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Highly dispersed iron oxide nanoclusters supported on ordered mesoporous SBA-15: A very active catalyst for Friedel–Crafts alkylations

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Abstract

Iron oxide supported on ordered mesoporous SBA-15 was prepared by impregnating as-synthesized SBA-15 with a methanolic solution of $Fe(NO_3)_3 \cdot 9H_2O$, characterized by X-ray diffraction (XRD), N_2 sorption, transmission electron microscopy (TEM), and UV–vis spectroscopy. Characterization revealed that iron oxide was present as highly dispersed nanoclusters in the well-ordered mesoporous channels of SBA-15. The supported material still maintained its ordered mesoporous structure similar to SBA-15 and possessed high surface area, large pore volume and uniform pore size.

The benzylation of benzene by benzyl chloride showed that iron oxide nanoclusters-supported SBA-15 was a very active catalyst and able to activate the reactant at relatively low temperature such as 313 K. Moreover, the catalyst could be reused. Such outstanding catalytic performance should be attributed to the presence of active sites from iron oxide nanoclusters, large surface area, open pore channels, and high pore volume. Additionally, the catalyst has found potential applications in other Friedel–Crafts alkylations, especially to large molecular reactions due to its ordered mesoporous structure.

Keywords: Iron oxide; Nanoclusters; SBA-15; Ordered mesoporous; Friedel–Crafts; Alkylation; Benzyl chloride; Benzylation

1. Introduction

Friedel–Crafts alkylations are very important class of reactions in organic chemistry [1,2]. Among these reactions, the liquid phase benzylation of benzene and other aromatic compounds by benzyl chloride, or benzyl alcohol is important for the production of diphenylmethane and substituted diphenylmethanes which are key industrial compounds used as pharmaceutical intermediates or fine chemicals. Generally, such reactions were carried out using strong homogeneous acid catalysts such as $AlCl_3$, $FeCl_3$ and H_2SO_4 [1–4]. However, these catalysts are associated with problems such as corrosion, toxicity, handling, and difficulty in separation and recovery of the catalyst. Therefore, there has been lots of interest to replace these homogenous catalysts by heterogeneous solid catalysts [5–8].

Zeolites like H-ZSM-5 and HY, as a member of solid catalysts, have received much attention because of their strong acidity and regular porous structure with excellent stability. Thus, some studies reporting their catalytic performance in the benzylation reaction have been carried out [9–11]. However, the results indicated that highly acidic zeolite catalysts showed poor activity for the reaction, because of diffusion limitation caused by their microporous network [9,10].

Recently, the discovery of a new family of ordered mesoporous silica materials (M41S) is of considerable interest

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because of their regular pore array with uniform pore diameter (2.0–8.0 nm), high surface area and pore volume [12]. However, the pure-silica mesoporous materials are of limited use in many catalytic reactions because of their lack of active sites. Thus, according to the requirement of various catalytic reactions, various active species were introduced into the ordered mesoporous silica materials by various methods. For example in the benzylation of benzene, iron species have been directly introduced into the synthesis of Si-MCM-41 [13]; various Lewis acidic catalysts ($AlCl_3$, $ZnCl_2$, $FeCl_3$, $GaCl_3$ and $InCl_3$) [14–16] and metal oxides (Ga_2O_3, In_2O_3, Tl_2O_3 and Fe_2O_3) [17,18] have been supported in ordered mesoporous Si-MCM-41 by incipient wetness technique. The studies indicated that mesoporous materials containing iron species exhibited outstanding catalytic activity in the reaction. It has been suggested that for the reaction nano-sized Fe_2O_3 clusters with high degree of coordinative unsaturation should be much more reactive iron species and even that isolated iron species are inactive [19,20].

More recently, SBA-15, another new type of ordered mesoporous material prepared by using a tri-block copolymer as structure-directing agent, has attracted more attention [21]. SBA-15 material possesses a high surface area and uniform tubular channels with tunable pore diameters in the range of 5–30 nm, which are significantly larger than those of MCM-41. Especially due to its thicker walls, SBA-15 provides a thermal stability and hydrothermal stability that exceed those for MCM-41 with thinner walls. Additionally, cheaper surfactant was used during its preparation. Obviously, SBA-15 is a more ideal catalytic support than MCM-41. However, to the best of our knowledge, up to now only Al-SBA-15 was studied for the benzylation of benzene and exhibited poor reactivity in the reaction due to the presence of less active catalytic species [22].

In the present work, we report that iron oxide nanoclusters have been successfully supported on ordered mesoporous SBA-15, which were characterized by XRD, UV–vis spectroscopy and TEM. The catalytic performance of the sample was evaluated by using the model reaction of the benzylation of benzene.

2. Experimental

2.1. Preparation of catalyst

Mesoporous SBA-15 silica was prepared according to the literature procedure using Pluronic P123 tri-block polymer ($EO_{20}PO_{70}EO_{20}$, $M_{av} = 5800$; Aldrich) as surfactant in acidic conditions [21]. Briefly, a solution of $EO_{20}PO_{70}EO_{20}$-2M HCl–TEOS–H_2O (2:60:4.25:15) (mass ratio) was prepared, stirred for 20 h at 313 K, and then hydrothermally treated at 373 K for 24 h. The obtained products were filtered, washed and dried in air at room temperature, labeled as u-SBA-15. By the weight loss before and after calcination, it is estimated that the weight percentage of surfactant is 43% in u-SBA-15.

The iron oxides-supported SBA-15 catalysts were prepared by incipient wetness technique. Typically, u-SBA-15 was impregnated with a calculated amount of $Fe(NO_3)_3{\cdot}9H_2O$ in methanol solution and stirred at room temperature. Finally, the resulting material was dried, and calcined at 773 K for 5 h in air. According to the expected Fe loading (2.9%, 5.6%, 10.5%, 14.7% and 24.5%), the samples were labeled as FSA-3, FSA-5, FSA-10, FSA-15 and FSA-25, respectively.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer equipped with a SolX detector – Cu Kα radiation with wavelength of $\lambda = 1.5406$ Å. UV–vis spectroscopy was recorded with a Perkin Elmer lambda 9 UV–vis-NIR spectrometer and a Harrick Praying Mantis diffuse reflectance optical accessory. A 1% attenuator was placed in the reference beam. The background correction was performed with a piece of Spectralon in either the cell or the sample holder. The measurement parameters were scan speed 240 nm/min, slit width (UV–vis) 2.0 nm, sensitivity (NIR) 2.0. TEM images were recorded on Philips CM 200 LaB6 operated with an acceleration voltage of 200 kV. Nitrogen adsorption isotherms were obtained at 77 K on a Micromeritics Tristar Gas Sorption and Porosimetry system. Samples were normally prepared for measurement after degassing at 423 K under vacuum until a final pressure of 1×10^{-3} Torr was reached.

2.3. Catalyst tests

The liquid phase benzylation of benzene with benzyl chloride (BC) was carried out in a two necked round-bottomed flask equipped with a reflux condenser and heated in a precisely controlled oil bath under atmospheric pressure. In a typical run, 10 ml of benzene and 0.9 ml of 1,2-dichlorobenzene as internal standard were added to the catalyst (which had been activated overnight at 383 K). The reaction mixture was maintained for 30 min at the required reaction temperature, and then 0.9 ml of benzyl chloride was added. The moment was regarded as initial reaction time. Liquid samples were withdrawn at regular intervals and analyzed by gas chromatography on a HP 5890 Series II with an FID detector using a 30 m packed column PONA. Since benzene was in excess, conversion was calculated based on the benzylating reagent, i.e. BC.

The reused catalyst was obtained based on the method that the catalyst after the first complete conversion was separated from the reaction solution and then calcined at 773 K at 5 h.

3. Results and discussion

3.1. Catalytic activity of the samples with various Fe loading

Generally, in the benzylation of benzene by benzyl chloride, the loading of catalyst for each test was 0.1 g. A mild reaction temperature (333 K) to test the catalytic activities of our samples has been chosen. Fig. 1 shows the conversion of various samples after the reaction time of 30 min. It is seen that