



Supported iron catalysts for Michael addition reactions

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ARTICLE INFO

Article history:

Received 5 November 2017

Received in revised form

17 December 2017

Accepted 19 December 2017

Available online 4 February 2018

Keywords:

Iron

Heterogeneous

Michael addition

Dendrimer

Silica

ABSTRACT

Heterogeneous catalysts have been widely used for chemical transformations and offer easy product separation in addition to their high activity. Iron is an earth-abundant metal, but it has not been studied thoroughly as heterogeneous catalysts for organic reactions. In this work, supported iron catalysts were synthesized via loading FeCl₃ onto a mesoporous silica SBA-15. These catalysts were highly active for Michael addition reactions, a synthetic pathway for forming C–C bonds that is typically achieved by homogeneous catalysts. Our studies show that for the supported iron catalysts, larger pore sizes of the silica resulting from the loading of iron and the oxidation state of iron being Fe(III) are essential for the high reaction rates. Notably, the catalysts show stability against leaching, regardless the presence or absence of a dendrimer as an additional stabilizing agent. The catalysts could be used for at least three runs without the loss of activity. The successful Michael addition reactions of indole or 2-methylindole and different α,β -unsaturated ketones corroborate the synthetic scope of the catalysts. These results show promises of using supported iron catalysts as inexpensive and effective alternatives for the formation of C–C bonds.

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1. Introduction

The large majority of catalysts consist of metals, specifically precious metals such as Pt, Pd, Au, and Rh [1]. Many of these catalysts have been synthesized in the form of heterogeneous catalysts, which offer many benefits, including easy product separation, recyclability, and efficiency. These metal-containing heterogeneous catalysts can be loaded into porous supports, such as silica [2], in order to achieve heterogeneity. However, precious metals are vulnerable to leaching in organic solutions as sometimes they cannot attach strongly to the silica framework [3–6]. Heavy metals, such as Pt, have been shown to be toxic depending on the dose and type of exposure, acute or chronic [7]. Aside from toxicity, metal leaching reduces the catalytic efficacy of a catalyst over time. Dendrimers have been used to prevent toxic metal leaching and to improve the overall stability and recyclability of metal-containing heterogeneous catalysts [8–10].

Iron is an inexpensive earth-abundant metal and has been an attractive element for catalysis [11–16]. The synthesis and characterization of Fe salts loaded onto mesoporous silica SBA-15 has been explored by Kuhn et al. [17] and Tilley et al. [18], but the catalytic performances of these materials have yet to be studied in comparison to those containing dendrimers [17–19]. In this study, the hydroxyl-terminated generation-4 polyamidoamine (PAMAM) dendrimer, denoted as G4OH, are investigated as a potential stabilizer of iron, as they are known to encapsulate and stabilize the nanoparticles of noble metals including Pt, Pd, Au, and Rh [9,20–24]. Supported iron catalysts with or without G4OH were synthesized, characterized, and compared in catalytic Michael addition reactions. A Michael addition reaction involving indole and butenone was used as a model reaction to test the ability of supported iron catalysts to catalyze C–C bond formation. C–C bond formation reactions remain one of the most useful but challenging chemical processes for use in synthetic industries [25], among which Michael addition reactions are an important part of the total synthesis for many complex organic compounds [26]. The formation of C–C bonds under mild conditions is necessary for the commercial production especially in the pharmaceutical industry [27,28]. Previously, Pitchumani et al. showed that Michael addition reactions were achieved by an acidified silica under mild conditions with high yields [29]. In this work, the characterization of supported iron catalysts, reaction kinetics studies, metal-leaching tests, and cata-

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lyst recyclability tests were carried out to understand the catalytic properties of supported iron catalysts. Supported iron catalysts show promises in that they are not only highly active but also stable as they bind strongly to the silica support framework.

2. Experimental

2.1. General information

Unless otherwise noted, all commercial materials were used as received without purification. All glassware was dried at 100 °C for 8 h before use.

2.2. Chemicals

Iron (III) chloride ($\geq 99.99\%$), iron(II) sulfate heptahydrate ($\geq 99.0\%$), indole (98%), 2-methylindole (98%), butenone (99%), 2-cyclopenten-1-one (98%), 2-cyclohexen-1-one ($\geq 95\%$), 4-phenyl-3-buten-2-one (99%), and 1,3-diphenyl-2-propenone ($\geq 98.0\%$) were purchased from Sigma-Aldrich. All PAMAM dendrimers, G4OH, G4NH₂, and G4SA were purchased from Dendritech Inc. as water solutions. Deuterated solvents (chloroform, toluene, benzene, water, methanol, and acetonitrile) were purchased from Cambridge Isotope Laboratories, Inc.

2.3. Instruments

The catalyst loading was analyzed by Optima 7000 DV Inductively coupled plasma optical emission spectroscopy (ICP-OES). The transmission electron microscopy (TEM) images were taken with an FEI Tecnai TEM at an accelerating voltage of 200 kV. All NMR spectra were obtained at ambient temperature on Bruker AVB-400 and AVQ-400 spectrometers. Centrifugation was performed on a Thermo Scientific IEC Centra[®] CL2. Physisorption experiments were recorded on Micromeritics 3Flex with Ultra-high-purity grade N₂ (Praxair, 99.999% purity). A liquid nitrogen bath was used for the measurements at 77 K. Powder X-ray diffraction (PXRD) patterns were recorded using a Rigaku Miniflex 600 (Bragg–Brentano geometry, Cu K α radiation $\lambda = 1.54 \text{ \AA}$) diffractometer. X-ray photoelectron spectrometric (XPS) experiments were performed on a Perkin-Elmer PHI 5300 XPS spectrometer with a position-sensitive detector and a hemispherical energy analyzer in an ion-pumped chamber (evacuated to 2×10^{-9} Torr). The Mg K α ($h\nu = 1253.7 \text{ eV}$) X-ray source of the XPS spectrometer was operated at 350 W with 15 kV acceleration voltage.

2.4. Synthesis of the support

The procedure established by Zhao et al. was followed for the synthesis of the support SBA-15 [30]. Briefly, 8 g of Pluronic 123 was dissolved in 60 g of deionized H₂O and 240 g of 2 M HCl with stirring at 35 °C for 1 h. Then, 17 g of tetraethyl orthosilicate was added and allowed to stir for an additional 20 h. Next, the mixture was aged at 80 °C for 24 h overnight without stirring. The resulting solid was collected by filtration and washed with water and ethanol, and then finally dried at 100 °C. The solid was then heated to 500 °C in 8 h and held at 500 °C for 6 h and then allowed to cool. The resulting solid, SBA-15, was grinded using mortar and pestle and stored before usage.

2.5. Synthesis of catalysts

For the synthesis of the supported iron catalyst Fe/SBA-15, approximately 0.06 mmol of FeCl₃ (9.73 mg), 1 g of SBA-15, and 60 mL of H₂O was mixed for 24 h at room temperature with stirring. Care was taken to quickly weigh FeCl₃ as it is extremely

Table 1
Loading amount of iron in catalysts.

catalyst	Fe concentration (mmol/g) ^a	percent loaded (%) ^a
Fe/G4OH/SBA-15	4.49×10^{-2}	74.9
Fe/G4OH/SBA-15(10 \times)	1.97×10^{-1}	65.7
Fe/SBA-15	4.54×10^{-2}	75.7
Fe/SBA-15(10 \times)	2.13×10^{-1}	71.0

^a Approximately 10 mg of each catalyst was used in ICP-OES analyses. Samples were prepared by digesting approximately 10 mg of a solid catalyst in a centrifuge tube with 0.2 mL HF, 0.2 mL HNO₃, and 0.6 mL HCl, and then diluted to 10 mL with deionized water. The total amount of iron in the sample was calculated accordingly, which was divided by that amount of iron used in the synthesis process to calculate the loading percentage.

hygroscopic. The mixture was centrifuged at 4000 rpm for 5 min, the supernatant was discarded and the resulting solid was dried at 100 °C for 20 h. In addition, a version was synthesized with the G4OH dendrimer, and the resulting catalyst was called Fe/G4OH/SBA-15. The synthesis of Fe/G4OH/SBA-15 is similar to that of Fe/SBA-15. First, 1 g of SBA-15, 1.5 μmol of G4OH dendrimer, and 30 mL of deionized H₂O were allowed to stir for three hours at room temperature. Then the solution was centrifuged for 5 min at 4000 rpm, and the supernatant was discarded. Next, 0.06 mmol of FeCl₃ was added and allowed to mixed for 24 h at room temperature with stirring. The mixture was centrifuged at 4000 rpm for 5 min, the supernatant was discarded and the resulting solid was dried at 100 °C for 20 h. Two other catalysts were also synthesized using 0.6 mmol of FeCl₃ without or with 15 μmol of G4OH in the same way, which are denoted as Fe/SBA-15(10 \times) and Fe/G4OH/SBA-15(10 \times), respectively.

2.6. Representative procedure for catalytic reactions

To a dry 2 mL reaction vial equipped with a stir bar, were added 0.05 mmol of butenone, 0.06 mmol of indole, 0.2 mL CDCl₃, and a catalyst. The reaction mixture was heated with stirring at the desired temperature for 22 h. The mixture was then cooled to room temperature, and the solid catalyst filtered using a polytetrafluoroethylene syringe filter. The filtrate was transferred to a NMR tube for analysis.

3. Results and discussions

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to determine iron concentrations of the supported iron catalysts, and the results are summarized in Table 1. 75.7% and 74.9% of iron used in the synthesis were found to be loaded into Fe/SBA-15 and Fe/G4OH/SBA-15, respectively (Table 1). While the Fe/SBA-15(10 \times) catalyst had 4.7% lower loading percent compared to Fe/SBA-15, the Fe/G4OH/SBA-15(10 \times) catalyst had a decrease of 9.2% in loading compared to Fe/G4OH/SBA-15. The dendrimer decreases the loading percent of iron, which is more significant at higher concentrations of iron.

N₂ physisorption isotherms show that the addition of iron increased the pore size of the SBA-15, which is likely due to the restructuring of the pores during the loading process, while the G4OH dendrimer decreased the pore size because of their steric bulk (Fig. 1A). The physisorption isotherms for all four samples are Type IV isotherms which are indicative of multilayer adsorption [31]. The supported iron catalysts retain their mesoporous structure after the synthetic process, as expected. In the case of Fe/G4OH/SBA-15(10 \times), the non-negligible amount of G4OH greatly decreased the pore size, which outweighed the effect of the iron on the SBA-15. In addition, the lower S_{BET} of Fe/G4OH/SBA-15(10 \times) shows that surface areas decrease with the addition of dendrimers (Table 2). Similarly, the V_{micro} was reduced for samples contain-

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