

A novel, zeolite-encapsulated μ_3 -oxo Co/Mn cluster catalyst for oxidation of *para*-xylene to terephthalic acid

Suhas A. Chavan, D. Srinivas and Paul Ratnasamy*

National Chemical Laboratory, Pune 411 008, India. E-mail: prs@ems.ncl.nes.in

Received (in Cambridge, UK) 2nd March 2001, Accepted 10th May 2001

First published as an Advance Article on the web 31st May 2001

Trinuclear, μ_3 -oxo mixed metal acetato complexes, $[\text{CoMn}_2(\mu_3\text{-O})(\text{MeCO}_2)_6(\text{py})_3]$ (py = pyridine) encapsulated in zeolite HY, exhibit high catalytic efficiency in the selective aerial oxidation of *para*-xylene to terephthalic acid; interestingly, the formation of 4-carboxybenzaldehyde, the worrisome impurity in the conventional process, is suppressed significantly over these solid catalysts.

Terephthalic acid, one of the largest volume commodity chemicals, is commercially manufactured by dioxygen oxidation of *para*-xylene using cobalt and manganese salts, at 473–500 K, in acetic acid (MeCO_2H) solvent and bromide ion as promoter.^{1,2} High yields and selectivity for terephthalic acid are obtained. Replacement of the homogeneous catalyst with a solid catalyst is a desirable alternative which will eliminate toxic metal ions from the waste effluents in the process. One such method of preparing solid, heterogeneous catalysts is encapsulation of active metal complexes inside the pores of zeolites or zeolitic materials.^{3–5} We had reported earlier the presence of reactive μ_3 -oxo Co/Mn mixed cluster complexes in homogeneous reaction medium.⁶ In this communication we report, for the first time, the encapsulation of these complexes, $[\text{CoMn}_2(\mu_3\text{-O})(\text{MeCO}_2)_6(\text{py})_3]^n$ ($n = +1$ or 0) inside the cages of zeolite HY [hereafter referred to as $\text{CoMn}_2(\text{O})\text{-Y}$]. The hydrothermal stability and catalytic activity of these solid cluster catalysts in the *heterogeneous* dioxygen oxidation of *para*-xylene are also reported. It is found that these heterogeneous catalysts were highly active and selective for the oxidation of *para*-xylene to terephthalic acid. A comparative study indicates that the zeolite-Y-encapsulated *heteronuclear*, cluster complex, $\text{CoMn}_2(\text{O})\text{-Y}$ is more efficient than the corresponding *homonuclear* cobalt and manganese cluster complexes, $[\text{Co}_3(\mu_3\text{-O})(\text{MeCO}_2)_6(\text{py})_3]$ and $[\text{Mn}_3(\mu_3\text{-O})(\text{MeCO}_2)_6(\text{py})_3]$, respectively, in HY [hereafter referred to as $\text{Co}_3(\text{O})\text{-Y}$ and $\text{Mn}_3(\text{O})\text{-Y}$, respectively].

Co(II) , Mn(II) and mixed Co(II)/Mn(II) exchanged HY zeolites were prepared by the ion exchange method, wherein zeolite HY was contacted with aqueous solutions of $\text{Co}(\text{MeCO}_2)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{MeCO}_2)_2 \cdot 4\text{H}_2\text{O}$ in requisite proportions at 338 K with stirring for 4 h. The ion-exchanged zeolites (Co-Y , Mn-Y , Co,Mn-Y) were washed with distilled water several times and dried at 373 K. In a typical preparation of the encapsulated metal cluster complex, the corresponding ion exchanged zeolite Y sample (1.5 g) was suspended in 15 ml glacial MeCO_2H . To this slurry was added pyridine (3 ml), NaBr (0.5 g), aq. H_2O_2 (50%, 10 ml) and distilled water (5 ml). The mixture was stirred, while bubbling air through the solution, for 2 h at 298 K. The solid product [$\text{Co}_3(\text{O})\text{-Y}$, pink; $\text{Mn}_3(\text{O})\text{-Y}$, pale brown; $\text{CoMn}_2(\text{O})\text{-Y}$, purple] was filtered off, washed with glacial MeCO_2H and dried under vacuum. 'Neat' cluster complexes of the composition $[\text{Co}_3(\mu_3\text{-O})(\text{MeCO}_2)_6(\text{py})_3]\text{ClO}_4$ [referred to as $\text{Co}_3(\text{O})$], $[\text{Mn}_3(\mu_3\text{-O})(\text{MeCO}_2)_6(\text{py})_3]\text{ClO}_4$ [referred to as $\text{Mn}_3(\text{O})$] and $[\text{CoMn}_2(\mu_3\text{-O})(\text{MeCO}_2)_6(\text{py})_3]$ [referred to as $\text{CoMn}_2(\text{O})$] were prepared, for comparative studies, by known procedures.^{7–9} The formation and purity of the complexes was confirmed by elemental analysis, FT-IR, UV-VIS and EPR spectroscopies.

The FT-IR spectra of the encapsulated complexes showed characteristic bands corresponding to acetate groups at *ca.*

2924, 1624, 1458, 1340, 1221, 680 and 623 cm^{-1} . The FT-IR bands due to pyridine were observed at around 1545, 1489 and 790 cm^{-1} . A shift in the position of the bands due to encapsulation was observed. Representative FT-IR spectra of encapsulated clusters, $\text{Mn}_3(\text{O})\text{-Y}$ and $\text{CoMn}_2(\text{O})\text{-Y}$, are shown in Fig. 1. The 'neat' cluster complexes in $\text{MeCO}_2\text{H-H}_2\text{O-NaBr}$ medium showed a characteristic band of ligand origin and a charge transfer band ($\text{O} \rightarrow \text{Mn/Co}$) in the UV-VIS spectra, the positions of which were sensitive to the metal ions [$\text{Co}_3(\text{O})$: 250, 355 nm; $\text{Mn}_3(\text{O})$: 254, 320 nm and $\text{CoMn}_2(\text{O})$: 254, 345 nm]. The encapsulated clusters in zeolite-Y exhibited a marked shift in the band positions (Fig. 2). The diffuse reflectance UV-VIS spectra (Fig. 2) are dominated by the band of ligand origin; the weak charge transfer band could be seen only in $\text{Co}_3(\text{O})\text{-Y}$.

EPR spectra provided evidence for the formation and stability of cluster complexes in zeolite-Y. $\text{Mn}_3(\text{O})$ and $\text{Co}_3(\text{O})$ complexes showed a broad EPR signal at $g = 2.008$ (peak-to-peak line width = 500 G) and 2.259 (peak-to-peak linewidth of 1050 G), respectively. The intensity of these signals decreased with temperature to 77 K corresponding to an antiferromagnetic behaviour of the complexes. For $\text{Co}_3(\text{O})$, the signal arises from the low lying excited states while $\text{Co}_2\text{Mn}(\text{O})$ was EPR silent. $\text{Mn}_3(\text{O})$ in frozen solutions of 38 ml HOAc –5.6 ml H_2O –86.5 mg NaBr [Fig. 3(a)] at 82 K, showed an EPR signal with partially resolved Mn hyperfine features. These hyperfine features could not be seen in the solid complexes due to intermolecular interactions. Encapsulated $\text{Mn}_3(\text{O})$ clusters showed EPR signals ($g = 2.012$) similar to that of frozen solutions [see Fig. 3(a) and (b)] and indicate the formation and isolation of cluster molecules in zeolite-Y. $\text{CoMn}_2(\text{O})\text{-Y}$ exhibited signals at $g = 2.026$. $\text{Co}_3(\text{O})\text{-Y}$ showed a broad signal

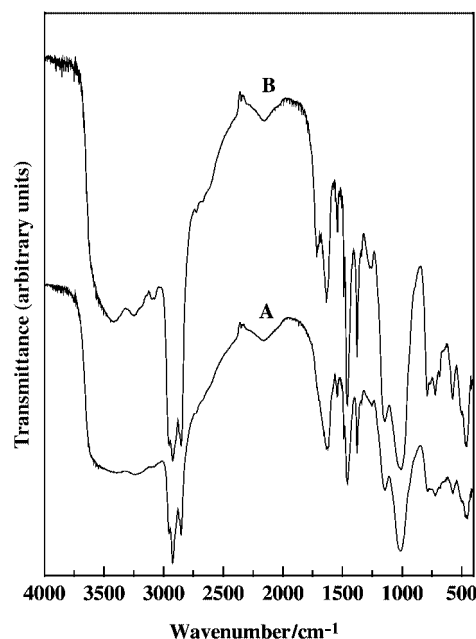


Fig. 1 FT-IR spectra (Nujol mull) of cluster complexes $\text{Mn}_3(\text{O})$ (A) and $\text{CoMn}_2(\text{O})$ (B) encapsulated in zeolite HY.

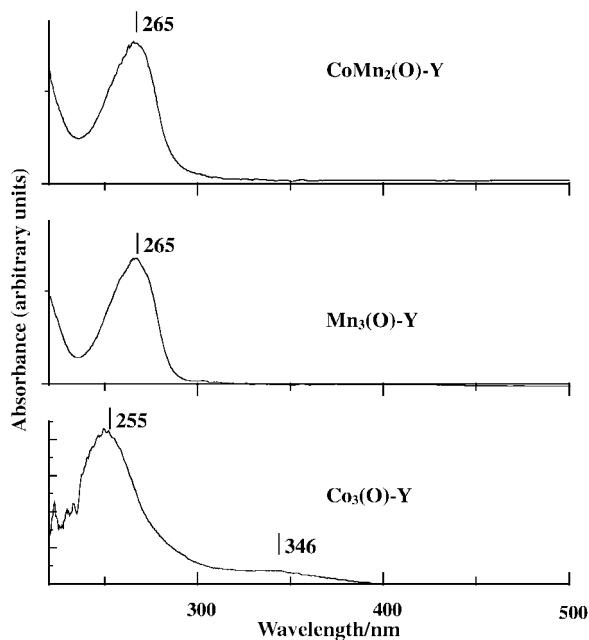


Fig. 2 Diffuse reflectance UV-VIS spectra of solid encapsulated clusters.

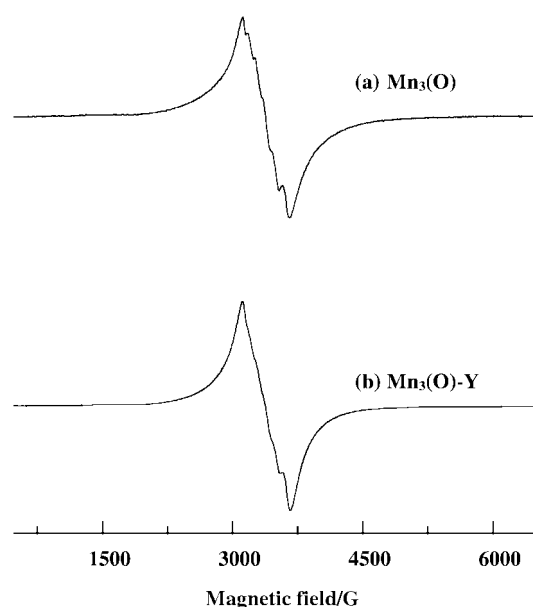


Fig. 3 X-band EPR spectra of $\text{Mn}_3(\text{O})$ in 38 ml HOAc–5.6 ml H_2O –86.5 mg NaBr at 82 K (a) and $\text{Mn}_3(\text{O})\text{-Y}$ (b) at 298 K.

at $g = 2.220$ at 298 K which disappeared on lowering the temperature below 120 K.

The encapsulated cluster catalysts are highly active in the dioxygen oxidation of *para*-xylene at 550 psig (air) and 473 K (Table 1). The oxidation products (identified by GC and GC-MS) are *para*-tolyl alcohol (A), *para*-tolualdehyde (B), *para*-toluic acid (C), 4-carboxybenzaldehyde (D) and terephthalic acid (E). Small amounts of benzoic acid (F) were also observed. Among the 'neat' complexes, the mixed metal cluster complex, $\text{CoMn}_2(\text{O})$ exhibited high catalytic activity similar to that of the conventional catalyst system⁶ [$3\text{Co}(\text{MeCO}_2)_2 + 1\text{Mn}(\text{MeCO}_2)_2$] with 100% *para*-xylene conversion and >97% selectivity for terephthalic acid. The solid, heterogenized catalyst, $\text{CoMn}_2(\text{O})\text{-Y}$, at 100% conversion of *para*-xylene, was even more selective (99.4% selectivity for terephthalic acid; only 0.01% of 4-carboxybenzaldehyde, a worrisome impurity in the conventional process which imparts colour to the terephthalic acid product and whose concentration must be reduced at great cost by post-oxidation processes) than the 'neat' cluster and conventional homogeneous catalysts. A longer reaction

Table 1 Catalytic activity of μ_3 -oxo metal cluster complexes in selective oxidation of *para*-xylene^a

| Catalyst | Time/h | Conv. (wt%) | Product distribution (wt%) ^c | | | | | |
|---|--------|-------------|---|------|------|------|------|-----|
| | | | A | B | C | D | E | F |
| $\text{Co}_3(\text{O})$ | 2 | 73.1 | 0.7 | 32.4 | 20.4 | 28.9 | 16.6 | 1.0 |
| $\text{Mn}_3(\text{O})$ | 2 | 77.0 | — | 35.8 | 8.6 | 1.6 | 53.8 | 0.2 |
| $\text{CoMn}_2(\text{O})$ | 2 | 100 | — | — | 1.8 | 0.4 | 97.8 | — |
| $\text{Co}_3(\text{O})\text{-Y}$ | 4 | 69.9 | — | 28.4 | 49.5 | 7.7 | 12.7 | 1.7 |
| $\text{Mn}_3(\text{O})\text{-Y}$ | 4 | 99.9 | — | — | 20.1 | 0.7 | 79.2 | — |
| $\text{CoMn}_2(\text{O})\text{-Y}$ | 4 | 100 | — | — | 0.6 | 0.01 | 99.4 | — |
| $\text{Co}(\text{MeCO}_2)_2 \cdot 4\text{H}_2\text{O} + \text{Mn}(\text{MeCO}_2)_2 \cdot 4\text{H}_2\text{O}$ (3:1) ^b | 2 | 100 | — | — | 0.7 | 1.4 | 97.9 | — |

^a Reaction conditions: medium *para*-xylene (2 ml)–NaBr (86.5 mg)– H_2O (5.6 ml)– MeCO_2H (38 ml); weight of 'neat' cluster catalyst = 34.2 mg; weight of encapsulated cluster catalyst = 299.5 mg; pressure = 550 psig; reaction temperature = 473 K; oxidant = air. ^b Conventional catalyst system [$\text{Co}(\text{MeCO}_2)_2 \cdot 4\text{H}_2\text{O} = 107$ mg; $\text{Mn}(\text{MeCO}_2)_2 \cdot 4\text{H}_2\text{O} = 35.7$ mg]. ^c A = *para*-tolyl alcohol, B = *para*-tolualdehyde, C = *para*-toluic acid, D = 4-carboxybenzaldehyde, E = terephthalic acid, F = benzoic acid.

time (4 h) was required for complete conversion of *para*-xylene (Table 1). The 'neat' and conventional catalysts required only 2 h. This is probably due to diffusional limitations in the zeolite catalysts. The solid catalysts were separated by simple filtration from the terephthalic acid by converting the latter into a water-soluble sodium salt. The separated catalyst has similar activity (on recycling) and spectroscopic characteristics as that of the fresh catalyst indicating the preservation of its structural integrity and reusability. The EPR spectra of the catalysts, at 82 K, before and after the reaction were almost the same confirming the stability of these complexes under the reaction conditions. Leaching of metal ions (Co and Mn) into solution at the end of the oxidation reaction [550 psig (air), 473 K and 4 h] was investigated by AAS and EPR spectroscopies. While AAS did not reveal any leaching of metal ions, EPR spectral measurements revealed trace amounts of Mn ions (*ca.* 0.5% of the metal in the zeolite; about 50 ppm of Mn in solution) leached into the reaction solution which is too low to account for the catalytic activity. Catalytic runs with this trace amount of metal ions in solution exhibited low *para*-xylene conversions (25 wt%) with *para*-tolyl alcohol (A) and *para*-tolyl aldehyde (B) as products; terephthalic acid was not detected.

Our studies also revealed that mixed metal heteronuclear catalysts [$\text{CoMn}_2(\text{O})$] are more active than the homonuclear catalysts [$\text{Mn}_3(\text{O})$ and $\text{Co}_3(\text{O})$]. To our knowledge this is the first example of a solid catalyst for the oxidation of *para*-xylene to terephthalic acid with catalytic efficiencies comparable, if not superior to that of state-of-art homogeneous catalysts.

Notes and references

- W. Partenheimer, *Catal. Today*, 1995, **23**, 69; A. K. Suresh, M. M. Sharma and T. Sridhar, *Ind. Eng. Chem. Res.*, 2000, **39**, 3958; *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*, ed. D. H. R. Barton, A. E. Martell and D. T. Sawyer, Plenum Press, New York, 1993.
- US. Pat.*, 2833816, 1958; *PCT Int. Appl.*, WO 9,931,038 A1 (24 June 1999).
- M. J. Sabater, A. Corma, A. Domenech, V. Fornés and H. Garcia, *Chem. Commun.*, 1997, 1285.
- G. J. Hutchings, *Chem. Commun.*, 1999, 301.
- P. Piaggio, P. McMorn, C. Langham, D. Bethell, P. C. Bulman-Page, F. E. Hancock and G. J. Hutchings, *New J. Chem.*, 1998, 1167.
- S. A. Chavan, S. B. Halligudi, D. Srinivas and P. Ratnasamy, *J. Mol. Catal. A: Chem.*, 2000, **161**, 49.
- C. E. Sumner Jr. and G. R. Steinmetz, *Inorg. Chem.*, 1989, **28**, 4290.
- J. B. Vincent, H.-R. Chang, K. Folting, J. C. Huffman, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1987, **109**, 5704.
- R. D. Cannon, U. A. Jayassooriya, L. Montri, A. K. Saad, E. Karu, S. K. Bollen, W. R. Sanderson, A. K. Powell and A. B. Blake, *J. Chem. Soc., Dalton Trans.*, 1993, 2005.