High catalytic efficiency of transition metal complexes encapsulated in a cubic mesoporous phase

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Copper(II) acetate dimer and [Mn^{II}(bipy)$_2$]$^{2+}$ encapsulated in cubic Al-MCM-48 show high catalytic activity in the oxidation of phenol to catechol by oxygen activation, and of styrene to styrene oxide by singlet oxygen, respectively.

Transition metal complexes encapsulated in the cavities of zeolites are known to exhibit high catalytic activity in certain oxidation reactions, suggesting that these catalytic systems are good enzyme mimics.[1] Oxidation of phenols with O_2 by copper acetate dimer incorporated in MCM-22 or VPI-5 is a case in instance wherein the copper(II) complex mimics the phenolase activity of tyrosinase.[2,3] Besides the activation of O_2, there have been studies of the oxidation of organic compounds with singlet oxygen sources such as H_2O_2, by metal complexes encapsulated in molecular sieves. Selective oxidation of alkenes by bis(2,2′-bipyridyl)manganese, [Mn(bipy)$_2$]$^{2+}$, encapsulated in zeolites X and Y is one such example.[4] The [Mn^{II}(bipy)$_2$]$^{2+}$ complex immobilized in mesoporous Al-MCM-41 has been recently shown to exhibit high catalytic activity for styrene oxidation.[5] Based on the geometry of the pore structures of mesoporous solids, it was our view that the cubic phase should be an excellent host for enhancing the catalytic activity of metal complexes. We have therefore investigated the catalytic activity of two transition metal complexes incorporated in mesoporous Al-MCM-48, in oxidation reactions. The metal complexes examined are copper(II) acetate dimer which has the structural features of Cu-containing monooxygenase enzymes[2,3] and [Mn^{II}(bipy)$_2$]$^{2+}$. While copper(II) acetate incorporated in Al-MCM-48 was primarily meant to examine the catalytic activity for oxygen activation at ambient conditions, the manganese(II) complex system was intended to study the oxidation of styrene by singlet oxygen.

Al-MCM-48 was prepared by employing a modified procedure. To a solution of 2.9 g of cetyltrimethylammonium bromide in 40 ml of deionised water, 2.8 ml of 5 M NaOH was added and the solution stirred for 30 min. To this, a solution containing 0.09 g of aluminium sulfate dissolved in 10 ml of water was added followed by the dropwise addition of 6.2 ml of tetraethylorthosilicate. The mixture was stirred for 1 h, transferred to a stainless steel autoclave and kept at 383 K for 5 days. The final product was filtered, washed several times with deionised water, dried at 353 K for 3 h and calcined at 773 K for 10 h in air to remove the template. The Si/Al ratio in the product was *ca.* 50. The cubic nature of the mesoporous phase was confirmed by X-ray diffraction (Fig. 1). Distinct (211), (220), (321), (400) and (332) reflections were seen in the pattern. Cu-acetate-Al-MCM-48 was prepared by stirring 0.4 g of Al-MCM-48 with 0.2 g of copper acetate monohydrate in distilled, deionised water for 12 h. The product was filtered, washed with water and dried at 383 K for 24 h in vacuum. The Cu/Al ratio in the final product was 0.15. The XRD pattern given in Fig. 1 shows the cubic mesoporous nature of the catalyst. The surface area of the catalyst was 600 m^2 g^{-1}. Al-MCM-48-[Mn(bipy)$_2$]$^{2+}$ was prepared by the treatment of Al-MCM-48 (0.3 g) with a solution of 0.3 g of [Mn(bipy)$_2$][NO$_3$]$_2$ in 20 ml of 1 : 9 (by volume) DMF–acetonitrile mixture at room temperature for 48 h. The sample was filtered, washed with acetonitrile and dried at 353 K under vacuum for 1 h. Chemical analysis showed that the Mn/Al ratio in the product was 0.14. The XRD pattern (Fig. 1) confirmed that the cubic mesoporous structure was retained. The surface area of the catalyst was 770 m^2 g^{-1}.

The second derivative EPR spectrum of Cu-acetate-Al-MCM-48 ($g_\perp$ = 2.06, $g_\|$ = 2.18) exhibited the expected

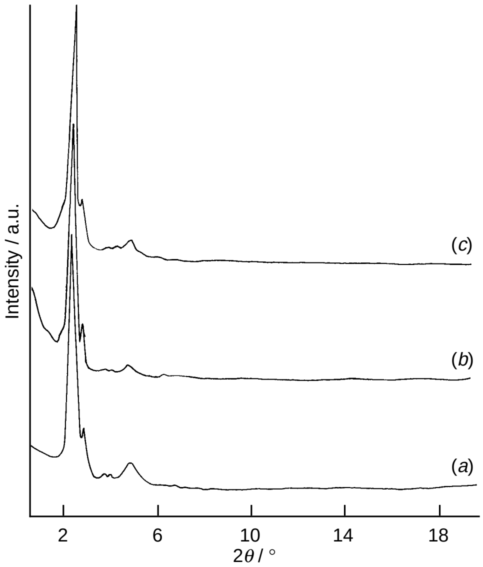

Fig. 1 X-Ray diffraction patterns of (*a*) calcined Al-MCM-48, (*b*) copper acetate dimer encapsulated Al-MCM-48 and (*c*) [Mn(bipy)$_2$]$^{2+}$ encapsulated Al-MCM-48

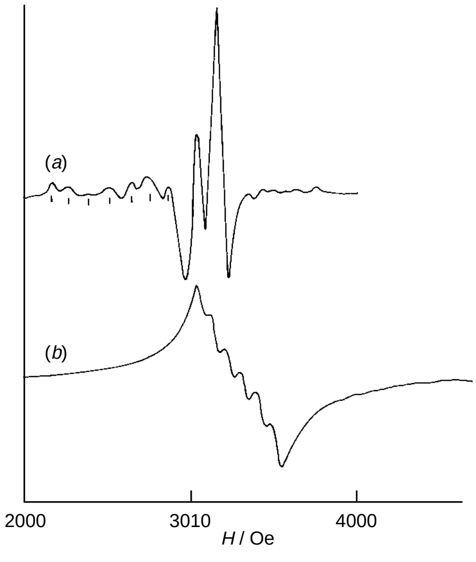

Fig. 2 EPR spectra of (*a*) copper acetate dimer and (*b*) [Mn(bipy)]$^{2+}$ encapsulated in Al-MCM-48

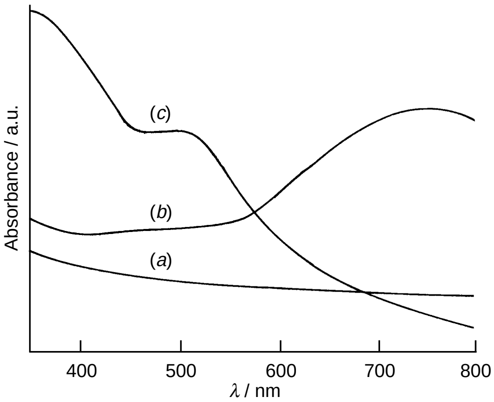

Fig. 3 Electronic absorption spectra of (*a*) Al-MCM-48, (*b*) copper acetate dimer encapsulated in Al-MCM-48

hyperfine structure [Fig. 2(*a*)], establishing the presence of the copper(II) acetate dimer.[3] The IR spectrum showed the carboxylate absorption at 1629 cm^{-1}. The diffuse reflectance spectrum [Fig. 3(*b*)] gave a band around 740 nm, just as in the case of the copper acetate encapsulated zeolites. Oxidation of phenol by the Cu-Al-MCM-48 catalyst was studied by stirring 100 mg of the catalyst in a phosphate buffer solution with 0.57 mmol of phenol in an oxygen atmosphere at 303 K. Gas chromatographic analysis of the product indicated 36% conversion, with catechol as the primary product. The turnover number was 37, a value considerably higher than that found (*ca.* 4) with copper(II) acetate alone. This result demonstrates the high catalytic activity of Cu-Al-MCM-48 in the orthohydroxylation of phenol by oxygen activation.

The Al-MCM-48-$[Mn(bipy)_2]^{2+}$ gave an EPR spectrum with the expected hyperfine structure due to Mn^{2+} [Fig. 2(*b*)]. It was pink with a broad band around 490 nm in its DRS, due to the metal–ligand charge transfer transition [Fig. 3(*c*)]. The IR spectrum showed bands at 760 and 773 cm^{-1} due to the out-of-plane C–H deformation of the bipy. Oxidation of styrene was studied by taking 100 mg of the catalyst in a solution of 0.87 mmol of styrene in 5 ml of acetonitrile, to which 3.5 mmol of H_2O_2 was added. Gas chromatographic analysis showed the conversion to be *ca.* 40% with styrene oxide as the primary product. The turnover number was 82 compared with *ca.* 7 for the $[Mn(bipy)_2]^{2+}$ complex alone. In the hexagonal mesoporous host, Al-MCM-41, the maximum turnover number was 58.[5] This result establishes Al-MCM-48-$[Mn(bipy)_2]^{2+}$ to be an excellent catalyst for such oxidation reactions. It is to be noted that the turnover number for styrene oxidation with Cu-acetate-Al-MCM-48 catalyst was 46, but there was hardly 5% conversion to styrene oxide, the main product being benzaldehyde. Similarly, the turnover number of the manganese catalyst for the oxidation of phenol through the activation of molecular oxygen was 14 and the product contained almost no catechol. These results reveal the specificity of the metal complexes encapsulated in the cubic mesoporous phase.

The present study not only demonstrates the high catalytic potential of transition metal complexes encapsulated in cubic mesoporous phases in oxidation reactions, but also the need to explore other reactions as well as mesophase compositions with different Si/Al ratios.

Notes and References

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