

# OMS-2 molecular sieves doped with ceria for the development of new emission control catalyst

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## Introduction

Manganese oxide octahedral molecular sieves (OMS) are microporous, inorganic nanostructures. Manganese oxides with cryptomelane type structures (OMS-2), has a one-dimensional tunnel structure composed of edge shared  $\text{MnO}_6$  octahedra that form a  $2 \times 2$  arrangement. [1] OMS-2 materials are hydrophobic and hence have improved hydrolytic stability under oxidation conditions. The mixed valency in OMS-2 contributes to its highly active and selective catalysis. [2] Functionality of OMS-2 can be further extended by structural incorporation of various dopants. In this work we have synthesized a range of OMS-2 based supports doped with Ce, CeZr and Pt for emission control. Materials often used for emission control applications are precious metals supported on a Ceria Zirconia mixed oxide [3-5]. Currently, one of the main challenges is to provide a catalyst which is active at low temperature, due to the high emissions of combustion engines during cold start cycles [6]. In particular, we have investigated the use of these OMS-2 hybrid catalyst supports for their activity in the oxidation reactions of CO,  $\text{C}_3\text{H}_6$  and  $\text{CH}_4$  and compared with a commercial diesel oxidation catalyst. The new catalyst samples were tested under representing those in the catalytic filter of a light duty diesel vehicle. The effect of doping the OMS-2 support with Ceria and Zirconia have been studied both pre and post loading with 1 wt% Pt.

## Materials and Methods

OMS-2 molecular sieves were prepared by a sol-gel method.  $\text{KMnO}_4$  (12.65 g, 0.08 mol) was dissolved in deionized water (800 ml). Maleic acid (3.09 g, 0.027 mol) was added slowly to the  $\text{KMnO}_4$  solution and stirred for the desired duration. After stirring, the mixture was allowed to settle, and the top water layer decanted. The resultant gel was then washed 4 times with deionized water. During washing the gel and water were stirred for approximately 5 min each time, the gel was allowed to settle then the water was decanted off. The remaining water was then removed *via* vacuum and the gel transferred to an oven and dried overnight at 90 °C. The gel was then crushed into a fine powder and calcined in air at 450 °C for 4 h. Ce doped OMS-2 was prepared by addition of Ce nitrate during the synthesis of OMS-2 prior to the addition of maleic acid. 1 wt% Pt materials were prepared by incipient wetness impregnation.

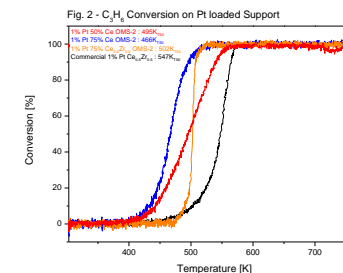
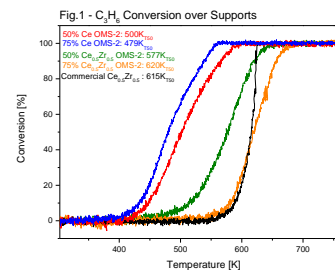
To investigate the effect of the dopants on the catalytic activity of the OMS-2 supports, temperature programmed reactions were carried out. A reaction mixture composed of 10%  $\text{O}_2$ , 4.5%  $\text{H}_2\text{O}$ , 2000ppm CO, 2000ppm  $\text{CH}_4$ , 2000ppm  $\text{C}_3\text{H}_6$ , and 200ppm NO with a total flow of 100ml/min. The temperature was increased from 303 K to 773 K at a rate of 5 K/min and held for 20 mins before being cooled to room temperature. A temperature programmed desorption was carried out immediately after the reaction with 100 ml/min of Ar, using the same temperature ramp. Commercial  $\text{Ce}_{0.5}\text{Zr}_{0.5}$  from Sigma Aldrich and commercial Pt 1wt%  $\text{Ce}_{0.5}\text{Zr}_{0.5}$  were used as a reference. This cycle was repeated 3 times on each sample. The exit stream was analysed using a Pfeiffer Vacuum quadrupole mass spectrometer. Further characterisation has been carried out including XRD, ICP metal analysis and BET surface area.

## Results and Discussion

Figure 1 shows the  $\text{C}_3\text{H}_6$  conversion as a function of temperature in a typical oxidation cycle for each support prepared. It is shown that the addition of Ceria and Zirconia has an impact on

the activity of the OMS-2 support. The addition of  $\text{CeO}_2$  has improved the activity with 50% Ce OMS-2 and 75% Ce OMS-2 reducing the  $T_{50}$  value by 115 K and 136 K respectively, compared to the commercial  $\text{Ce}_{0.5}\text{Zr}_{0.5}$  support. Less enhancements are observed when  $\text{Ce}_{0.5}\text{Zr}_{0.5}$  is added, with the  $T_{50}$  values of 577K and 620K for 50% $\text{Ce}_{0.5}\text{Zr}_{0.5}$  OMS-2 and 75% $\text{Ce}_{0.5}\text{Zr}_{0.5}$  OMS-2 respectively, compared with the commercial  $\text{Ce}_{0.5}\text{Zr}_{0.5}$  support.

Figure 1 shows the  $\text{C}_3\text{H}_6$  conversion as a function of temperature for each support loaded with Pt 1wt%. It can be seen that the enhancements of the support are maintained when loaded with Pt. The  $T_{50}$  values are reduced by 52 K, 81 K and 45 K for 1% Pt 50% Ce OMS-2, 1% Pt 75% Ce OMS-2, and 1% Pt 75%



$\text{Ce}_{0.5}\text{Zr}_{0.5}$  OMS-2 respectively when compared with the commercial 1%Pt  $\text{Ce}_{0.5}\text{Zr}_{0.5}$  sample.

## Significance

These results demonstrate that the addition of  $\text{CeO}_2$  to OMS-2 has a significant impact on the oxidation of these catalysts in the low temperature region. The catalysts doped with  $\text{CeO}_2$  showed a catalytic enhancement than  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  with OMS-2, due to the higher reduction temperature of Zirconia. Therefore, only oxygen stored within the Ceria lattice is available for the oxidation reaction, of which the concentration is lower than that of the supports which are doped with Ceria only. This would also explain why 75% Ce OMS-2 performs better than 50%Ce OMS-2. Furthermore, the enhancement observed when loading Pt was much greater in the 75%  $\text{Ce}_{0.5}\text{Zr}_{0.5}$  OMS-2 and commercial samples, where  $T_{50}$  were decreased by 118 K and 68 K respectively. Both 75% and 50% Ce OMS-2 samples where  $T_{50}$  value were decreased by only 13 K and 5 K respectively. This could also be an indication to the metal-support interaction in each group of material.

## References

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**List of Orals 2019**

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PI01	Design and implementation of <i>de novo</i> biosynthetic cascades	Sabine Flitsch
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K10	Biocatalyst – artificial metalloenzyme cascade based on alcohol dehydrogenase	Simone Morra and Anca Pordea
K11	Magnetocatalysis for selectivity manipulation	Pip Hellier, Michael Bowker, Adli Peck and Michael Claeys
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