Synthesis, characterization and application of a nano-manganese-catalyst as an efficient solid catalyst for solvent free selective oxidation of ethylbenzene, cyclohexene, and benzylalcohol

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ABSTRACT

The object of this study is to synthesize the heterogeneous Mn-nano-catalyst (MNC) which has been covalently anchored on a modified nanoscale SiO_2/Al_2O_3, and characterized by FT-IR, UV-Vis, CHN elemental analysis, EDS, TEM, and EDX. The method is efficient for the highly selective oxidation of ethylbenzene, cyclohexene, and benzylalcohol without the need to any solvents, using *tert*-butyl hydroperoxide (TBHP) as an oxidant. Oxidation of ethylbenzene, cyclohexene, and benzylalcohol gave acetophenone, 2-cyclohexene-1-one and benzaldehyde, respectively, as major products. Reaction conditions have been optimized by considering the effect of various factors such as reaction time, amounts of substrates and oxidant, Mn-nano-catalyst and application of various solvents.

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1. Introduction

The oxidation of organic substrates into useful organic compounds is a fundamental reaction in the organic chemistry both for basic researches and chemical industries [1,2]. Recently, significant amounts of transition metal complexes accompanied by Schiff base as ligand have been used as heterogeneous catalysts, due to their high activity, eco-friendly and selectivity [3–5]. Production of benzylic and allylic ketons were carried out before by oxidizing the C—H bond using stoichiometric amount of $KMnO_4$ [6], H_2O_2 [7,8], CrO_3—SiO_2 [9], and *tert*-butyl hydroperoxide (TBHP) [10–16] as oxidizing agents. Transition metal complexes mainly used as catalyst to promote the oxidation reaction as the manganese complexes have considerable advantages [17–20]. Considerable researches have been devoted to find efficient catalysts for the selective side chain oxidation of alkyl aromatics and allylic substrates. The following catalytic systems were used for the oxidation of ethylbenzene(EB) to acetophenone (AP) such as, metal acetylacetone [21], metalloporphyrins [22,23], macrocyclic [24] and metal complexes supported on alumina/silica [25], salen-Mn (III)/MCM-41 [26], Si/Al-Pr-NH-et-N = methyl-2-Pyridylketone-Mn [15], SF-ATPS-Mn(III) TMCPP [27], Mn(salen)-POM [28], M-APO-11 (M = Co, Mn and V) [29], Zeolite encapsulated metal complexes [30], Co tetraphenylporphyrins [31] and the PS-PAR-Co [32]. The allylic oxidation of olefin to α,β-unsaturated ketone is an important transformation in natural product synthesis [33]. For the article reported in oxidation of cyclohexen to 2-cyclohexen-1-one, $[Mn(H_4C_6N_6S_2)]$ [34], [Mn(Sal-1.3-phen)]-NaY [35], $[Mn(bpy)_2]Cl_2$-Al_2O_3 [36], manganese porphyrin [37] and salophen Mn(III) complexes [26] can be mentioned.

In addition, to study the variation of the Mn catalyst, we report a simple and general synthesis of manganese ions immobilized onto the factionalized SiO_2-Al_2O_3 mixed oxide with the Schiff base ligand, and a methodology planned for the selective and eco-friendly oxidation of ethylbenzene, cyclohexene and benzylalcohol with TBHP.

2. Experimental

2.1. Materials and instruments

All reagents were purchased from the Merck and Fluka chemical companies. Reagents were used without extra purification, but solvents were purified with standard methods. Inductively coupled

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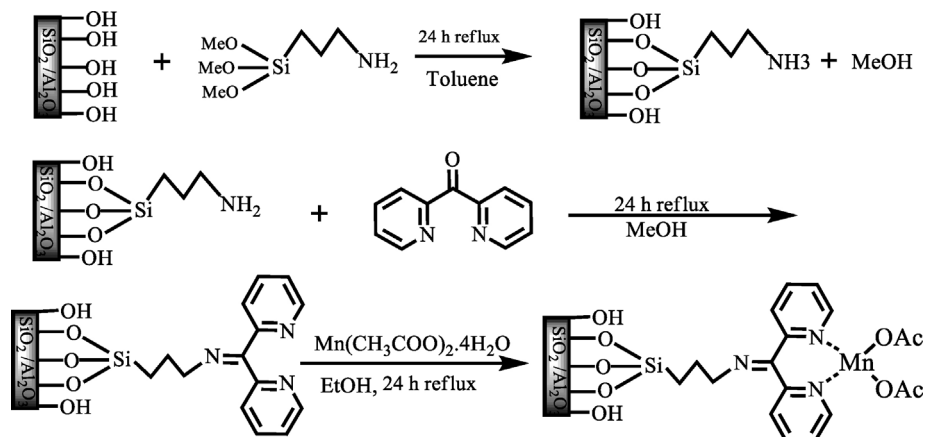
Scheme 1. Typical preparation procedure of Si/Al-APTMS-BPK-Mn catalyst.

plasma (ICP) measurements for Mn content evaluation were performed using a Perkin-Elmer ICP/6500. Infrared was collected on KBr pellets using a JASCO FT/IR (680 plus) spectrometer and the position of an infrared band is given in reciprocal centimeters (cm^{-1}). Diffuse reflectance spectra were registered on a JASCO-550 UV–vis spectrophotometer which was equipped with a diffuse reflectance attachment in which $BaSO_4$ was used as the reference. Type and quantity of the resulting products from oxidation were determined by a HP 6890/5973 GC/MS instrument and analyzed by a Shimadzu GC-16A gas chromatograph(GL-16A gas chromatograph with a $5\,m \times 3\,mm$ OV-17 column, 60–220 °C (10 °C/min), Inj. 230 °C, Det. 240 °C). For elemental analysis a CHN-Rapid Heraeus elemental analyzer (Wellesley MA) was used. Before carrying out the Nitrogen (99.999%) adsorption experiments, the sample was outgassed at 393 K for 14 h, then the experiment was carried out at 76 K using a volumetric apparatus (Quantachrome NOVA automated gas sorption analyzer). The specific surface areas were calculated, using the BET (Stephen Brunauer, Paul Hugh Emmett, and Edward Teller) method. The images of scanning electron micrograph (SEM) and transmission electron microscopy (TEM) were taken using a Philips 501 microscope and a Tecnai F30TEM operating at 300 kV, respectively. In addition, energy dispersive X-ray analysis was conducted on each sample. In order to count nanoparticles in reverse microemulsion, size distribution was measured by Zetasizer Nano-ZS-90 (ZEN 3600, MALVERN instruments).

2.2. Preparation of Organometallic nanosized SiO_2/Al_2O_3

SiO_2/Al_2O_3 nanosized was used as the support prepared by the sol–gel method [15]. At first, 3.5 g of nanosized SiO_2/Al_2O_3 was activated at 500 °C for 5 h under air and then refluxed with 4.3 mL of trimethoxysilylpropylamine (3-APTMS) in dry toluene (50 mL) for 24 h. The solid achieved during this process was filtered and washed off with dry methanol at 100 °C under vacuum for 5 h. Then bipyridylketone (BPK) was added to the suspended solution of SiO_2/Al_2O_3-APTMS in dry methanol. To synthesize the SiO_2/Al_2O_3-APTMS-BPK-Mn (Scheme 1), 2.0 g of SiO_2/Al_2O_3-APTMS-BPK was suspended in 50 ml of ethanol in a round bottom flask followed by adding of 3.0 mmol $Mn(OAc)_2 \cdot 4H_2O$. The mixture was refluxed during 24 h under magnetically stirring.

2.3. General procedure for the oxidation of ethylbenzene, cyclohexene and benzyl alcohol

In this procedure the heterogeneous catalyst (5.0 mg), the substrate (9.0 mmol) and an oxidant (9.0 mmol, 80% aqueous solution TBHP) were added in three necked round bottom flask equipped with a refluxed condenser. The mixture was stirred at desired temperature. After filtering and washing with solvent, the filtrate was monitored by GC analysis. The products were identified by GC–MS techniques. The conversion and selectivity were calculated with GC area normalization. Finally, comparative experiments were performed under different conditions.

3. Results and discussion

3.1. Characterization

Using BPK and $Mn(OAc)_2 \cdot 4H_2O$ through the covalently immobilization, caused heterogeneous Mn catalyst synthesized onto the SiO_2/Al_2O_3 mixed oxides, as illustrated in Scheme 1. The formation of Mn catalyst onto the SiO_2/Al_2O_3 was verified using CHN, FT-IR, UV–vis, SEM, TEM and EDX. The surface area, pore size and volume of the modified support were significantly reduced compared to the parent SiO_2/Al_2O_3 (this decrease indicates the decrease in interaction between adsorbate, N_2 molecules, and the nano-sized SiO_2/Al_2O_3 surface after modification with organic chains). The loading of manganese in the heterogeneous manganese catalyst was characterized by elemental analyses. The final metal content was around 0.35 mmol/g, indicating that 74.4% of the immobilized ligands were complexed with manganese ions (Table 1).

3.1.1. The FT-IR spectra

In Figure 1, the FT-IR spectra of SiO_2/Al_2O_3-APTMS, SiO_2/Al_2O_3-APTMS-BPK, and SiO_2/Al_2O_3-APTMS-BPK-Mn are shown. The strong absorption bands related to Si—O—Si stretching vibrations
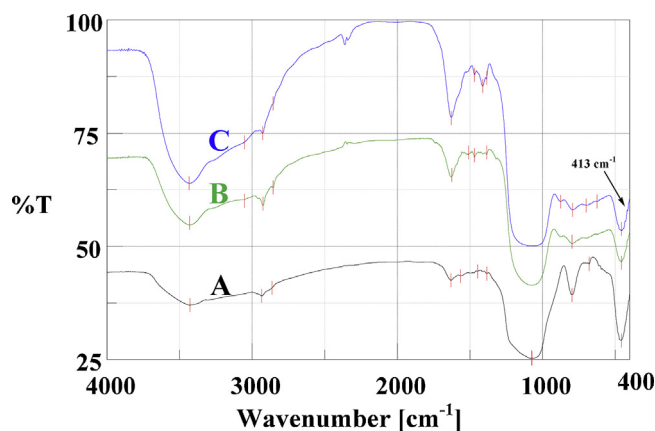
Fig. 1. FTIR spectra of: (A) SiO_2/Al_2O_3-APTMS; (B) SiO_2/Al_2O_3-APTMS-BPK; (C) SiO_2/Al_2O_3-APTMS-BPK-Mn.