Synthesis and structural characterization of cerium incorporated manganese oxide OMS-2 type catalysts

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Cerium incorporated ordered phase of manganese oxide OMS (octahedral molecular sieve) materials have been synthesized by ion exchange and hydrothermal methods. The cerium incorporated OMS-2 type catalysts have been prepared from potassium birnessite as well as from potassium containing cryptomelane. XRD, TGA, BET and SEM analyses have been used to characterize the cerium incorporated manganese oxide OMS-2 materials.

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Cryptomelane is one of the major manganese oxide minerals found in the deep-sea manganese nodules and in soil sediments. Cryptomelane (K-OMS-2) has a tunnel-structure. The tunnels consist of (2×2) matrix of edge-shared MnO₆ 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 form has been exploited as a potential catalyst for oxidation and oxidative dehydrogenation reactions. Synthetic forms of cryptomelane and potassium birnessite are designated as K-OMS-2 and K-OL-1, respectively. Synthetic cryptomelane and birnessite type porous manganese oxides have been used for the removal of radionuclides from radioactive wastes and as catalysts. Synthetic routes such as reflux and sol-gel methods have been used to synthesize cryptomelane type manganese oxide materials (K-OMS-2), having a composition of KMn₉O₁₆. Divalent and trivalent transition metal ions incorporated OMS-2 materials have been used as catalysts for oxidation reactions.

Potassium birnessite is a layer structure manganese oxide material with water molecules present inside the layer structure. Potassium in the interlayer acts as an exchangeable cation in the ion exchange process. The interlayer space of potassium birnessite is nearly 7 Å. Recently, Fe (III) doped cryptomelane type tunnel structure manganese oxide material prepared from sodium birnessite has been reported.

Bulk cerium oxide is an excellent catalyst for redox reactions and it is used as an important additive in the three-way catalyst (TWC) for automotive exhaust gas treatment. Supported ceria and cerium-manganese composite (disordered form) on oxide catalysts are potential catalytic materials for low temperature selective catalytic reduction (SCR) of NOₓ species, carbon monoxide oxidation and catalytic wet oxidation of phenolic compounds. The synthetic methodology to dope the cerium ion into the ordered phase of layer structure potassium containing birnessite and cryptomelane type porous manganese oxide materials is discussed here. Our previous study regarding cerium incorporation into cryptomelane type manganese oxide OMS-2 material via impregnation and ion-exchange methods is discussed in detail. In the present study, potassium containing birnessite and cryptomelane type manganese oxide materials have been used as precursors for the preparation of cerium incorporated manganese oxide OMS catalysts.

Materials and Methods

Reagent grade chemicals were purchased from E-Merck and SRL (India). The synthesized cerium incorporated manganese oxide OMS-2 materials 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 (λ= 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 instrument, at 10°/min heating rate. Chemical compositions of the catalysts were evaluated by SEM-EDAX method (JEM-35, JEOL, Co.). Surface area of the as-synthesized materials was determined by BET (Brunauer-Emmett-Teller) method using Carlo-Erba sorptometer (Model 1800).
Preparation of cryptomelane type 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 permanganate in strong acidic medium under suitable reflux condition. 100 mL 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 (MnO₄⁻/Mn²⁺ = 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 dropwise to the mixed solution for maintaining the strong acidic medium (pH = 2) 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.

Preparation of cerium incorporated manganese oxide OMS-2 from cryptomelane by 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. After 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.

Synthesis of cerium incorporated manganese oxide OMS material from potassium birnessite by hydrothermal method

Potassium birnessite was synthesized in an alkaline medium using 5.0 M potassium hydroxide solution as the precipitating agent. Required amount (30 mL) of manganese (II) sulphate was added to 50 mL of 5.0 M KOH solution by dropwise addition, where pH was maintained between 12-13. As-synthesized Mn(OH)₂ suspension was oxidized by dropwise addition of (40 mL of 0.10 M) potassium permanganate followed by aging for 4 days resulting the formation of layer structure potassium birnessite. The molar ratio between potassium permanganate and manganese (II) ion was fixed at 0.36. As-synthesized potassium birnessite type layer structure manganese oxide material was used as the precursor for the formation of cerium incorporated manganese oxide OMS catalyst. The synthesized potassium birnessite was ion exchanged with 25 mL of 0.30 M aqueous solution of cerium (III) nitrate for 3-4 cycles. As-synthesized cerium incorporated potassium birnessite, when subjected to hydrothermal treatment for 2-3 days at 110°C resulted in the formation of cerium incorporated manganese oxide OMS catalyst.

Results and Discussion

Cerium incorporated manganese oxide OMS-2 catalysts were prepared from cryptomelane and potassium birnessite by ion exchange and hydrothermal methods. Figure 1 shows the structures of potassium birnessite (Fig. 1a) and cryptomelane type tunnel structure manganese oxide (Fig. 1b). Figure 2a shows the XRD pattern of cerium exchanged cryptomelane type manganese oxide OMS-2 catalyst. Major d-spacing values of as-synthesized cerium incorporated OMS-2 catalyst matched with the reported d-spacing data of mineral cryptomelane. Figure 2b shows the XRD pattern cerium incorporated OMS-2 type manganese oxide catalyst synthesized from potassium birnessite. Major d-spacing values of as-synthesized materials matched with JCPDS data of cerianite (JCPDS 43-1002) and cryptomelane (JCPDS 34-168). Thermal stability of the cerium incorporated OMS-2 catalysts was obtained by thermogravimetric
Fig. 2 — XRD pattern of cerium incorporated OMS-2 catalysts. [(a) ion-exchange method, (b) hydrothermal method].

Fig. 3 — TGA of cerium incorporated OMS-2 catalysts [(a) ion-exchange method, (b) hydrothermal method].

Table 1 — Surface area and chemical composition of cerium incorporated OMS catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (mL/g)</th>
<th>EDX composition (at %)</th>
<th>Ce/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce-K-OMS-2</td>
<td>145</td>
<td>0.33</td>
<td>O: 53.04, K: 2.63, Ce: 9.05, Mn: 27.36</td>
<td>0.034</td>
</tr>
<tr>
<td>Ce-K-OMS-2b</td>
<td>166</td>
<td>0.51</td>
<td>O: 71.48, K: 0.62, Ce: 8.6, Mn: 19.31</td>
<td>0.44</td>
</tr>
</tbody>
</table>

*Synthesized from cryptomelane

*Synthesized from potassium birnessite

analysis (TGA). Figures 3a and 3b show the TGA of cerium incorporated manganese oxide OMS-2 catalysts (ion exchange and hydrothermal method), respectively. The ion-exchange method synthesized cerium incorporated OMS-2 catalyst (Fig. 3a) shows an initial weight loss at 100-110°C due to evolution of water molecules present in the material and the major weight loss observed at around 610°C with a weight loss value of 6.36% due to the decomposition of tunnel structure manganese oxide OMS-2 material into more stable Mn₂O₃ phase. The hydrothermal method synthesized cerium incorporated OMS-2 catalyst (Fig. 3b) shows an initial weight loss around 80°C due to the presence of water molecules and the second weight loss value was obtained around 620°C with a value of 9.06% due to the decomposition of OMS-2 tunnel structure into more stable manganese oxide phase (Mn₂O₃). Table 1 shows the surface area, pore volume and elemental composition of the synthesized cerium incorporated manganese oxide OMS-2 catalysts prepared by ion exchange and hydrothermal methods. Surface area values of as-synthesized cerium incorporated manganese oxide OMS-2 catalysts was found to be high compared to that of conventionally synthesized cryptomelane type manganese oxide (91 m²/g) catalyst. Cerium to manganese atomic ratio of ion exchange method synthesized cerium incorporated manganese oxide OMS-2 catalyst was found to be less compared to the material synthesized by hydrothermal method. The size and shape of cerium incorporated OMS-2 materials strongly depend on the preparation method. The SEM micrographs demonstrated that OMS-2 materials obtained by ion exchange method consisted of relatively large globular particles of 5-25 µm (Fig. 4a) due to the agglomeration of densely packed small K-OMS-2 nanocrystals of needle and globular shapes (Fig. 4b). These particles could be considered as densely packed crystals of octahedral molecular sieve K-OMS-2 materials with crystal size of 20 nm in agreement with XRD data, this conclusion is consistent with the texture of K-OMS-2 material observed recently with high resolution TEM (transmission electron microscopy). The sample prepared by hydrothermal method represented 0.25-1 µm agglomerates of crystals with globular or needle shape (Figs 4c,4d). This explains the high sur-
face area (166 m²/g) and pore volume (0.51 mL/g) of Ce-K-OmS-2 (hydrothermal method prepared) materials that could be caused by significant contribution of external surface of small crystals and voids between them, due to their better accessibility in substantially smaller agglomerates.

XRD, TGA and BET analyses was confirm the crystal structure, thermal stability, increased surface area and porous structure of cerium incorporated OMS-2 catalysts (ion exchange as well as hydrothermal method synthesized catalysts). Cerium incorporated manganese oxide OMS-2 type catalysts with high surface area and specific pore volume may function as a possible catalysts for oxidation of phenolic compounds and degradation of volatile organic compounds.

References
1. Luo L, Qiuhua Zhang, Aimin Huan & Suib S L. Micropor

Fig. 4—SEM micrographs of cerium incorporated OMS-2 catalysts [a & b, ion-exchange method; c & d, hydrothermal method].