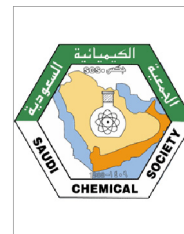




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ORIGINAL ARTICLE

[CTA]Fe/MCM-41: An efficient and reusable catalyst for green synthesis of xanthene derivatives

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Abstract Iron was incorporated into MCM-41 via direct synthesis and wet impregnation methods. Removal of the surfactant occluded in Fe/MCM-41 pores has been performed by using two procedures: solvent extraction and calcination. For comparison, a series of template-containing mesoporous Fe/MCM-41 were also synthesized without surfactant removal. The catalysts were examined in three component reaction to afford benzoxanthene derivative. A high yield of 91% was achieved over template-containing Fe/MCM-41 catalyst. This high activity is due to both Lewis acid sites and ionic template. This catalyst could be easily recovered by filtration and reused without loss of its catalytic activity because the organic template does not leach during the reaction. It is also very efficient for the synthesis of a hydroxanthene derivative.

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1. Introduction

Xanthenes and benzoxanthenes are important categories of organic compounds. They have various pharmacological activities such as antibacterial (Omolo et al., 2011), antiviral (Ion et al., 1998), antiplasmodial (Azebaze et al., 2006), and anti-inflammatory properties (Poupelin et al., 1978), and have been utilized as antagonists for drug-resistant leukemia lines (Nguyen et al., 2009).

There are several methods for the synthesis of xanthene derivatives; these compounds are conventionally prepared using condensation of aromatic aldehydes and β -naphthol with dimedone in the presence of acid catalysts such as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and [bmim][BF₄] ionic liquid (Fan et al., 2005), Fe^{3+} -montmorillonite (Song et al., 2007), silica-sulfonic acid (Mohammadi Ziarani et al., 2011), heteropolyacid supported MCM-41 (Karthikeyan and Pandurangan, 2009) and nanospherical mesoporous Lewis acid polymer Sc(OTf)₂-NSMP (Zhang et al., 2014).

Recently, mesoporous molecular sieves (like MCM-41 and MCM-48), have attracted much interest in catalysis, due to the high surface area, well defined pore shape, narrow pore size distribution, and good thermal stability. These are particularly attractive for heterogeneous reactions of large organic molecules for which microporous zeolites cannot be used. These mesoporous material, are prepared by using ionic surfactants (Beck et al., 1992). Generally, the residual templates inside the pores are removed by calcination or extraction. As ionic surfactants contain an organic cation such as cetyltrimethylammonium ($\text{C}_{19}\text{H}_{42}\text{N}^+$) and an inorganic anion, we hypothesized

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that could resemble ionic liquid. Herein, we report for the first time the preparation of two xanthene derivatives in the presence of template-containing Fe/MCM-41 as heterogeneous catalyst under solvent free conditions.

2. Materials and methods

2.1. Materials

Cetyltrimethylammonium bromide (CTAB) was purchased from Sigma-Aldrich Inc. and the other reagents were purchased from Merck company.

2.2. Methods

2.2.1. Catalyst preparation

– Direct Synthesis method (DS)

Fe/MCM-41 samples were synthesized according to standard literature procedure (Tantirungrotechai et al., 2011). In a typical non-hydrothermal synthesis, 2.74 mmol of CTAB was dissolved in 480 mL of NaOH aqueous solution (15.0 mM), followed by a drop wise addition of 22.4 mmol of tetraethylorthosilicate (TEOS). Then, a solid powder of iron nitrate (0.18 g) was slowly added. The mixture was vigorously stirred and heated to 80 °C for 2 h. Subsequently, the product powder was isolated by hot filtration, washed with deionized water and air-dried.

In some preparations, the cationic surfactant was removed either by hot solvent extraction or by calcination in air at 640 °C for 6 h. The solvent extraction was performed by stirring 1 g of the air-dried product with a 1 M HCl solution in ethanol (liquid: solid 300 mL/g) at 333 K for 24 h. Then the mesoporous material was collected by filtration and dried at room temperature. In order to compare the effect of the template, a series of as-synthesized molecular sieves, containing their organic template, were also tested for benzoxanthene synthesis without further modification. Moreover physical mixture of Fe/MCM-41 WI (0.1 g) and CTAB (0.02 g) was also used for synthesis reactions.

– Wet Impregnation method (WI)

0.18 g of $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 10 ml distilled water. 0.9 g calcined MCM-41 was added to the iron nitrate solution. After stirring for 3 h at room temperature, the solid was filtered from the solution and dried at 60 °C.

2.2.2. Catalyst characterization

XRD measurements were performed on a Philips-PW 17C diffractometer with Cu K_α radiation over the 2θ range 1–10°. The elemental chemical compositions of the samples were determined by EDX (VEGA\\TESCAN-LMU, Czech Republic) under vacuum mode for precise measurement of both light and heavy elements. FTIR spectra were recorded on a Bruker Tensor 27 instrument using KBr pressed powder discs. A Mettler Toledo thermogravimetry (TG/SDTA 851) was used for thermogravimetric analysis (TGA). About 10 mg of the sample was heated at 10 °C/min to 700 °C in air flow (100 ml/min).

2.2.3. Synthesis of 12-phenyl-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthene-11(1H)-ones (Compound 1)

A mixture of β -naphthol (0.144 g, 1 mmol), dimedone (0.140 g, 1 mmol), benzaldehyde (1 ml, 1 mmol) and Fe/MCM-41 (0.1 g), was stirred in an oil-bath (110 °C). After completion of the reaction, as monitored with TLC, the reaction mixture was cooled to room temperature; ethyl acetate (15 mL) was added to it, stirred for 10 min. Then the catalyst was separated by filtration (for separation of calcined catalysts, a magnet was put at the bottom of the reaction flask). Finally, ethyl acetate was evaporated under vacuum to give the crude product. The crude product was recrystallized from EtOH to yield pure xanthene-11-one derivatives.

All of the pure products were characterized by comparison of their physical (melting point) and spectral data ($^1\text{H NMR}$) with those of authentic samples (Supplementary information).

2.2.4. Synthesis of 9-phenyl-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydroxanthene-1(1H),8(2H)-dione (Compound 2)

This xanthene derivative was synthesized by the above mentioned procedure with 2 mmol dimedone without introducing of β -naphthol.

3. Results and discussion

Most attempts to introduce surface-bound active sites have centered on aqueous impregnation methods. Wet impregnation involves bringing the precursor solution into the pore space of the support. However, it has been found that catalysts prepared by this method have a limited reusability, since in this method, active species leach out from the support due to a weak interaction of metal ions with silica. To avoid this problem we used direct synthesis approach for incorporating the metal into the MCM-41, where an iron precursor salt is present in the MCM-41 synthesis gel.

The low angle XRD pattern of MCM-41 exhibits four well-resolved peaks with a very intense diffraction peak (100) at $2\theta \approx 2.5^\circ$ and three peaks with lower intensity at higher degree (3–5°) which were indexed to the 110, 200, and 210 reflections of the hexagonal P6mm honeycomb lattice (Kresge et al., 1992). The XRD results suggested that the ordered mesoporous structure of as-synthesized MCM-41 was preserved after the introduction of iron species (Fig. 1a). Although after incorporation, Fe/MCM-41(WI) changed into more disordered structure in comparison with Fe/MCM-41(DS), as the whole metal precursor retained on the support (Fig. 1b).

The elemental concentration on the catalyst is reported in Table 1. EDX results show that WI method can achieve a high metal loading, because there is no intermediate washing step involved in the wet impregnation approach, in contrast to the direct synthesis procedure. Furthermore, the solvent extraction method decreases metal loading because during this process, the iron ions leaches out of the support.

3.1. Influence of the template removing method

Two methods have been widely used to remove the organic templates molecules: calcination at 500–600 °C, in air or oxygen atmosphere, and extraction with a hot conventional

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