

## Effect of the Preparation Method on the Structural and Catalytic Properties of MnO<sub>x</sub>-CeO<sub>2</sub> Manganese Cerium Mixed Oxides

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MnO<sub>x</sub>-CeO<sub>2</sub> catalysts (molar ratio Mn/Ce = 1) were prepared using two methods: co-precipitation and citrate methods. The prepared solids were calcined at 500°C, and characterized by XRD, nitrogen adsorption-desorption technique and SEM morphological, they were, then, tested in the toluene combustion reaction. The catalytic performances of the prepared solids were evaluated in the temperature range 150-400°C. The XRD analysis of the two solids showed that the only crystalline phase detected is cerium oxide. BET surface area measurements showed that the incorporation of manganese led to an increase in the specific surface area of ceria, the solid prepared by the co-precipitation method led to the highest specific surface area (156 m<sup>2</sup>/g). The solids showed good performances in the toluene combustion reaction that depend strongly on the preparation method. The best catalytic activity was obtained for the catalyst prepared by the citrate method achieving a complete conversion of toluene at 250 ° C.

**Keywords:** MnO<sub>x</sub>-CeO<sub>2</sub> mixed oxides, Solid solution, VOC, Catalytic combustion, Toluene.

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### 1. INTRODUCTION

Mixed oxides are often used as heterogeneous catalysts for many chemical reactions; both cerium and manganese cations may be the effective component in oxide-based catalysts suitable for oxidation reactions [1-10].

Manganese oxides have been widely used in a broad range of reactions and have received a strong intention as catalysts, or as structural and electronic promoters of heterogeneous catalysts formulations [11-13].

Ceria has been the subject of thorough investigations, mainly because of its use as an active component of catalytic converters for the treatment of exhaust gases. Moreover, ceria-based catalysts have also been developed for different applications and chemical reactions. Ceria is known for its particular activity in catalytic oxidation reactions, due to the oxygen storage capacity property [14-17].

Volatile organic compounds (VOCs), are a major class of atmospheric pollutants, that are released in the atmosphere by different manufacturing processes, motor vehicles and domestic activities. In addition to be directly harmful for human health, the COV's are involved into the formation of ambient ozone by chemical reactions with nitrogen oxides (NO<sub>x</sub>)[18-20]. The VOC's generated by industrial processes are generally eliminated by thermal combustion, however, the catalytic combustion is more advantageous as it enables to operate at lower temperatures (200-400°C instead of 1000°C) which leads to the limitation of the formation of by-products, such as dioxins and nitrogen oxides and carbon monoxide [20].

In the present work, two MnO<sub>x</sub>-CeO<sub>2</sub> solids were prepared using co-precipitation and citrate methods to check the influence of the preparation method on the textural and structural properties of the solids and then the catalytic performance of these systems was probed in the toluene combustion reaction.

### 2. EXPERIMENTAL

#### 2.1 Catalysts Preparation

The solids, MnO<sub>x</sub>-CeO<sub>2</sub> with a molar ratio Mn/Ce = 1, were prepared by two methods:

a-Carbonate route [MnCe-CPC]. A solution of manganese and cerium nitrates was poured, under vigorous stirring, into a solution of excess (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> held at 60°C. Upon contact, a precipitate immediately forms and the pH of the slurry stabilizes at 8. The slurry is aged at 60°C for 3 h and then filtered to separate the solid. The obtained cake is thoroughly washed to remove nitrates and excess carbonates. Subsequently, the solid was dried at 100 °C overnight. The dried samples were calcined, in air, at 500°C for 4 hours (heating rate 5 °C/min). The solid prepared via this carbonate route was labeled MnCe-CPC-500. Pure oxides were also prepared using the same method and were labeled MnO<sub>x</sub> and CeO<sub>2</sub>.

b-Citrate route [MnCe- Cit]. Manganese and cerium nitrates were dissolved in water and mixed in a molar ratio Mn/Ce = 1. A citric acid solution was added to the previous mixture. The molar ratio of the total metallic cations (Mn+Ce):citric acid (CA) was 1:1 which represents an excess over the stoichiometric proportion. After homogenization of this solution, the temperature was raised to 60°C, and the solution maintained under stirring to remove excess water and to convert it to a yellowish gel. The gel was then dried at 80°C overnight. The precursors were calcined at 500°C, in air, during 5 hours with a heating rate of 5°/min. The solid prepared via the citrate route were noted as MnCe-CIT-500.

#### 2.2 Catalysts characterization

The X-ray diffraction experiments were performed on a Philips PW 1710 f powder diffractometer using the Cu K $\alpha$  radiation ( $\lambda = 1.5406$  nm). The data was collected at

0.02° with a counting time of 2 s per step, in the (2 $\theta$ ) range from 20° to 80°. The crystalline phases were identified by reference to the powder diffraction data (JCPDS) with the use of standard spectra software and the average crystallite size was estimated from the line broadening with the Scherrer formula.

Nitrogen adsorption and desorption isotherms were determined on a Micromeritics ASAP 2010 instrument. The specific surface areas were calculated by the BET method.

Scanning electron microscopy (SEM) was performed using a (Hitachi S 2460 N) apparatus Figure 2.

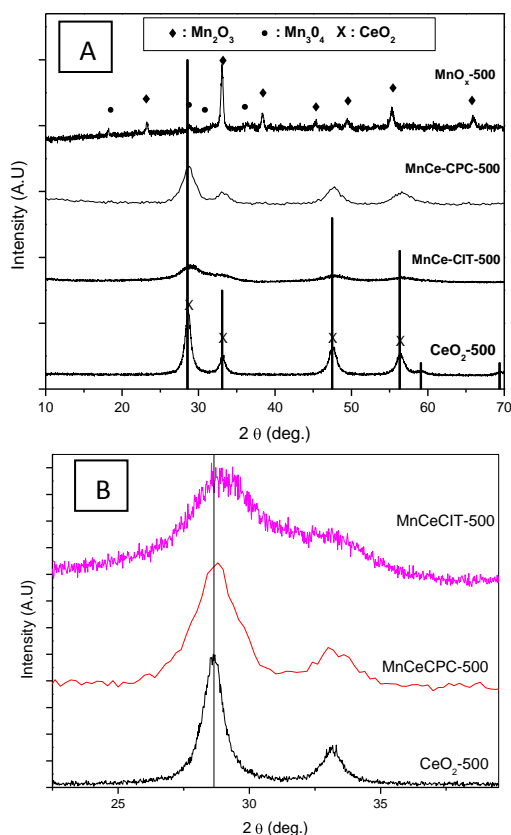
### 2.3 Catalytic activity

Catalytic activity tests were carried out in a fixed-bed flow reactor (10mm i.d) under atmospheric pressure loaded typically with 0.2g catalyst. For the catalytic activity evaluation, a mixture of 8000 ppm mol of toluene and air flowing at 100 ml min<sup>-1</sup> was admitted and the temperature was raised up to 400 °C in steps of 50°C. The reactants and reaction products were analyzed by an on-line gas chromatograph Perkin Elmer, GC Clarus 500, equipped with an FID detector and using a Porapak Q column.

## 3. RESULTS AND DISCUSSION

### 3.1 Solids characterization

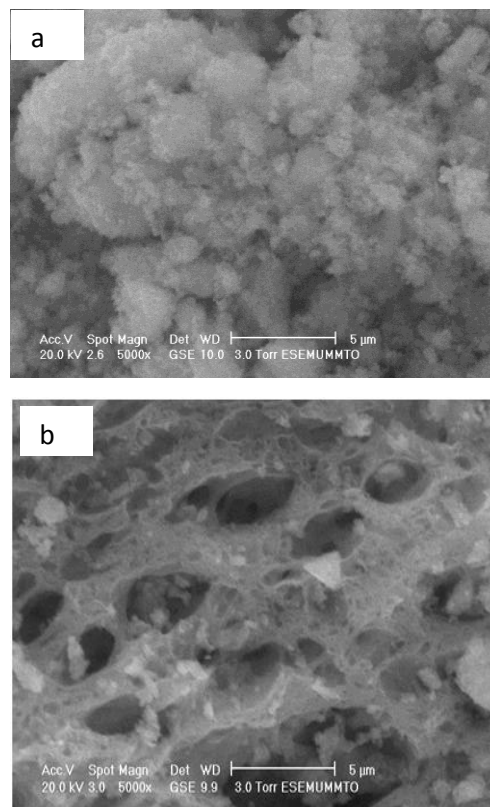
The XRD patterns of the pure and mixed oxides are shown in figure 1.



**Fig. 1** – (A) XRD patterns of pure and mixed manganese-cerium oxides the vertical lines correspond to the position of diffraction lines of CeO<sub>2</sub> JCPDF#34-0394 B :shift XRD lines.

The manganese oxide consisted mainly in Mn<sub>2</sub>O<sub>3</sub> oxide phase (JCPDF#411442) with traces of Mn<sub>3</sub>O<sub>4</sub> (JCPDF#240734). Pure ceria prepared by the precipitation of carbonate precursor showed the characteristic diffraction lines of cubic fluorite structure (JCPDF#34-0394). The mixed oxides prepared by the two synthesis protocols showed both broad diffraction lines of the cubic ceria, nevertheless these lines were shifted to higher 2  $\theta$  values, this shift may be attributed to the introduction of manganese ions into the ceria lattice, resulting in the formation of a Mn-Ce-O solid solution as reported in several studies in the literature [21-23], the partial replacement of Ce<sup>4+</sup> by Mn<sup>3+</sup> is possible knowing that the radius of Mn<sup>2+</sup> (0.0117nm), Mn<sup>3+</sup> (0.066 nm) and Mn<sup>4+</sup> ions(0.06nm) is smaller than the Ce<sup>4+</sup> one (0.094). The formation of the solid solution results in the decrease in the ceria cell parameter (Table 1).

The synthesis method is known to influence the textural properties of solids, in the present study, the two methods used to prepare the Mn-Ce mixed oxides lead to solids with different textural characteristics as it can be noticed in table 1. The citrate method lead to the formation of a solid with smaller surface area, pore volume and average pore diameter. Nevertheless, the mixed oxides prepared via both methods showed greater surface areas than the pure oxides. Moreover, the preparation method seemed to influence also the particle size, and the citrate method lead to the solid with the smallest particles compared to the one prepared via the carbonate precursor precipitation (Table 1) indicating that the co-precipitation lead to a better crystallization.



**Fig. 2** – SEM of the MnCe-CPC-500(a) and MnCe-CIT-500 (b).

**Table 1** – Cell parameter and ceria particle size, BET, pore volume and pore diameters of the solids

Catalyst	Preparation method	$d_{111}$ (Å)	Cell parameter (Å)	Particle Size* (nm)	BET Area ( $m^2/g$ )	Pore Volume ( $cm^3/g$ )	A.P.D* (nm)
MnO <sub>x</sub>	Carbonate			22.31	48	0.33	2.6
CeO <sub>2</sub>	Carbonate	3.135	5.429	8.04	113	0.16	9
MnO <sub>x</sub> -CeO <sub>2</sub>	Carbonate	3.111	5.388	4.07	156	0.42	10

\*APD : average pore diameter

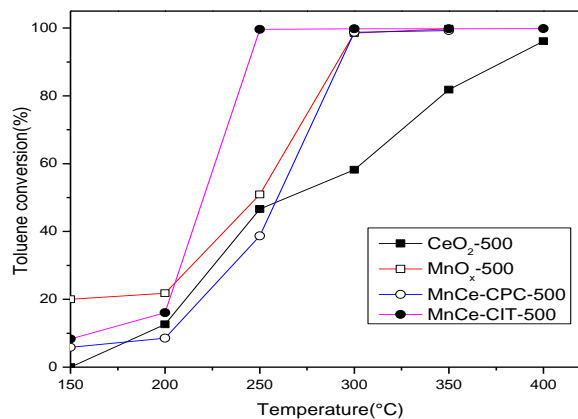
The morphological structure depends strongly on the preparation protocol as shown on figure 2, the coprecipitation method led to an agglomerated particles and the citrate route led to a highly porous foam microstructure.

### 3.2 Catalytic Activity

Fig. 3 shows the result of the oxidation of toluene as expressed by the conversion of toluene versus reaction temperature. At low temperatures, the solid MnO<sub>x</sub> showed the best conversion among the studied solids whereas ceria presented no activity at 150°C. For both pure oxides, the toluene conversion increases gradually to reach 99.8 % at 300°C for MnO<sub>x</sub> and 96.1% at 400°C for ceria. In the temperature range 200-300°C, the solid prepared by the citrate method exhibited the best toluene conversion, leading to a total conversion at 250°C, where the solid MnCe-CPC-500 showed a total conversion at 300°C and showed lower activity than the MnO<sub>x</sub> in the temperature range 200-300°C.

The fact that CeO<sub>2</sub> is less active than MnO<sub>x</sub>, indicates that the higher activity of the solid MnCe-CIT-500 is not due to the inherent activity of Ce. Imamura [24] showed that doping the manganese oxide with cerium resulted in higher valence for manganese and this resulted in a better CO oxidation activity, so, the higher activity of the MnCe-CIT-500 could be attributed to the interaction between Ce and Mn that implies that oxygen is activated by ceria and then transferred to manganese. The superior activity of the solid prepared via the citrate route over the carbonate prepared one may be due to its particular texture properties as it showed the smallest particle size and the small-

est average diameter pore.

**Fig. 3** – Toluene conversion Vs reaction temperature over the pure and Mn-Ce single oxides.

### 4. CONCLUSION

MnO<sub>x</sub>-CeO<sub>2</sub> Mixed oxides prepared by the coprecipitation and citrate methods lead to a good catalytic activity in the total oxidation of toluene. The textural properties and catalytic behavior of these oxides depend strongly on the preparation method. The XRD analysis suggested the formation of a solid solution between manganese and cerium oxide. The citrate method formed the solid with the best catalytic performance, a strong interaction between cerium and manganese and the small particle size seem to be at the origin of this performance.

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