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Preparation, characterization and catalytic properties of cerium incorporated porous manganese oxide OMS-2 catalysts

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Abstract

Tunnel structured manganese oxide octahedral molecular sieve (OMS) materials have been recently exploited as potential materials in the field of heterogeneous catalysis and battery technology. In the present study cerium incorporated manganese oxide OMS-2 catalysts have been synthesized by ion-exchange and impregnation methods. Crystal structure, thermal stability, textural property and morphology of as synthesized materials have been characterized using XRD, TGA, BET and TEM techniques.
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1. Introduction

Bulk cerium oxide is an excellent catalyst for redox reactions and is used as an important additive in the three-way catalyst (TWC) for automotive exhaust gas treatment [1–3]. Partially reduced ceria is used as a catalyst in CO hydrogenation [2]. Supported ceria and cerium-manganese oxide composite catalysts have been used as potential catalytic material for low temperature SCR (selective catalytic reduction) of NO_x [4], carbon monoxide oxidation [5] and catalytic wet oxidation of phenolic compounds [6,7]. The effect of addition of copper and silver to cerium oxide catalysts for complete oxidation of methane has also been studied [8]. The prominent role of ceria has been recognized in various fields such as oxidation, combustion catalysis and solid oxide fuel cell. Cryptomelane is one of the major manganese oxide minerals found in the deep-sea manganese nodules and in soil sediments. Cryptomelane (OMS-2)

has a tunnel-structure, which is shown in Fig. 1. The tunnels consist of (2×2) matrix of edge-shared MnO_6 octahedral chains that are corner shared to form a one-dimensional tunnel structure. Recently, a new class of octahedral molecular sieves (OMS) of manganese oxide with specific porous structure in the ordered phase material has been exploited as a potential catalyst for oxidation and oxidative dehydrogenation process [9].

Synthetic cryptomelane possess many applications such as ion exchange material, removal of radioactive nuclides from radioactive waste and in the field of heterogeneous catalysis [10,11]. Synthetic routes such as reflux and sol–gel methods have been used to synthesize cryptomelane type manganese oxide material (K-OMS-2) [12], which has a composition of KMn_8O_{16}. Divalent or trivalent transition metal ion incorporated OMS-2 materials have also been used as the catalyst for oxidation reactions [5]. The present communication deals with the synthetic strategies of incorporating cerium ions into the ordered phase of manganese oxide OMS-2 catalysts by ion exchange process as well as by wet impregnation method. The synthesized cerium modified OMS-2 catalysts have been tested for gas phase decomposition of cyclohexanol.

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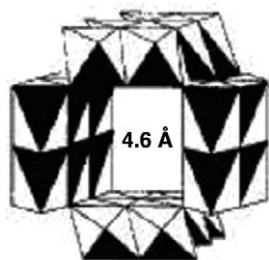*E-mail address:* bvnathan@iitm.ac.in (B. Viswanathan).

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

2. Experimental

All chemicals purchased from E-merck, CDH and SRL (India), were reagent grade and the samples were 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 Kα ($\lambda = 1.97$ Å) radiation at a scanning speed of 2°/min. Thermal stability and phase transitions were analyzed by using Perkin–Elmer Delta Series DSC 7 instrument, at 10°/min scanning rate. Transmission electron micrographs (TEM) were recorded using Philips CM12/ STEM, Scientific and Analytical Equipment. TEM sampling grids were prepared by placing 2 μl 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). The products of the catalytic reactions were analyzed by gas chromatography (Nucon 5600, FID, OV 17).

Vapour phase decomposition of cyclohexanol was performed in a fixed bed flow reactor working at atmospheric pressure. The reactants were fed into the reactor by a motar-driven syringe infusion system. The inlet tube was spiraled around three fourth of the length of reactor before its inlet through the top of the reactor. This enabled the vaporization of the reactants and preheating of the vapour to the set reaction temperatures before entering the catalyst zone. For vapour phase reaction, about 1.0 g of the catalyst was used for each run. Products collected for the first 20 min were discarded to ensure the attainment of the steady state.

3. Results and discussion

3.1. Preparation of parent manganese oxide OMS-2 material

Cryptomelane type parent tunnel structure manganese oxide OMS-2 material was synthesized by oxidation of manganese(II) sulphate by potassium per-manganate in strong acidic medium under suitable reflux condition. Hundred millilitre of 0.4 M solution of potassium permanganate was added to a 500-ml round-bottom flask, and 31.0 ml of 1.7 M solution of manganese(II) sulphate hydrate solution was mixed with 100 ml of 0.4 M solution of potassium permanganate. The molar ratio between potassium permanganate to manganese(II) sulphate fixed as 0.76 ($MnO_4^-/Mn^{2+} = 0.76$) for preparing parent OMS-2 material in acidic medium. After the addition of manganese(II) sulphate aqueous solution to the potassium permanganate, the concentrated nitric acid (15–20 ml of 6.0 M) was added drop wisely to the mixed solution for maintaining the strong acidic medium and the mixed solution was stirred for 24 h at 90 °C. The synthesized manganese oxide suspension was filtered, washed several times with distilled water and the solid brown-black manganese oxide material was dried at 110 °C for 10 h. As synthesized manganese oxide material is designated as parent OMS-2 material.

3.2. Preparation of cerium incorporated manganese oxide OMS-2 catalysts

Cerium cation incorporated ordered manganese oxide OMS-2 catalysts were prepared by ion exchange and wet impregnation methods.

3.2.1. Ion-exchange method

The synthesized parent manganese oxide OMS-2 material was used to prepare the cerium modified manganese oxide OMS-2 catalysts. The as-synthesized parent OMS-2 material (1 g) was stirred with 30 ml aqueous solution of 0.2 M cerium(III) nitrate for 24 h at room temperature and every 4 h the aqueous cerium(III) nitrate solution was decanted and 20 ml of fresh aqueous cerium(III) nitrate solution was added to facilitate the ion-exchange process. Cerium(III) ion exchanged OMS-2 material was filtered, washed with distilled water and dried at 120 °C for 8 h. As synthesized cerium ion incorporated OMS-2 material was calcined in air at 400 °C for 4 h, and the calcined catalyst was used for catalytic study. Potassium ions were partially replaced by cerium(III) ion in the ion-exchange method.

3.2.2. Impregnation method

In impregnation method, 1.5 g of parent OMS-2 type manganese oxide material was added to the 0.5 g of cerium(III) nitrate dissolved in methanol. The mixture was stirred for 24 h, followed by evaporation of the methanol. The solid material directly dried at 120 °C for 8 h. The synthesized cerium incorporated OMS-2 material calcined at 400 °C in air for 4–5 h and the calcined catalyst was used for catalytic study.
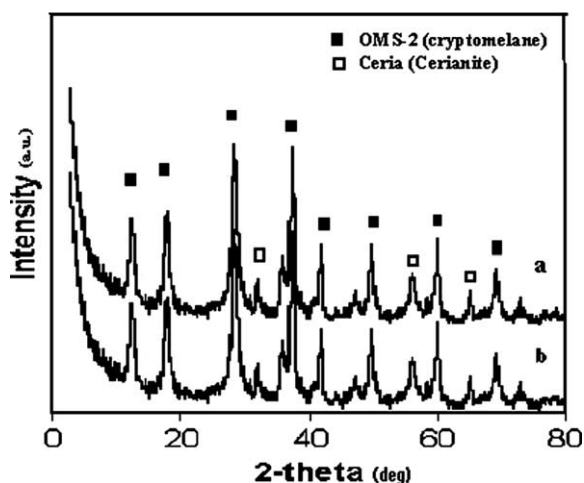
Fig. 2. X-ray diffraction pattern of cerium incorporated OMS-2 catalysts: (a) ion-exchange method prepared catalyst; (b) impregnation method prepared catalyst.

3.3. X-ray diffraction, thermal analysis and catalytic activity

X-ray diffraction pattern of cerium ion incorporated OMS-2 catalysts are shown in Fig. 2. Major d spacing values of ion exchange (Fig. 2(a)) and impregnation method (Fig. 2(b)) synthesized cerium incorporated OMS-2 catalysts matched with the reported data of OMS-2 type manganese oxide crystal structure such as cryptomelane (JCPDS = 34,168) and ceria phase has also been observed and it is indexed with reported data (JCPDS = 43,1002). Fig. 3 shows the TGA of cerium ion incorporated OMS-2 catalysts synthesized by ion exchange method (Fig. 3(a)) and impregnation method (Fig. 3(b)), respectively. TGA of the sample prepared by ion exchange method (Fig. 3(a)) shows an initial weight loss due to the presence of water molecules, at

around 110 °C with the weight loss of 1.26% and a major weight loss in the temperature range between 600 and 785 °C, due to decomposition of cerium incorporated OMS-2 phase into more stable manganese oxide phase such as Mn_2O_3, with weight loss of 6.4% (Fig. 3(a)). Impregnation method synthesized cerium ion incorporated OMS-2 catalyst shows a first weight loss around 100 °C with a weight loss value of 0.6% due to the loss of water molecules and a second weight loss in the temperature range between 550 and 600 °C with a weight loss value of 3.6%, due to decomposition of cerium incorporated OMS-2 phase into the more stable bixbyite type manganese oxide (Mn_2O_3) phase [13]. Fig. 4 shows the TEM pictures of cerium incorporated OMS-2 catalysts synthesized by ion exchange process (Fig. 4(a) and (b)) and impregnation process (Fig. 4(c) and (d)), respectively. TEM pictures of ion exchange process synthesized cerium ion incorporated OMS-2 material show the cerium ion incorporated in to the needle type fibrous structure of OMS-2 material (Fig. 4(a) and (b)), but in the case of impregnation method synthesized cerium incorporated OMS-2 material shows (Fig. 4(c) and (d)), agglomerated ceria particle was dispersed in the fibrous structure of manganese oxide surface. The physico-chemical properties of ion-exchange and impregnation method synthesized cerium ion incorporated OMS-2 catalysts are given in Table 1. 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 1). Cerium content of as synthesized OMS-2 catalysts was determined by spectro fluorometric analysis by standard calibration method [14]. BET surface area values of cerium ion incorporated OMS-2 catalysts (ion exchange and impregnation method synthesized catalyst) were found to be higher compared to conventionally synthesized OMS-2 type manganese oxide
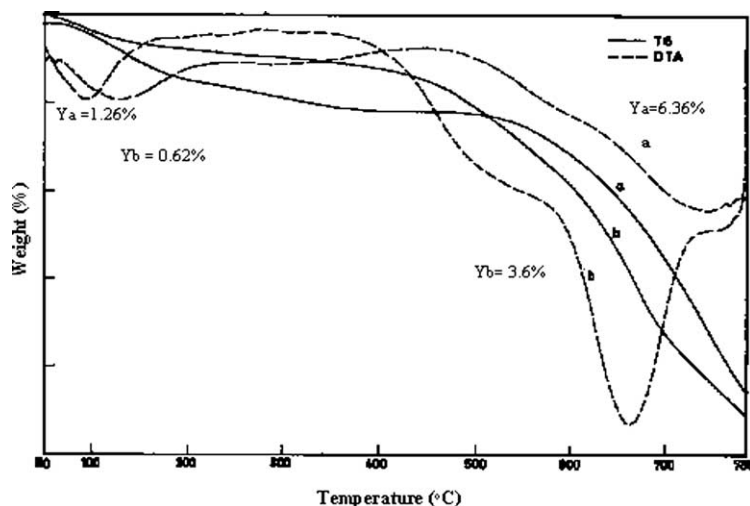

Fig. 3. TGA of cerium incorporated OMS-2 catalysts: (a) ion-exchange method prepared; (b) impregnation method prepared catalyst.
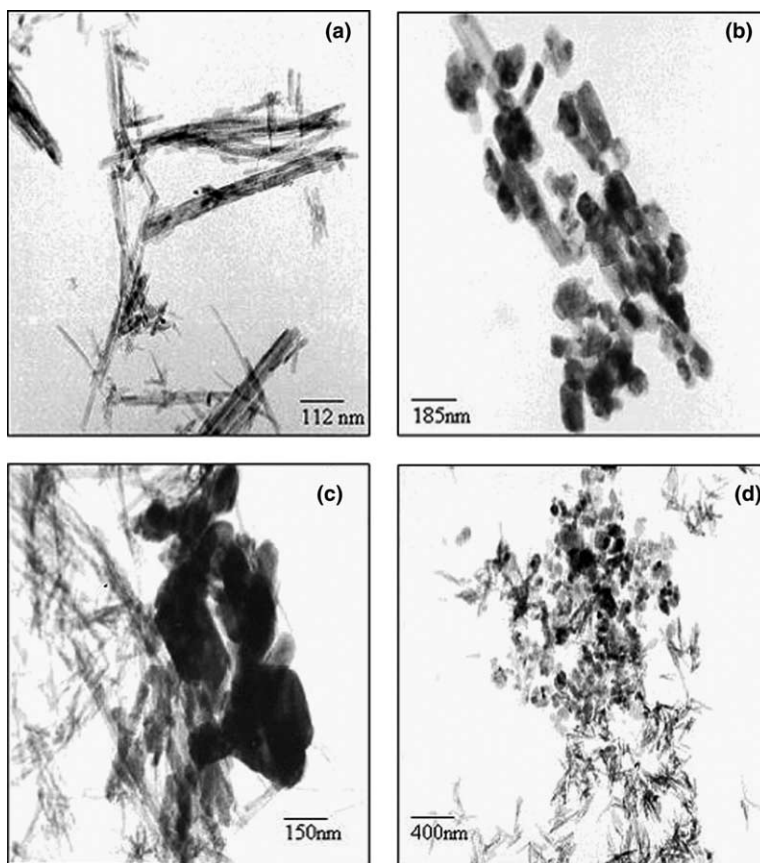
Fig. 4. TEM pictures of cerium incorporated OMS-2 catalysts: (1) ion-exchange method prepared (a,b); (2) impregnation method prepared catalyst (c,d).

materials [15]. In the present study, as synthesized cerium incorporated OMS-2 catalysts were tested for cyclohexanol decomposition at various substrate flow rates as well as at different temperatures. Alcohol decomposition reaction has been widely studied because it is a simple model reaction to determine the functionality of an oxide catalyst. Decomposition of isopropanol and that of cyclohexanol (CHOL) are the most widely studied reactions in this category. Dehydration activity is linked to the acidic property and dehydrogenation activity to the combined effects of both acidic and basic properties of the catalyst. Studies on cyclohexanol decomposition on spinel oxide have been reported [16,17]. Bezouha-

nova and Al-Zihari et al. [18], have recommended the dehydration activity of cyclohexanol conversion as a simple test to measure the Bronsted acid sites in a metal oxide. Bar diagram (Fig. 5) shows the effect of cyclohexanol conversion at various temperatures. Wet impregnation method synthesized catalyst showed higher conversion for cyclohexanol decomposition compared to that of ion exchange method synthesized catalyst. Both the catalysts (impregnation method and ion exchange method synthesized cerium incorporated OMS-2 catalysts) showed major selectivity towards cyclohexanone formation. Cyclohexanol dehydrogenation was more favorable than dehydration of cyclohexanol on

Table 1
Textural property and catalytic activity of cerium incorporated OMS-2 catalysts

Catalyst	Surface area (m^2/g)	Pore volume (mL/g)	Ce/Mn atomic ratio	Cyclohexanol conversion (%)	Selectivity	
					Cyclohexene (%)	Cyclohexanone (%)
Ce-K-OMS-2 (ion-exchange method)	145	0.33	0.034	20.4	35	65
Ce-K-OMS-2 (impregnation method)	297	0.36	0.03	23.2	6	94

Reaction condition: 1 g catalyst, 10 mL/h substrate and 350 °C, GHSV = 14,600 h^{-1}. Total reaction time = 40 min.
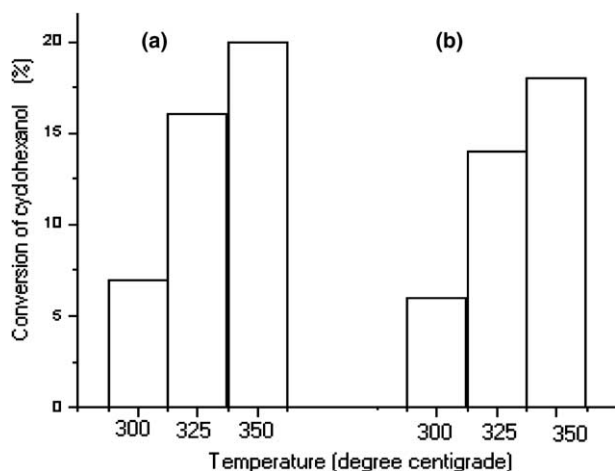
Fig. 5. Bar diagram of cyclohexanol conversion on cerium incorporated OMS-2 catalysts: (a) impregnation method prepared catalyst; (b) ion-exchange method prepared catalyst at various temperatures.

volatile hydrocarbons as well as for decomposition of phenolic compounds.

as synthesized cerium ion incorporated OMS-2 catalysts. It indicates that, cerium ion incorporated OMS-2 catalysts will provide the selective product formation depends on the nature of the acidic and basic properties of as-synthesized OMS-2 catalysts. Cerium incorporated OMS-2 catalysts favor the dehydrogenation of cyclohexanol due to the presence of basic sites in the cerium incorporated OMS-2 catalysts. Incorporation of cerium ions into the parent OMS-2 phase causes the alteration in the acidic and basic sites present on the manganese oxide surface. In summary, the simple synthetic route prepared cerium incorporated OMS-2 catalysts may be used as promising catalysts for complete oxidation of

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