ABSTRACT

The major challenging goal for fine chemical industry is to establish green, sustainable and economical processes. Catalytic oxidation plays a pivotal role and engages a prominent position in both academic research and modern chemical industry. Three dimensional mesoporous silicate have a distinctive advantage over 2D materials because of 3D interconnected pores that alleviate diffusion of reactants and products. Hence functionalisation of these materials with manganese is preferred as an alternative heterogeneous catalyst for various types of catalytic organic transformations. In comparison to homogeneous catalysts they have the advantages of easy recovery, high surface area, well-defined pore structure, and narrow pore size distribution than microporous materials.

Here in the present study, direct one pot synthesis of manganese containing ordered mesoporous silicate SBA-1 with $Pm3n$ cubic symmetry was synthesized by varying Si/Mn ratio ranging from 100-10. A maximum manganese loading of approximately 4.8 wt% was achieved under acidic synthesis conditions. XRD, N$_2$ sorption, TEM and SEM studies confirmed well-ordered cubic mesoporous structure typically of SBA-1 type materials. Diffuse Reflectance UV-Vis (DRS-UV-Vis), FT-IR and EPR studies concluded the framework incorporation of Mn$^{3+}$ ions as well as extraframework Mn$^{2+}$ ions at higher manganese loadings. Further, employing ethylbenzene oxidation with TBHP as probe reaction, Mn-SBA-1 catalysts performed marginally higher compared to Mn-MCM-41 and Mn-SBA-15 type materials. The presence of isolated tetrahedral Mn$^{3+}$ species is found to be responsible for desired product formation acetophenone.
Manganese was incorporated into three dimensional sponge-like amorphous mesoporous silica matrix of TUD-1 using tetra ethylene glycol (TEG) as the template under basic conditions. Nitrogen physisorption indicates that Mn-TUD-1 is a mesoporous material possessing surface area of 430–490 m$^2$/g with mesopore volume of 0.61–0.71 cm$^3$/g and an average adsorption pore diameter of 4.1–4.7 nm. The framework incorporation of manganese was confirmed by FT-IR, EPR and DRS-UV–Vis studies. Mn-TUD-1 is shown to be mesoporous with tetrahedrally coordinated Mn at lower manganese loading and nano-particles of manganese oxides observed with increase in the loading of manganese. Manganese exists in bivalent and trivalent states in all the materials. The catalytic activity of Mn-TUD-1 was explored in the liquid-phase oxidation of ethylbenzene with tert-butyl hydroperoxide (TBHP) as oxidant. Influence of various reaction parameters such as time, Si/Mn ratio, oxidant and solvent were studied. The catalytic activity of Mn-TUD-1 was found to be significantly higher compared to well-known microporous and mesoporous catalysts like Mn-AlPO-5, Mn containing SBA-1, MCM-41, MCM-48 and SBA-15 which could be due to 3D pore network structure of TUD-1 framework.

Further, testing these materials for liquid phase oxidation of cyclohexane with TBHP under solvent-less and mild reaction conditions Mn-TUD-1 showed good catalytic activity (13.5% cyclohexane conversion) and high selectivity (84.5%) to mono-oxygenated products. The activity of Mn-TUD-1 was found to be superior compared to Fe and Ti-TUD-1 and was comparable with Co-TUD-1. Hot-filtration studies confirmed the heterogeneity of Mn-TUD-1 under the reaction conditions.

Manganese containing 3D mesostructured FDU-5 ($Ia3d$ space group) silicates with varying Si/Mn ratios were synthesized for the first time via evaporation induced self assembly (EISA) technique under acidic
conditions at room temperature, employing Pl23 triblock copolymer as a structure directing agent. This method facilitates complete incorporation of higher amounts of Mn in the framework and extraframework locations of FDU-5 even under highly acidic synthesis conditions. The Mn-FDU-5 samples possessed surface area of 300–500 m$^2$/g, pore volumes of 0.42–0.55 cm$^3$/g and narrow pore size distributions of 4.1–4.9 nm. Homogeneous dispersion of Mn species and aggregated Mn oxide clusters were evidenced from FIB-SEM micrographs. Complementary analytical techniques such as diffuse reflectance UV–Vis, FTIR, TPR and EPR analyses provide insights into the nature of the different types of Mn species (Mn$^{2+}$, Mn$^{3+}$ and Mn$_3$O$_4$ nano-particles) that co-exist in FDU-5. The Mn-FDU-5 material is shown to be active for the epoxidation of trans-stilbene (TS, ~ 60 % conversion) to trans-stilbene epoxide (TSO, ~ 64 % selectivity) with TBHP as oxidant. Although the activity of Mn-FDU-5 (~ 45 % TS conversion) is similar to those observed with MCM-41 and MCM-48 supports containing similar amounts of Mn, higher epoxide selectivity (~ 64 %) was observed with Mn-FDU-5. The mixed oxidation states of Mn ($Mn^{2+}$, $Mn^{3+}$) along with the extraframework Mn$_3$O$_4$ are found to be beneficial in catalyzing TS epoxidation.