Direct catalytic oxidation of methane to methanol over zeolite encapsulated transition metal complexes

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Zeolite encapsulated metal complexes ML (M=Cu or Mn; L=salen or substituted salens or octaaza macrocyclic ligand) have been synthesized and their catalytic activities studied for the selective aerobic oxidation of methane at 273 K using TBHP as a promoter and acetonitrile or water as solvent. The zeolite encapsulated macrocyclic complex is found to be a better catalyst for the oxidation of methane with respect to conversion and selectivity towards methanol. Acetonitrile seems to be a good solvent for this reaction. Catalyst could be recycled and reused.

Zeolite encapsulated metal complexes have captured much attention in catalysis and biomimetic chemistry1-3. These new catalytic systems are of great interest not only because of their potential advantages in practical use but also because of the possibility that the zeolite framework may impose shape selectivity on the incoming reactant molecules. The high adsorption potential inside the zeolitic channels raises the effective concentration of a reagent at the catalyst active sites (complex) and thereby enhances their efficiency as catalytic centers. For example, a 200-fold increase in turn-over number was found for the oxidation of n-octane using zeolite encapsulated iron-phthalocyanine complex as the catalyst4.

The oxidation of methane with oxygen to C1 oxygenates has been widely investigated using Mo and V oxide catalysts5. Methane conversions are of particular interest due to large reserves of natural gas located in remote areas. Methane is one of the major greenhouse gases considered to be the primary causes of global warming. Technologies for the effective conversion of methane to value added fuels or more useful chemicals like methanol and formaldehyde are desirable. The higher temperatures required to activate methane and the oxidant, in most cases, resulted in oxidative coupling reaction6,7, but more recently there has been some success in the synthesis of catalyst active for the direct oxidation of methane to methanol8. A number of approaches have been made concerning the identification of suitable catalysts, but to date very little is known about the activation of methane molecule at low temperatures so that oxidative coupling products such as C2 formation and CO2 or CO may be neglected. Current technology for producing formaldehyde consists of a multi-step process, schematically represented by equation 1.

\[ \text{CH}_4 \rightarrow \text{CH}_2=\text{O} \rightarrow \text{H}_2 \text{O} \rightarrow \text{H}_2 \text{O} \rightarrow \ldots \] (1)

In the three-step process, methanol is the precursor of formaldehyde and approximately 60% of the cost of this precursor arises from the high temperature steam reforming of methane to produce synthesis gas (step 1). Thus there is a significant economic incentive to develop a one-step direct conversion of methane to formaldehyde and methanol. In the present communication we report our preliminary investigation into the use of salen or substituted salens and octaaza macrocyclic manganese and copper complexes encapsulated in zeolite X and Y for the oxidation of methane in an attempt to (1) design new catalytic system for the oxidation of methane and to improve (2) catalyst recovery, product selectivity and catalyst lifetime.

Materials and Methods
Acetonitrile, copper diacetate tetrahydrate, NaOH (E. Merck), TBHP, o-phthalonitrile, 2,6-diaminopyri...
dine, 1-chloronaphthalene, fumed silica, aluminium isopropoxide (all Aldrich) were commercially available samples and used as such.

Chemical analyses of the zeolite encapsulated manganese salen complexes were done by taking a known weight of the sample in a platinum crucible with lid and igniting at 393 K to get the dry weight of the sample. The sample was weighed after equilibration. The difference in weights gave the loss on ignition. The anhydrous sample was treated with sulphuric acid (75%) and hydrofluoric acid (40%) and was evaporated on a hot plate to remove the silicon in the form of SiF₆. This procedure was repeated three times and the sample was ignited, cooled and weighed. The loss in weight gave the amount of silica present in the sample. The residue was fused with potassium pyrosulphate and dissolved in a known volume of water in a standard flask. It was then analyzed for manganese, silicon, sodium and aluminium by atomic absorption spectroscopy (Hitachi Model Z-8000). Omnisorb 100 CX (COULTER Corporation, USA) was used for surface area measurements of the samples. XRD of the samples were done using a Rigaku Model D/Max III VC, (Japan) instrument. Infrared spectra were recorded using a Perkin Elmer 1600 FT IR spectrophotometer in the range 4000-200 cm⁻¹. The diffuse reflectance spectra of the solid catalysts were recorded using a Shimadzu UV-2101 PC UV-Vis spectrophotometer. Scanning electron micrographs of the solid catalysts were recorded on a Leica Stereoscan-440, Cambridge instrument.

**Catalyst preparation**

**Synthesis of tetraiminoctaazamacrocyclic ligand**

A slurry of 8.0 g of o-phthalonitrile (0.0625 mol) and 6.82 g of 2,6-diaminopyridine (0.0625 mol) in 75 ml of 1-chloronaphthalene was heated under gentle reflux for 24 hr. The tarry reaction mixture was allowed to cool and was diluted with 75 ml cold methanol and shaken vigorously for 1 hr. The required solid was filtered using a sintered glass filter and washed with cold methanol until the washings were pale yellow. The red needle type solid thus formed was dried. The macrocycle thus obtained was recrystallized from boiling nitrobenzene and vacuum dried. The yield was 7.43 g (0.01685 mol). Anal. Calc. C₂₆H₁₆NO₆Cu: C, 70.90; H, 3.36; N, 25.45. Found: C, 70.67; H, 3.89; N, 25.54%. Melting point=618 K.

**Copper complexes of the above prepared octaazamacrocyclic ligand**

Copper diacetate tetrahydrate (4.39 g, 0.022 mol) was dissolved in 50 ml of DMF. This solution was added to a slurry of 4.03 g (0.0091 mol) of L in 50 ml of hot DMF. The dark brown mixture was heated under gentle reflux for 3.5 hr. The reaction mixture was cooled, filtered and the solid product was washed with cold DMF and then with cold MeOH. The dark powder obtained was dried by suction and then stored in vacuo over silica gel. Anal. Calc. C₂₆H₁₆NO₆Cu: C, 62.2; H, 2.8; N, 22.3; Cu, 12.7. Found: C, 61.4; H, 3.0; N, 21.8%.

Copper or manganese complexes of salen or substituted salen and the encapsulation procedure of these complexes inside the supercages of zeolite X and Y have already been reported by us.⁹¹⁰

**Encapsulation of octaaza macrocyclic copper complex in the supercages of zeolite X**

Fumed silica (4.0 g) sodium hydroxide (3.2 g) copper macrocyclic complex (0.3 g) and water (16.0 g) were mixed in a plastic beaker and the mixture was kept on stirring for 30 min. To the above homogeneous solution was added aluminate solution (prepared from 9 g of aluminium isopropoxide and 3.2 g of sodium hydroxide in 40 g of water). The final mixture was stirred magnetically for another period of 15 min. The slurry thus obtained was transferred into a polypropylene bottle and stirred for an additional period of 24 hr at 273 K and then heated at 363 K for 15 hr. The mixture was then allowed to cool to room temperature and diluted with plenty of deionized water. The solid crystals were isolated by centrifugation at 8000 rpm for 5 hr. The solid thus obtained was dried at 363 K in vacuo for 15 hr.

**Catalytic oxidation reaction**

In a 300 ml Parr reactor (USA), 0.4 g of the respective solid catalyst, 30 g of acetonitrile, 120 psi methane, 120 psi air and 0.5 g of tertiary butyl hydroperoxide were stirred at 273 K for 8 hr. The temperature of the reaction vessel was maintained using a cryostat (Julabo, FT 901). In the case of oxidation using H₂O₂ as the oxidant in water, 10 g of H₂O₂ (30%) was introduced before methane was admitted to the autoclave. At the end of the reaction, the gas was collected in a glass bulb fitted with a three-way valve and analysed.
Product analysis

The solid catalysts were separated from the reaction mixture by filtration using filtration assembly fitted with a G4 crucible. Manganese and copper were not detected by atomic absorption spectroscopy (Hitachi model Z8000) which suggests absence of leaching of the catalyst-active species. The products of the methane oxidation reaction were analysed for unreacted methane, carbon dioxide, methanol, formaldehyde and formic acid using a Perkin Elmer auto system XL gas chromatograph equipped with an FID detector and a capillary column. The identities of the products were further confirmed by GC mass spectroscopy (Shimadzu GCMS-QP-5000) and also by injecting standard samples. The liquid products were analysed separately. Formic acid formed was esterified as methyl formate by the esterification of formic acid with boron trifluoride in methanol.

Results and Discussion

The elemental analyses of the octaazamacrocyclic ligand and its copper complex are consistent with the proposed structures. The high thermal stability of this complex is an added advantage to exploit its use as a catalyst. FTIR spectra (Table 1) do not show bands corresponding to nitrile (C=N) or primary amino (-NH₂) groups; instead, a new medium intensity band observed around 1610 cm⁻¹ assignable to C=N stretching vibration is observed. These evidences strongly support that the condensation has indeed taken place. The diffuse reflectance spectra of the octaazamacrocyclic copper complex exhibits two d-d bands at 13800 and 19700 cm⁻¹ respectively assignable to the tetrahedral geometry of the copper complex.

The X-ray diffractograms of the zeolite encapsulated complexes did not reveal any significant difference from that of the commercial grade pure zeolite X. Chemical analyses indicate that 0.27 wt % Cu has been encapsulated in the cavities of zeolite. The Si/Al (1.27) ratio is consistent with that of standard zeolite X. This information clearly suggests that the zeolite X structure is formed during the encapsulation step. The encapsulation of copper complex inside the zeolite cavities is indicated by the absence of extraneous material by scanning electron microscopy (SEM) and the average particle size of the zeolite was estimated to be about 1 μ. The structural integrity of the encapsulated macrocyclic complex was indicated by the FTIR and diffuse reflectance spectral data. The intensity of FTIR bands of encapsulated complex reduced considerably which may be due to the low concentration of complex inside the zeolitic cage. However, there was a red shift in the diffuse reflectance spectra of the macrocyclic copper complex on encapsulation. Thus, the absorption maxima for this complex after encapsulation shifted to 14100 and 2000 cm⁻¹ respectively. A similar behaviour was reported with the zeolite encapsulated phthalocyanine copper complexes. Such a shift may be explained to be due to the distortion of the complex species inside the zeolite cage. The surface area of zeolite encapsulated copper macrocyclic complex was reduced considerably to 98 m²/g in comparison to that of the commercial grade pure zeolite X (690 m²/g) without the inclusion of metal complex. Such reduction in surface area strongly supports the inclusion of complex in zeolite cavities.

The results for the oxidation of methane using oxygen or hydrogen peroxide as the oxidant, tertiary

<table>
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<th>Catalyst</th>
<th>νC=N</th>
<th>νC-O</th>
<th>νC=N</th>
<th>νC-H</th>
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<td>1165</td>
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butyl hydroperoxide as the initiator (2% wt of methane) and acetonitrile or water as the solvent at 273 K over various zeolite encapsulated copper and manganese catalysts are shown in Table 2. It is interesting to note that when the octaazamacroyclic copper complex is employed as the catalyst, methane conversion increases appreciably. Another feature observed with this catalyst is that no formaldehyde is detected and a steep increase in formic acid formation is observed. This shows copper macrocyclic complex, like phthalocyanine complex, is much more active catalyst compared to salen complexes. Methanol and formaldehyde are the two major products when zeolite encapsulated salen complexes are employed as the catalysts. The catalyst was filtered after every reaction (Table 2) and washed with acetone, dried and reused. The catalyst maintained almost same activity after recycling. This information along with the absence of metal ions in the solution (by atomic absorption spectroscopy) strongly indicates that the any appreciable leaching of the catalyst active species into the reaction mixture is unlikely.

When the reaction is performed in water with hydrogen peroxide as the oxidant (Table 2), a lower conversion of methane with high selectivity to methanol are noticed compared with the catalytic reaction in acetonitrile medium. The reason for such a difference in catalytic activities is still unclear.

Blank reactions (without the presence of solid catalyst) showed that no appreciable activation of methane molecule occurred and hence the present reaction is indeed catalytic in nature. It seems that the increase in order of catalytic activity of these zeolite encapsulated catalysts in the present oxidation reaction may be placed in the order: copper macrocyclic complex > manganese salen > copper salens, for the aerobic oxidation of methane. There is no apparent direct correlation between methanol, formaldehyde formation and the extent of conversion of methane. The nature of metal and ligand structure influence the conversion of methane. The turnover number values observed (Table 2) are higher than most of the values reported so far.

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References