

## Synthesis and characterization of cerium doped OMS-2 type manganese oxide materials – promising catalysts for oxidation of hazardous pollutants

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It is necessary to develop the new and active catalysts to oxidize or degrade the hazardous pollutants (phenol and atrazine like compounds) released from industrial effluents and wastewater. Bulk manganese oxide is used as simple and successful catalyst for many oxidation reactions in the past. This article discusses the synthetic methodology to prepare the new cerium doped OMS-2 type manganese oxide catalysts. The structure and textural properties of synthesized catalysts were characterized by XRD, TGA, BET and TEM techniques.

### 1. Introduction

In 1980, U.S. EPA (Environmental Protection Agency) announced 57,000 metric tones of solid waste in U.S. classified as hazardous substance; hazardous means it causes or it contributes serious illness or dieses to humans as well as pet animals health. EPA has also announced recently phenol like substance is the top list pollutant in industrial wastes, and table. 1 shows the different phenolic compounds released from U.S. industries per year.

**Table. 1** Release of toxic phenol-like pollutants in the U.S.A. for the year 2000 reproduced from [www.epa.gov/tri/](http://www.epa.gov/tri/).

Compound	Emission (ton/year)	Overall Ranking
Phenol	22	35
2,4-Dinitrophenol	11	50
Catechol	8.3	59
Aniline	5.8	70
Hydroquinone	1.9	95
Quinone	0.64	115
Pentachlorophenol	0.55	120
Chlorophenols	0.046	203
2-Nitrophenol	0.026	213
4-Nitrophenol	0.007	239

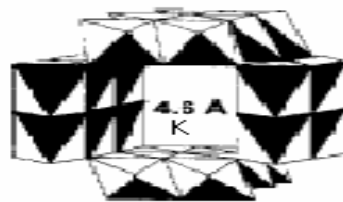
It is necessary to develop the suitable and sustainable engineering process and treatment plants for treating the toxic pollutant from industries like textile, dye, pharmaceutical etc,. Atrazine is the most common post emergent herbicide used for weed control on

agricultural and non-agricultural lands [1]. The presence of atrazine in water is particularly disturbing given recent findings that s-atrazine may have potentially carcinogenic effects [2]. Biological degradation of atrazine is well documented [3]. But, studies on the abiotic interactions of soil components with atrazine are generally limited to clay mineral catalyzed hydrolysis [4-5], sorption reactions on clays [6-7] and activated carbon [8]. Manganese oxide minerals, although generally present in small amounts are common components of soils, Synthetic forms of such oxides are known to oxidize a number of organic compounds, e.g. phenols and aniline [9-11]. The herbicides 2,4 D(2,4 dichlorophenoxyacetic acid) and atrazine are known to be oxidized by synthetic forms of the common soil component oxide mineral birnessite ( $\delta$ - $MnO_2$ ) and cryptomelane ( $\alpha$ - $MnO_2$ ) [12]. Interaction of atrazine with the surface of birnessite produced the metabolites such as deethylatrazine, deisopropyl-atrazine,  $CO_2$  and apparently liberated very small amounts of  $Mn^{2+}$ . Cheney et al. [13] reported the mechano-chemical degradation of atrazine adsorbed on synthetic manganese oxide materials. Manganese oxide surfaces in soils exemplify this possibility by their redox-catalyzed degradation of a number of

adsorbed xenobiotic organic compounds [14] and the widely applied herbicide, 2,4-D (dichloro-phenoxyacetic acid) is a model toxic compound.

Although metal oxides have been used in studies to mimic the transformations of pesticides in soil [15], surprisingly none has employed metal oxides for studies of 2,4-D (dichlorophenoxyacetic acid). But, chenny et al. [16] has studied the abiotic degradation of 2,4-D(dichlorophenoxyacetic acid) on synthetic birnessite type porous manganese oxide material. Phenol is another important pollutant present in the industrial effluents, and the ranking of phenolic compound released per year is shown in table. 1. Cerium mixed manganese oxide composite catalysts are proved as an effective catalyst for phenol oxidation. Doping of cerium ion into the ordered structure of manganese oxide OMS-2 material can act as a selective catalyst for oxidation of hazardous pollutants. Cryptomelane (OMS-2 type manganese oxide) is one of the major manganese oxide minerals found in the deep-sea manganese nodules and in soil sediments [17]. Cryptomelane has a tunnel-structure (Fig. 1) material. The tunnels consist of (2x2) matrix of edge-shared  $MnO_6$  octahedral chains that are corner shared to form a one-dimensional tunnel structure [18] and the synthetic form of cryptomelane is designated as K-OMS-2. Manganese oxide OMS-2 (octahedral molecular sieve) type materials are recently exploited as the potential catalysts for oxidation of volatile organic compounds [20] and it is widely used in many chemical processes because of their porous structure, mild surface acid-base properties and ion-exchange abilities. In the present study discusses the synthetic strategies to synthesize the cerium doped OMS-2

type manganese oxide catalysts. Doping of cerium ion into the ordered tunnel structure manganese oxide can alter the textural and catalytic properties of the manganese oxide material. Crystalline phase, thermal stability and morphology of as synthesized cerium doped manganese oxide material have also been discussed.



**Fig. 1** Manganese oxide OMS-2 type cryptomelane structure

## 2. Experimental

The synthesized catalytic materials are characterized by powder X-ray diffraction method using Philips Diffractometer (Philips Generator, Holland, Model PW 1140) provided with an online recorder. The diffraction patterns were recorded using  $Fe K\alpha$  ( $\lambda = 1.97\text{\AA}$ ) radiation at a scanning speed of 2 degree/min. Thermal stability and phase transitions were analyzed by using Perkin Elmer Delta Series DSC 7 instrument, at 10 degree /min scanning rate. Transmission electron micrographs (TEM) images were recorded using Philips CM12/STEM, Scientific and Analytical Equipment. TEM sampling grids were prepared by placing 2  $\mu$ l of the solution on a carbon-coated grid and the solution was evaporated at room temperature. Surface area values of as synthesized materials were obtained by BET (Brunauer-Emmett-Teller) method using Carlo-Erba sorptometer (Model 1800).

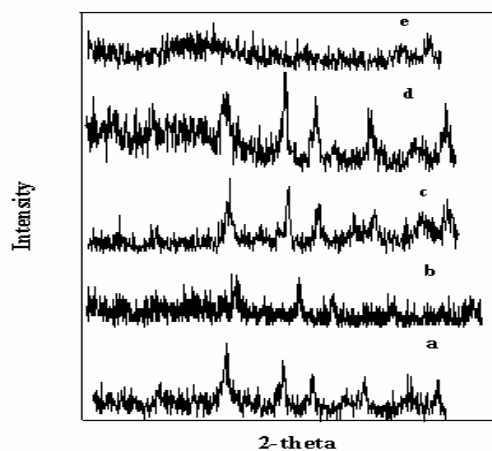
### 2.1 Catalysts preparation

Cerium ion doped ordered manganese oxide OMS-2 catalysts were prepared by

ion exchange process and wet impregnation method. Cryptomelane type doped tunneled manganese oxide K-OMS-2 material was synthesized by reflux method. 113 mL of 0.4M solution of potassium permanganate was added to a 500 mL round-bottom flask, and 33 mL of 1.75 M solution of manganese (II) sulphate hydrate solution was mixed with 113 mL of 0.4M solution of potassium permanganate. Concentrated nitric acid (3.4mL) was added drop wisely by maintain the pH between 2-3, followed by stirring the solution for 24 h. As synthesized cryptomelane type tunnel structure manganese oxide (K-OMS-2) material is filtered and dried at 110 °C for overnight. As synthesized K-OMS-2 material was used to prepare the cerium modified manganese oxide OMS-2 catalysts. In the present study, cerium doped OMS-2 catalysts was prepared by two ways, ion exchange as well as impregnation methods. As synthesized K-OMS-2 material was ion exchanged with aqueous solution of 0.25 M cerium (III) nitrate solution for a few cycles. Cerium ion exchanged OMS-2 material was filtered, washed with distilled water and dried overnight at 110 °C. As synthesized cerium doped OMS-2 material, calcined in air at 400 °C was used for catalytic study. 10wt%, 20wt% and 30 wt% cerium ion doped OMS-2 catalysts are synthesized by impregnation method. The synthesized OMS-2 type manganese oxide material was stirred with an appropriate amount (10wt%, 20 wt% and 30 wt%) cerium (III) nitrate in methanol medium for 24 h, followed by evaporation of the solvent. As synthesized cerium doped OMS-2 materials heat-treated at 400 °C for 5 hours in air for catalytic study.

### 3. Results and discussion

Fig.2 shows the X-ray diffraction pattern of cerium doped OMS-2 type manganese oxide catalysts. Major d spacing values of ion exchange (Fig. 2a) and impregnation method synthesized cerium doped OMS-2 catalysts (10wt%, 20 wt% and 30 wt %) (Fig. 2b, 2c, 2d) are matched with the reported data of OMS-2 type manganese oxide mineral such as cryptomelane (JCPDS = 34 168), upto 30 wt% cerium doped OMS-2 catalysts are shown the ordered XRD patterns. Higher doping of cerium ion (>30 wt%) into OMS-2 material didn't show the ordered XRD pattern.



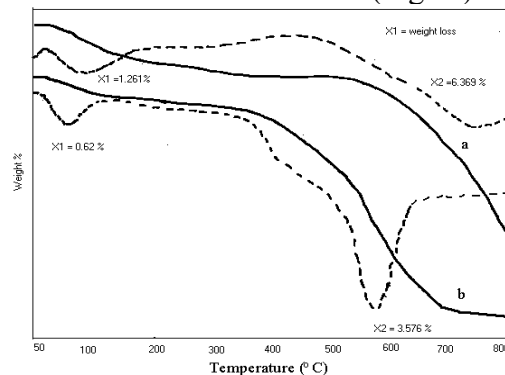
**Fig.2** X-ray diffraction pattern of cerium doped OMS-2 catalysts (a) ion exchange method prepared cerium doped OMS-2 catalyst (b) impregnation method prepared cerium doped OMS-2 catalyst (10wt %), (c) 20 wt % cerium doped OMS-2 (d) 30 wt %) cerium doped OMS-2 catalyst (e) 35 wt % cerium doped OMS-2 catalyst.

Fig 3 shows the TGA of cerium doped OMS-2 catalysts synthesized by ion exchange method (Fig. 3a) and impregnation method (Fig. 3b) respectively. Ion exchange method synthesized cerium doped OMS-2 catalyst (Fig 3a) show an initial weight at around 110 °C with weight loss of

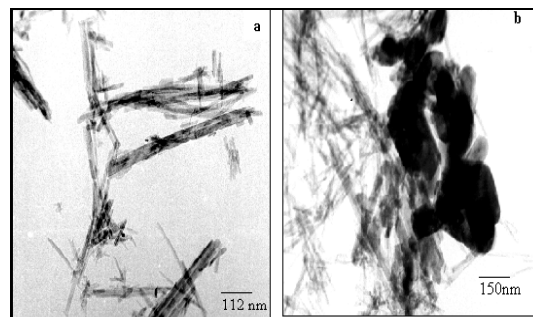
1.26 %, due to water molecules present in the catalyst, and the major weight loss was observed in the temperature range between 550 °C –700 °C, with weight loss of 6.37 % due to transformation of OMS-2 phase into more stable manganese oxide phase such as Mn<sub>2</sub>O<sub>3</sub>, (Fig 3a). Impregnation method synthesized cerium doped OMS-2 catalyst shows a first weight loss around 100 °C with a weight loss value of 0.62% due to the loss of water molecules present in the material and a second weight loss in the temperature range between 550 °C – 600 °C with a weight loss value of 3.58 %, due transformation of cerium doped OMS-2 phase into bixbyite type manganese oxide (Mn<sub>2</sub>O<sub>3</sub>) phase [19]. Ion exchange method synthesized cerium doped OMS-2 show the higher initial weight loss value (1.26 %) compared to impregnation method synthesized catalyst (0.62%), which is purely due to the preparation method. In ion exchange method, cerium ion exchanged with OMS-2 material in aqueous medium but in the case of impregnation method cerium ion doped into the OMS-2 material in methanolic medium. Second, difference in major weight loss value observed for ion exchange method and impregnation method synthesized catalysts. In impregnation method synthesized catalysts, cerium ion dispersed as ceria on manganese oxide surface as well as cerium ion doped into the defective sites, but in the case of ion exchanged method synthesized catalyst, cerium ion doped into the tunnel structure as well as doped into the defective sites present on the manganese oxide surface.

Fig. 4 shows the TEM pictures of cerium doped OMS-2 catalysts synthesized by ion exchange method (Fig. 4a) and impregnation method (Fig. 4b)

respectively. TEM picture of ion exchange method synthesized cerium doped OMS-2 material shows the cerium ion doped in to the needle type fibrous structure of OMS-2 material (Fig 4a).



**Fig. 3** TGA of cerium doped OMS-2 catalysts (a) ion exchange method prepared (b) Impregnation method prepared catalyst



**Fig. 4** TEM pictures of cerium doped OMS-2 catalysts (a) ion exchange method prepared (b) impregnation method prepared catalyst.

But in the case of impregnation method synthesized cerium doped OMS-2 material (Fig 4b), agglomerated ceria particle was deposited in the fibrous structure of manganese oxide surface.

The physico-chemical properties of ion exchange and impregnation method synthesized cerium doped OMS-2 catalysts are shown in table. 2. Cerium to manganese atomic ratio of impregnation method synthesized OMS-2 catalyst was found to be less compared to ion exchange method synthesized OMS-2 catalyst (table. 2). Cerium

content of as synthesized OMS-2 catalysts was determined by spectro fluorometric analyses [20]. BET surface area values of cerium doped OMS-2 catalysts (table. 2), (ion exchange and

**Table. 2** Comparison of surface area, (SA) pore volume (PV) and cerium content of ion exchange and impregnation method synthesized OMS-2 catalysts.

Catalysts	BET SA (m <sup>2</sup> /g) PV(ml/g)	Ce/Mn atomic ratio
Ce-K-OMS-2 (Ion-exchange method)	145 0.33	0.034
Ce-K-OMS-2 (Impregnation)	267 0.36	0.025

impregnation method synthesized catalysts) are found to be higher

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compared to conventional route synthesized transitional metal ion doped manganese oxide OMS-2 catalyst (91 m<sup>2</sup>/g) [21].

### Conclusion

Cerium doped OMS-2 type porous manganese oxide catalytic materials are synthesized by simple preparation route such as ion exchange method and impregnation method. The synthesized cerium doped OMS-2 type manganese oxide shows the higher surface area values compared to that of conventional route synthesized OMS-2 materials. TEM pictures confirm the cerium ion dispersion on fibrous structure of OMS-2 material.

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