

Mesoporous polymer–silica catalysts for selective hydroxylation of phenol

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Mesoporous polymer–silica nanocomposite materials with redox functional groups such as ferrocene were synthesized *via* controlled radical co-polymerization inside mesoporous silicas and exhibited very high activity and selectivity towards catalytic hydroxylation of phenol.

Introduction

Following the discovery of mesoporous materials, a strong desire to use more environmental friendly processes has been universally acknowledged and much effort has been devoted to this area during the last two decades.¹ This is due to their outstanding advantages such as extremely large surface area combined with large and well-defined pore sizes. In particular, the wide pore size range (2–20 nm) of ordered mesoporous silicas compared to microporous zeolites enables one to incorporate multifunctional organic moieties within the well-defined porous structures.^{1,2} The organic moiety can be functionalized to achieve the active centers for various applications in catalysis, adsorption, ion-exchangers, *etc.*, to design the new required materials. So far, co-condensation of organosilanes during the synthesis^{1,3,4} or direct grafting of the organosilanes into the as-synthesized mesoporous materials⁵ are the most common methods employed to obtain the organo–silica hybrid materials. In particular, the synthesis of novel organic–inorganic hybrid mesoporous materials with an homogeneous distribution of organic fragments and inorganic oxide within the framework was reported.³ However, the limited scope and density of the functional groups achievable and relatively low hydrothermal stability of the siloxane bond under reactive conditions limit the practical utilization. Choi and Ryoo⁶ have disclosed the synthetic strategy towards ordered nanoporous organic polymers using mesoporous carbon as the retaining framework and the design of silica polymer-composite material through controlled radical polymerization of monomers postfunctionalized with sulfonic acid groups for adsorption and acid catalysis.⁷ In this communication, we report the synthesis of new mesopore polymer–silica (KIT-6 with cubic *Ia3d* symmetry) composite materials through *in-situ* radical controlled polymerization of vinylmonomers (styrene and vinyl ferrocene as a functional monomer) inside the silica mesopores for hydroxylation of phenol. The endeavor of incorporating the polymer (styrene) is to make the nature of the surface more hydrophobic that may result in the desired selective products. The use of H₂O₂ as oxidant over

titanosilicate by Enichem has opened vistas for environmentally benign approaches for selective oxidation/hydroxylation reactions.⁸ In continuation, many recent efforts have been emphasized for metal oxides, supported metal complexes, metallosilicates, hydrotalcites, heteropoly-compounds and Cu-exchanged zeolites.⁹ Recently, direct grafting of ferrocene into SBA-15 material was reported for oxidation of benzene.¹⁰ Recently, ferrocene immobilization in MCM-41 types of material was used for hydroxylation/polymerization of phenol wherein only traces of hydroxylated products were formed leading to the polymerization of phenol.¹¹

Experimental

The synthesis methodology involves the incorporation of vinyl monomers, cross linkers and radical initiators into the KIT-6 mesopore walls *via* the wet-impregnation method and equilibrated under reduced pressure to achieve a uniform distribution. The monomers adsorbed on the mesopore walls were subsequently polymerised with temperature programmed heating. Typically, for 30 wt% polymer loading, 0.114 g of styrene (80 mol%), 0.0358 g divinylbenzene (20 mol%), 0.0065 g of AIBN, *a,a'*-azoisobutyronitrile (3% relative to the total vinyl group) and 0.01143 g of vinyl ferrocene (9 : 1 wt ratio; styrene : vinyl ferrocene) were dissolved into 2 ml of solvent (dichloromethane). The role of styrene is to solubilize vinyl ferrocene and to make the nature of the surface more hydrophobic. After impregnating the solution, the sample was heated to 40 °C to remove the dichlorobenzene and subjected to freeze–vacuum–thaw to remove the residual solvent and air. The sample was sealed in a pyrex tube and subjected to controlled temperature programming for polymerization. The temperature scheme follows 45 °C for 24 h, 60 °C for 4 h, 100 °C, 120 °C and 150 °C for 1 h. Two different amounts (3 and 7 wt% vinyl ferrocene : styrene) were selected to synthesize the samples.

Results and discussions

The powder X-ray diffraction pattern (PXRD) of the polymer composite materials (Fig. 1) recorded on a Rigaku X-ray diffractometer ($\lambda = 1.5418 \text{ \AA}$, Cu K α) showed an increase in the intensity of the characteristic peak compared to KIT-6 due to the polymer formation inside the mesopores of silica materials resulting in an increase in the apparent density of the mesopore walls.⁷ The organic nanopores thus obtained exhibit high thermal stability due to the interpenetrating composite frameworks between the cross-linked polymers and silica material. N₂ adsorption isotherms were measured at 77 K using a Quantachrome AS-IMP volumetric adsorption analyzer. Before the adsorption measurements, all samples were outgassed for 12 h at 353 K in the

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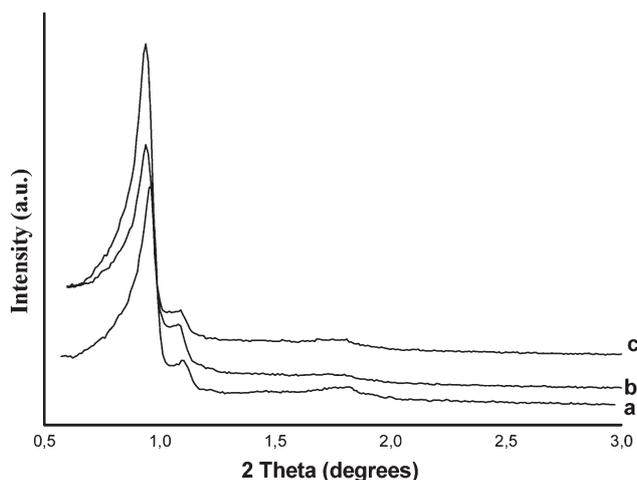


Fig. 1 PXRD pattern of (a) KIT-6, (b) 0.12% Fe/KIT-PS and (c) 0.35% Fe/KIT-PS.

degas port of the adsorption analyzer. The N_2 adsorption-desorption isotherm of KIT-6 shows a type IV adsorption isotherm.

Fig. 2 shows N_2 adsorption-desorption isotherms according to IUPAC classification, with a sharp capillary condensation step at relatively high pressure with an H1 hysteresis loop indicative of well-defined cylindrical pores. The total pore volume, pore size and surface area of the composite materials were reduced compared to the pure KIT-6 and reveals that the mesopores are filled with the polymers (Table 1).

The samples were named as x Fe/KIT-PS, where x presents the percentage of Fe content in vinyl ferrocene (Table 1), PS indicates the polymer composite. The elemental analysis was carried out by ICP-AAS. The thermogravimetric analysis indicated that 99% of the monomers were converted to polymers. The details of the synthetic methodology of KIT-6 has been published elsewhere.¹² Catalytic hydroxylation of phenol is carried out in a two-neck 50 ml glass reactor equipped with a condenser and septum using water as the solvent. 1 g of phenol is dissolved in the solvent containing 50 mg of the catalyst to the magnetically stirred solution kept at a desired temperature (2–65 °C) using H_2O_2 (substrate : oxidant molar ratio = 3 and 5) as an oxidant. A small amount of the samples was periodically withdrawn from the reaction mixture and analyzed by GC5890 equipped with a packed SE-30 column. The identification of the products was carried out by injecting the authentic samples after considering their response factors and using the internal standard, in this case 2-propanol. Catechol (CAT) and hydroquinone (HQ) were observed as the major products on all the catalysts and no benzoquinone was observed under our experimental conditions. Fig. 3 shows the

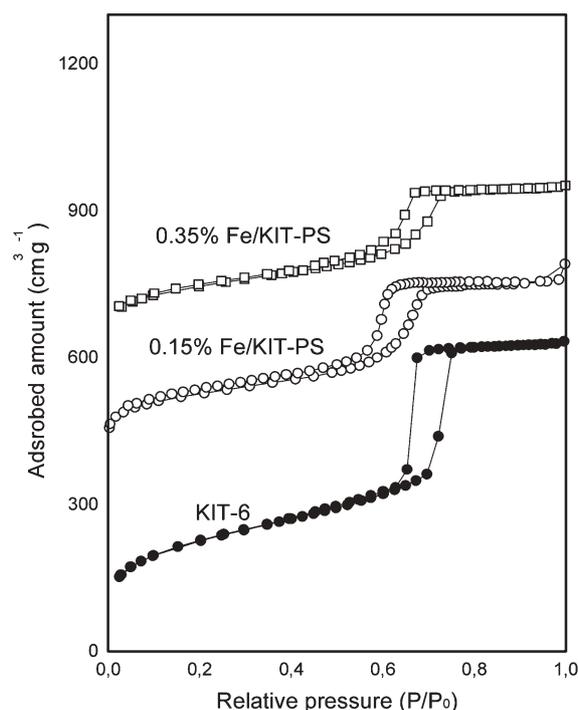


Fig. 2 N_2 adsorption-desorption isotherms for KIT-6, 0.12% Fe/KIT-PS and 0.35% Fe/KIT-PS samples. The isotherms are offset vertically by 400 and 600 cm^3 STP g^{-1} for 0.12 and 0.35% Fe/KIT-PS, respectively.

activity of the 0.35% Fe/KIT-PS (catalyst selected for detailed study) at 20 °C. The results indicated that nearly 30% conversion of phenol and 25.4% conversion based on the dihydroxybenzenes (Cat : HQ ratio = 3.4) with around 76.2% selectivity of H_2O_2 based on products was achieved in 24 h of the reaction time in the ferrocene-derived polymer materials. It should be mentioned here that no catalytic activity was observed for pure KIT-6 and KIT-PS, indicating that the catalytic activity is essentially due to the presence of Fe acting as the active center for this reaction. These results are quite different from some of the iron-containing mesoporous materials (ferrocene immobilization in MCM-41 type materials) where no hydroxylated products were observed under the same reaction conditions. This difference in the higher activity and selectivity of polymeric-derived materials for dihydroxylated product formation may be attributed to the different hydrophobic nature of the surface after the incorporation of polymer. To see the influence of amount of H_2O_2 , the experiments were performed using even lower concentration of H_2O_2 (5 : 1). The results obtained were quite interesting as 14.2% selective conversion to catechol was observed for 0.35%Fe/KIT-PS. This is the highest ever conversion of phenol, product selectivity and the selectivity of H_2O_2 on dihydroxybenzenes among the Fe-containing catalysts at

Table 1 Structural parameters of the samples^a

Catalyst	Surface area/ $m^2 g^{-1}$	Pore volume/ $ml g^{-1}$	Pore size/nm	^b Conversion (wt%)	H_2O_2 selectivity (%)
KIT-6 (silica)	821.74	0.97	8.3	0	0
0.12% Fe/KIT-PS	451.82	0.55	6.2	20.7	62.1
0.35% Fe/KIT-PS	432.32	0.54	5.1	25.4	76.2

^a Phenol (1 g), Catalyst (0.35% Fe/KIT-PS) 50 mg, solvent—water, oxidant— H_2O_2 , Phenol : H_2O_2 (molar ratio 3 : 1), reaction temp—293 K.

^b Conversion based on dihydroxybenzenes.

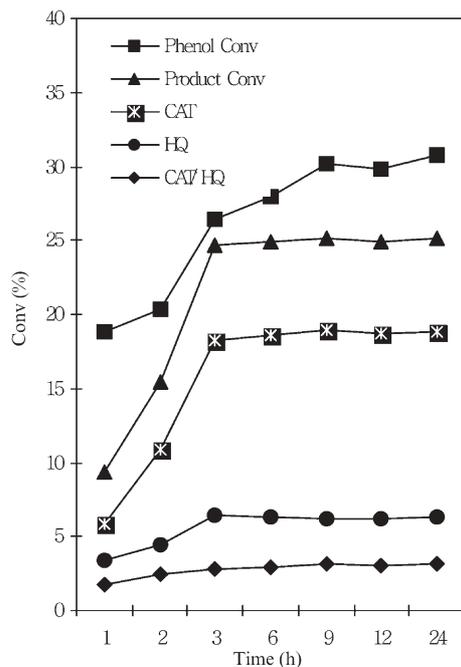


Fig. 3 Variation of conversion of phenol with time over 0.35% Fe/KIT-PS.

low temperature using water as a solvent. The interaction of the H_2O_2 with the catalyst generates hydroxyl radicals, thought to be active centres involved in the reaction, which subsequently attack at the *o*- and *p*-position to produce the desired dihydroxybenzenes. These results are quite significant for industrial perspectives and clearly corroborate the role of polymer incorporation on product selectivity. In order to check the reusability of the materials, the catalyst was centrifuged after the completion of the reaction, washed thoroughly with water several times until the filtrate becomes clear and subjected to fresh reaction. It was observed that 22.1% conversion of phenol was observed and the catalyst was recycled five times without any further decrease in the conversion.

Conclusion

In summary, we have synthesized large pore silica polymer nanocomposite materials through a radical polymerization technique for selective hydroxylation of phenol. The higher conversion of phenol on dihydroxybenzenes and selectivity of H_2O_2 using water as a solvent at 293 K may indicate the promising use of these materials for industrial applications. Further efforts are currently underway for the use of these materials in other applications.

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