consistent with the generally similar catalytic behaviors of materials prepared from diiron and monoiron precursors. The implications of these findings for the generality of molecular precursor techniques are discussed.

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**Keywords:** Molecular precursors; Hydrocarbon oxidation; Fe/SiO<sub>2</sub>; Diiron centers

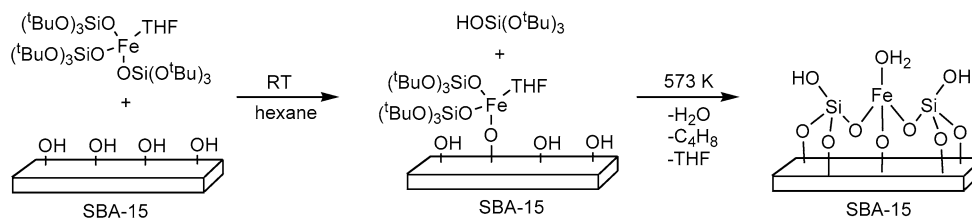
## 1. Introduction

Iron centers supported on inorganic oxides constitute a promising class of catalysts for the selective oxidation of hydrocarbons. Most prominently, iron-exchanged zeolites (Fe-ZSM-5) have proven to be uniquely effective catalysts for the monohydroxylation of benzene by N<sub>2</sub>O under relatively mild conditions [1,2]. To date, the structure of these

catalysts' active "α" sites remains a subject of vigorous debate; reports have proposed that the catalysis may occur at monoiron centers [3], diiron sites [4], or even larger iron clusters isolated within the zeolite matrix [5]. Both monoiron and diiron sites feature prominently in biological oxidation chemistry [6–15]; the development of synthetic mimics of iron-based oxidation enzymes for use as models and oxidation catalysts has been a subject of intense study for decades [16–24]. As such, the synthesis of related iron species in the context of a heterogeneous catalyst presents unique opportunities both to investigate diiron centers from a new perspective and to apply our knowledge of solution-phase systems

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Scheme 1.

to the understanding and improvement of the heterogeneous catalysts.

Many questions remain regarding fundamental characteristics of Fe-zeolite catalytic systems. A large body of knowledge regarding these catalysts has been compiled over many years of theoretical [25,26], spectroscopic [27–35], and microscopic [29,35] investigations of these materials, but these studies have yet to forge a consensus regarding the structure of the active catalyst. Findings from extended X-ray absorption fine structure (EXAFS) [36,37] and Mössbauer [27,31,34,38–40] spectroscopies have suggested the presence of both monoiron and diiron centers, and some studies have even demonstrated correlations between catalytic activity and specific spectroscopic features [34]. X-band electron paramagnetic resonance (EPR) spectroscopy [39,41] and transmission electron microscopy [29,42] have been used to follow the state of iron over the course of activation procedures, and the extra-framework iron (rather than framework iron or bulk iron oxide) have been identified as being crucial to catalytic activity. Nonetheless, conflicting results have frustrated the development of any widespread agreement regarding the specific structure of the active site.

A major obstacle to the unambiguous characterization of supported iron centers lies in the limitations of the methods conventionally used in their syntheses. Common approaches offer little rational control over the molecular detail of a material's structure, and thus no means of independently preparing and investigating proposed active structures. Iron is generally introduced to inorganic oxides as a simple inorganic salt [43–46], either during support synthesis or thereafter, and the active catalyst is prepared by subjecting the resulting material to steaming at high temperature [2,47]. Many studies have demonstrated the importance of this activation process, but it appears to serve chiefly to facilitate adoption of the most thermodynamically favorable iron distribution [28,31,34,35,42]. These methods thus offer no means by which to control the specific structure of the iron sites, and thus no opportunity to systematically compare the reactivities of the different structures proposed as active sites. Current methods also generally require the use of relatively low loading regimes to guarantee site isolation [48], which has been demonstrated to be a key to activity in many catalytic systems [49–52]. By overcoming these limitations, new methods allowing for the direct control of active site structure at the molecular level would pave the way for useful investigations and the rational preparation of improved materials.

One such method is the use of molecular precursors, wherein carefully designed metal complexes are introduced to the support under conditions in which they retain their original structure. There is growing evidence that this technique can be useful in the controlled preparation of well-defined inorganic materials [53–58]. We recently reported the application of such an approach to the preparation of strictly isolated monoiron centers on mesoporous silica SBA-15 [59] (chosen for its large pores and relatively simple surface structure) [60]. Introduction of the bulky iron siloxide complex (THF)Fe[OSi(O<sup>t</sup>Bu)<sub>3</sub>]<sub>3</sub> (**1a**) to a hydroxylic support results in the attachment of iron atoms to the surface through the formation of new Fe–O bonds (and concomitant liberation of silanol) (Scheme 1). Subsequent calcination yields an inorganic catalyst active in the oxidation of hydrocarbons by hydrogen peroxide. Initial spectroscopic investigations and more recent EXAFS studies [61] have demonstrated that the iron centers are isolated. This structural feature can be credited both to the bulky structure of the precursor and to the clean, mild, nonaqueous conditions of its grafting. Formation of isolated iron centers in this system is an outcome that stands in marked contrast to the results of conventional impregnation conducted at similar iron loadings; materials prepared by the latter route contain substantial amounts of bulk iron oxide [43–46], as do all known Fe/SiO<sub>2</sub> materials subjected to high-temperature steaming [38,62,63]. Thus, the molecular precursor approach affords a material with an iron distribution subject to kinetic control and permits tuning of the local iron structure through precursor design.

As an extension of our work on isolated monoiron catalysts, we sought to prepare and graft diiron precursors to investigate the stability and oxidation activity of isolated diiron centers on oxide surfaces.  $\mu$ -Oxo diiron centers are also ubiquitous in homogeneous oxidation systems of both biological [7,9,10] and synthetic [64,65] origin. Herein we report the results of efforts to support diiron centers on mesoporous silica using the molecular precursor technique, and the catalytic behavior of the resulting materials.

## 2. Experimental

### 2.1. General procedures

Unless otherwise indicated, all procedures were carried out under nitrogen atmosphere using standard Schlenk tech-

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