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Manganese porphines-NH_2@SBA-15 as heterogeneous catalytic systems with homogeneous behavior: Effect of length of linker in immobilized manganese porphine catalysts in oxidation of olefins

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ABSTRACT

Two types of SBA-15 mesoporous silica were functionalized with different nitrogen-carbon chain lengths (long and short-chain) and then used as solid supports for immobilization of manganese(III) complex of *meso*-tetrakis(4-carboxyphenyl)porphine, [SBA-15-short-chain-NH_2@Mn(TCPP)OAc] and [SBA-15-long-chain-NH_2@Mn(TCPP)OAc]. The prepared catalysts were characterized by powder X-ray diffraction (XRD), FT-IR and UV–vis spectroscopy. The loading of catalyst onto porous materials was determined by atomic absorption spectroscopy. Thermal analysis also demonstrated that the immobilized catalysts are thermally stable up to almost 400 °C. A comparative study based on the difference in chain length of the functional groups of SBA-15 in the oxidation of olefins was carried out in the presence of urea hydrogen peroxide (UHP) as oxidant and acetic anhydride as an activator. The novel long-chain catalyst was designed to improve performance of the catalytic activity.

1. Introduction

In order to achieve useful and practical intermediates and products, metal complexes have been considered as catalysts for the oxidation of various compounds. Meanwhile, the development of approaches for designing efficient catalytic systems has attracted much interest in recent years [1]. Even though the homogeneous catalytic systems are often more effective than the heterogeneous analogues, the difficulties in separation of the catalyst is the disadvantage of them and therefore the researchers are interested to design and construct more effective heterogeneous catalytic systems. Synthetic metalloporphines as model catalysts for cytochrome P450 have been extensively studied for oxidation of variety compounds using various oxidizing agents [2–8]. However, the oxidative degradation of these valuable macromolecules is often encountered in the oxidation reactions [9]. Therefore, immobilization of the metalloporphine complexes onto solid supports such as mesoporous materials with high specific surface area, make them stable toward degradation [10–18]. The supporting of the large metal complexes such as metalloporphines through an organic spacer onto the mesoporous materials is often preferred and also, the solidity of the attachment to the support is an important factor that should be considered during immobilization process [10,19]. Among different mesoporous silica, Santa Barbara Amorphous (SBA-15) due to its unique properties such as thick walls (4–6 nm), thermal and mechanical stability, highly ordered mesostructure, large specific surface area (above 1000 m^2/g) and regular 2D hexagonal array of channels with a narrow pore-size distribution of 1.5–300 Å has attracted more attentions as solid support [17,20–23]. The functionalization and modification of SBA-15 could enhance its capability as a support for supporting the large metal complexes such as metalloporphines. On the other hand, covalent immobilization of the catalyst, decrease catalyst leaching during catalytic reactions [24–29].

In the present study, we have utilized two types of functionalized SBA-15 with 3-aminopropyltriethoxysilane and *N*-(3-trimethoxysilylpropyl)diethylenetriamine which have short and long chain lengths relative to the surface of support and then a Mn-complex of *meso*-tetrakis(4-carboxyphenyl)porphine (H_2TCPP) has been covalently anchored onto them, [(SBA-15-short-chain-NH_2@Mn(TCPP)OAc] and [SBA-15-long-chain-NH_2@Mn(TCPP)OAc)]. Hydrogen peroxide and its derivatives are well-known as green oxidants which extensively used in the oxidation of various compounds [30,31]. One of the methods for the activation of hydrogen peroxide and its derivatives is the formation of peroxycarboxylic acids from the reaction of carboxcylic acid anhydrides and H_2O_2 [30,32].

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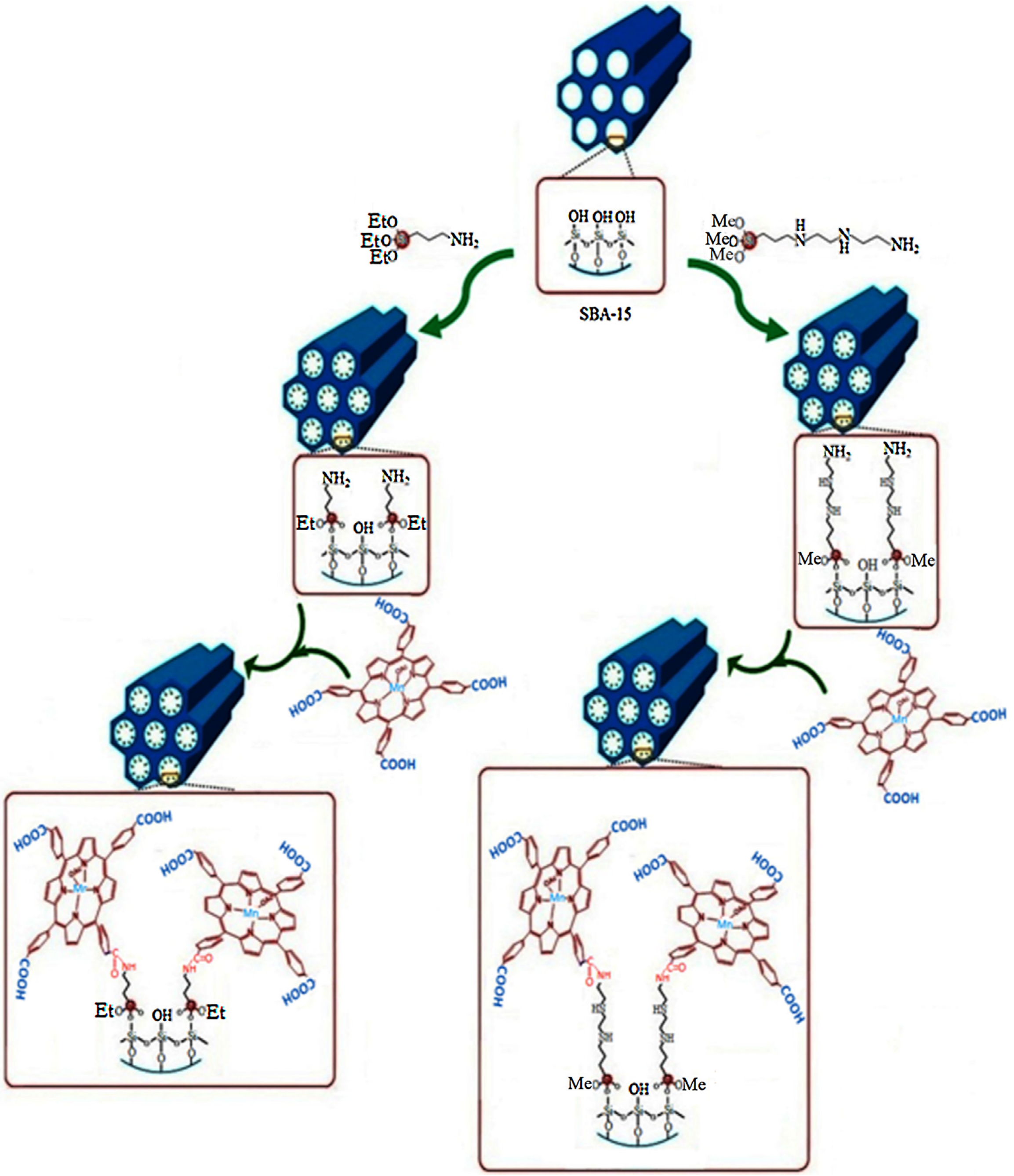

Scheme 1. Schematic representation of the preparation of [SBA-15-short-chain-NH_2@Mn(TCPP)OAc] and [SBA-15-long-chain-NH_2@Mn(TCPP)OAc].

2. Experimental

2.1. Materials and physico-chemical characterization techniques

The chemicals, reagents and solvents were purchased from Aldrich, Merck or Fluka chemical companies and were employed without further purification. The electronic absorption spectra were recorded on PerkinElmer Lambda 25 UV–vis spectrophotometer. The mesoporous materials and heterogenous catalytic systems were identified by X-ray powder diffraction (XRD) using a STOE diffractometer with Cu-Kα radiation (λ = 0.15418 nm) at 40 kV and 40 mA. The diffraction patterns were recorded in the Bragg angle (theta) range from 0.5° to 10° for small angle XRD with a position sensitive detector using a step size of 0.06°. Infrared spectra were recorded (KBr pellets) on an ABB Bomem: FTLA 2000-100 in the range of 400–4000 cm^{-1}. Thermal analysis (TGA/DTA) was carried out on a Bahr STA-503 instrument in air at a heating rate of 10 °C min^{-1}. Gas chromatography experiments (GC) were performed with a Shimadzu GC–14 B equipped with a flame ionization detector (FID) with a SAB-5 capillary column (phenyl methyl siloxane 30 m × 320 mm × 0.25 mm). A Varian AA 240 atomic absorption spectrometer was used for manganese determination.

2.2. General procedure for the preparation of porphine and metalloporphine

H_2TCPP was prepared by refluxing 4-carboxybenzaldehyde (300 mg, 2 mmol) and pyrrole (0.12 mL, 1.8 mmol) in propionic acid