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Synthesis, characterization and phenol hydroxylation reaction of zeolite-Y encapsulated metal-salen complexes

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Zeolite-Y encapsulated Mn-SALEN, Fe-SALEN and VO-SALEN complexes have been prepared and characterised by XRD, TGA, UV-Visible, IR and ESR spectra. They confirm the presence of complex inside the zeolite cages. These composites are found to be active redox catalysts. They hydroxylate phenol to the extent of 23-28 wt%.

The procedure for preparing zeolite encapsulated complexes involves exchange of desired metal ion, followed by complexation of metal ion by ligands and purification of the resulting composite. Once complex is formed in zeolite cages, it cannot come through the pores and is also not available to neighbouring cages because of its bulky nature. Such zeolite encapsulated metal-SALEN (metal = Co, Mn, Pd, Rh, Ni and Cu), metal phthalocyanine (metal = Ru, Fe and Co) and metal tetramethylporphyrin (metal = Fe, Mn, Co and Ru) complexes have been reported in the literature[1-3]. These encapsulated complexes have been found to be good redox catalysts. These encapsulated complexes, mimic properties of cytochrome P450 enzyme and are termed as inorganic enzymes/zeozymes. As against enzymes, in zeozymes, the protein part is replaced by a rigid inorganic matrix[2].

Metal-schiff-base complexes with SALEN ligand have been prepared, to mimic synthetic respiration[4], for selective epoxidation[5] and for many other reactions[6]. On melting SALEN (1,6-bis(2-hydroxy phenyl)-2,5-diaza-1,5-hexadiene) ligand with metal exchanged zeolite-Y the two ionisable protons are readily lost and easily enter into faujasite cages to form, metal-SALEN complex (Scheme 1). In this investigation, zeolite-Y encapsulated metal-SALEN complexes (metal = Mn, Fe and V) have been prepared, characterised and used for hydroxylation of phenol.

Experimental

Preparation

Sodium form of zeolite-Y ($SiO_2/Al_2O_3 = 2.6$) obtained from Union Carbide, Tarydown (lot 13076-91) was used in this study. Ion exchange of zeolite-Y was done using dilute solutions of metal salts at low *p*H (adjusted with acetic acid) in order to avoid precipitation of metal hydroxides. 10 g of Na − Y zeolite with 500 ml of 0.004 *M* solution was exchanged at room temperature for 6 h. Finally, the materials were filtered and washed thoroughly. The initial *p*H values of Mn, Fe and V complexes are 3.15, 2.57 and 3.10 respectively and the corresponding final values are 3.76, 3.50 and 3.74.

The required SALEN was prepared by refluxing 1:1 molar salicylaldehyde (66.8 ml) and ethylenediamine (13.4 ml) in ethanol (150 ml) for 2-5 h. The obtained SALEN was recrystallised in ethanol and its purity checked by its melting point (Expt = 140°, lit. value = 141°C).

The ion exchanged dried zeolite-Y (7-8 g) and SALEN (8 g) were taken in a round bottom flask fitted with a condenser. The mixture was heated at 140°C for 6 h in an atmosphere of nitrogen. The resulting material was washed with chloroform and subjected to soxhlet extraction using chloroform to remove the uncomplexed ligands and extractable complexes. This was done until the extract becomes colourless (4-6 h). The solid obtained was exchanged with brine solution for 4 h at room temperature to remove uncomplexed metal ions in zeolite, washed with water, finally with acetone and dried at 50°C. The resulting solids Mn-SALEN-Y, Fe-SALEN-Y and VO-SALEN-Y are bright yellow, blackish red and greenish yellow respectively in colour indicating encapsulation of complexes in zeolite matrix.

The resulting composite materials were analysed by powder XRD (Philips PW1710) in the scan range 2O between 5 and 50° with scan speed 2°/min using CuKα as X-ray source. TGA analysis was performed by Mettler TA 3000 instrument at a heating rate of 20°/min up to 800°C in ambient air.

Chemical analysis of the metals (Mn, Fe and V) was done by wet method. A known amount of material was calcined at 800°C in a platinum crucible till a black residue disappeared (4-6 h). To the calcined material, drops of 40% HF were added and warmed and then heated strongly to dryness. This procedure was repeated for 5-6 times and finally heated to 800°C for 1 h and the loss of SiO_2 was noted. After this, the material was fluxed with 2-3 g potassium persulphate to form clear molten solid, which after cooling was dissolved in water and if necessary, with dil HCl. The solution was made upto 25 ml. From known amount of this solution, the metals were estimated spectrophotometrically[7]. Vanadium was estimated as peroxyvanadyl complex obtained by the addition of hydrogen peroxide ($\lambda_{max} = 450$ nm), iron as phenanthroline complex ($\lambda_{max} = 508$ nm) and Mn as $KMnO_4$ by oxidising it by KIO_3 ($\lambda_{max} = 545$ nm).

The complexes released on destruction of zeolite by con. sulphuric acid were dissolved in water and analysed by UV-Visible spectral (Hitachi U2000). FTIR spectra were recorded using Brucker IFS-66V spectrometer by KBr pellet technique. Prior to the analysis, the spectrometer was evacuated to 10^{-6} torr and the recording were done in the region 400-1300 cm^{-1}. Similarly, the free complex was also recorded. ^{13}C MAS-NMR of the zeolite encapsulated complexes were recorded by Brucker MSL-300 spectrometer in the frequency 75.47 MHz over 1976 scan using TMS as reference compound. ESR spectra of the composites were recorded at room temperature using JEOL FE1X spectrometer operating at 9.2 GHz with 2 gauss modulation and 20 mW power.

The catalytic activity of these composites were tested for hydroxylation of phenol. The reactions were performed at 70°C with 200 mg catalyst, 1.95 ml phenol, 5 ml water and 5 ml of 30% hydrogen peroxide for 5 h under magnetic stirring in an oil bath. The products obtained were homogenised by 15 ml of water and analysed by HP5890A gas chromatograph using OV-17 column.

Results and discussion

The XRD patterns of the composites show that the framework of zeolite-Y is maintained. Only in the case of iron complex, a partial collapse of zeolite structure is observed which may be due to ion exchanging at *p*H 2.5. The absorption spectra of the complex released from zeolite matches with that of free complex, confirming the presence of complex in zeolite. The presence of trace amount of free SALEN was also observed from the weak transitions of $\pi \rightarrow \pi^*$ at 320 and 420 nm[8]. The estimated metals in zeolite cages were calcualted per unit cell; Mn = 1.61, Fe = 0.42 and V = 1.32. The amount of Mn and V are more than 1 per cage.

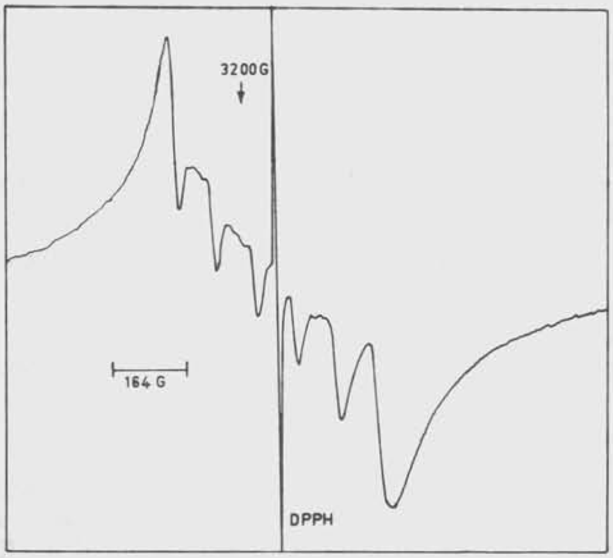

Fig. 1—ESR spectra of zeolite-Y encapsulated Mn-SALEN complex

TGA analysis shows loss of solvent or water at ≈ 70°C. Subsequent losses, which occurs in the temperature range 350-450°C are due to decomposition of complexes. Based on temperature at which major loss occurs, the stability of the complexes are in the order: Fe(SALEN)-Y < VO(SALEN)-Y < Mn(SALEN)-Y. The analysis further indicates the presence of 4.85, 4.67 and 5.27 Mn-SALEN-Y, Fe-SALEN-Y and VO-SALEN-Y ligands per unit cell respectively. These values are higher than the expected values for these complexes. The excess SALEN ligand might be occupying the sodalite cages while the complexes are occupying the supercages. The uncomplexed ligand in sodalite cages are not removed by chloroform extraction.

In the FTIR spectra, the vibrations due to Mn complex occur at 1461 and 1401 cm^{-1}, Fe complex at 1546, 1448 and 1401 cm^{-1} and for VO complex at 1545, 1507, 1469 and 1400 cm^{-1}. The metal complex peaks in zeolite matrix indicates the presence of complex in zeolite cages. Due to overlapping of zeolite and complex peaks, all the complex peaks are not distinctly observed.

^{13}C MAS-NMR spectra of VO(SALEN)-Y gives a broad signal between 125-135 ppm for aromatic carbons instead of sharp lines for them. Chemical shift anisotropies of the aromatic carbons in this sample is not reduced to their isotropic averages. As the encapsulated SALEN can have multitudes of interactions with zeolite sites, there is high degree of chemical shift dispersion contributing greatly to broadened NMR signal which is also applicable to aliphatic carbons.

The ESR spectra of Mn-SALEN-Y (Figure 1) shows six peaks, characteristic of $I=5/2$ of Mn(II) ion. The Spin-Hamiltonian parameters were calculated to be, $g=2.01$ and $A=90.7$ G. The Mn(II) ion exchanged zeolite ESR was also recorded and the corresponding values are $g=2.02$ and $A=86.9$ G. On complexing the Mn ion, the g values are not affected, but there is small increase in A value from 87.7 to 100 G. A similar increase in A value from 87.7 to 100 G for Mn(II) in zeolite 3A was observed by Sur *et al*[9] on increasing its coordination to form MnF_6^{4-}.

The ESR spectrum of Fe-SALEN-Y shows two iron peaks, one at $g_1=2.15$ ($A_1=181$ G, more intense) and the other at $g_2=4.08$ ($A_2=67.6$ G). These two were characteristic of iron species[19]. The g value ~ 2.0 is attributed to hexa-coordinated species and the g value around 4 to Fe(III) in cation sites, of slightly distorted coordination.

The VO-(SALEN)-Y complex as such does not show any intense peak in ESR. This is because of the oxidation of vanadium to V(V). The material on reduction with hydrazine hydrate gave ESR peaks. The spectrum shows eight peaks characteristic of $I=7/2$ of ^{51}V and the calculated parameters are given below:

VO(SALEN) Complexes	$g_\parallel$	$A_\parallel$(G)	$g_\perp$	$A_\perp$(G)	$\Delta g_\parallel/\Delta g_\perp$
Encapsulated in Zeolite-Y	1.953	180	1.990	51.4	3.96
Free complex (Ref. 11)	1.995	171.1	1.987	58.0	3.09

The parameters of free VO-(SALEN) reported by Pandey and Khare[11] are also presented. The ratio $\Delta g_\parallel/\Delta g_\perp$, measures the tetragonality of the vanadium site which is calculated to be 3.96 for the complex encapsulated in zeolite Y and 3.09 for free complex. The higher value of $\Delta g_\parallel/\Delta g_\perp$ compared to free complex, indicates that vanadyl complex in cages are in more tetragonally distorted state[12].

The hydroxylation of phenol by metal-SALEN-Y composites revealed that the conversion of phenol ranged between 23 and 28 wt% with more than 99% selectivity to dihydroxybenzenes. Among the three composites, Fe-SALEN-Y is found to be less active than the others. The reason for the low activity could be due to partial destruction of zeolite-Y matrix because of metal ion exchange at *p*H 2.5.

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