

# Insights on the active phase and mechanism for NO oxidation on MnO<sub>x</sub>-CeO<sub>2</sub> mixed oxide

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## Introduction

The oxidation of engine-generated NO to NO<sub>2</sub> is an important step in the reduction of NO<sub>x</sub> in lean engine exhaust because NO<sub>2</sub> enhances the activities of both ammonia selective catalytic reduction (SCR)<sup>1</sup> and Lean-NO<sub>x</sub> Trap (LNT)<sup>2</sup>. Platinum is highly active for NO oxidation, and is widely used in diesel oxidation (DOC) and LNT catalysts. However, because of the high cost and poor thermal durability of Pt-based catalysts, there is substantial interest in the development of alternatives.

Recently, MnO<sub>x</sub>-CeO<sub>2</sub> mixed oxide has been found to exhibit high activity for NO oxidation and is a promising catalyst to lower the loading or completely eliminate the need for Pt.<sup>2</sup> In this work, we investigate the Ce-Mn mixed oxide system using a suite of theoretical and experimental tools to provide insights on the active structure and reaction mechanism.

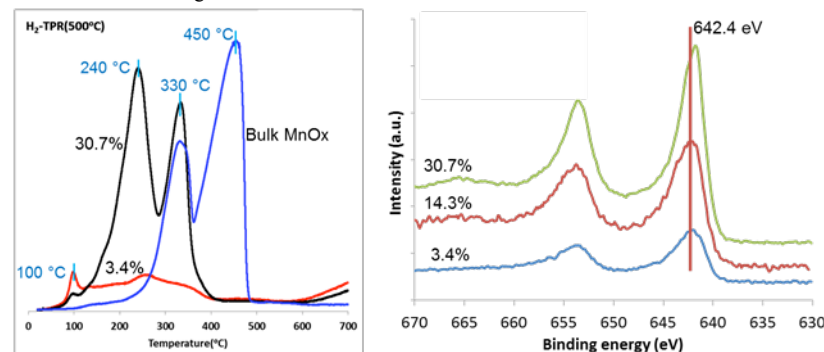
## Materials and Methods

The MnO<sub>x</sub>-CeO<sub>2</sub> catalysts were prepared by incipient wetness. The catalysts were characterized by temperature programmed reduction (TPR), BET surface area, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), X-ray diffraction (XRD) and extended X-ray absorption fine structure spectroscopy (EXAFS). The NO oxidation activity experiments were run in a fixed bed reactor at space velocity of 300,000 hr<sup>-1</sup>, using 200 ppm NO, 10% O<sub>2</sub>, 10% H<sub>2</sub>O (balance N<sub>2</sub>). The products were quantified using an infrared (IR) spectrometer. The NO interaction and NO oxidation mechanism were investigated with infrared spectroscopy in transmission mode. To provide fundamental insights on the reactivity of the MnO<sub>x</sub>-CeO<sub>2</sub> catalysts, we performed DFT calculations to compare the NO oxidation on Mn doped CeO<sub>2</sub> with clusters of MnO<sub>2</sub> supported on the ceria surface.

## Results and Discussion

A comparison of the TPR and XPS of the oxidized catalysts is shown in **Figure 1**. The TPR of the MnO<sub>x</sub>-CeO<sub>2</sub> catalysts with different loading in **Figure 1** show that the lower loading of MnO<sub>x</sub> results in lower reduction temperatures. Even the 30.7 wt% MnO<sub>x</sub>-CeO<sub>2</sub> shows a much lower reduction temperature compared with the pure MnO<sub>x</sub>. The XPS spectra in **Figure 1** show that the Mn is stabilized in a higher oxidation state for the lower MnO<sub>x</sub> loadings. These results are consistent with the EXAFS results shown in **Table 1** where the Mn-O and Mn-Mn bond distances for the 3.4% are shorter than for the 30.7% MnO<sub>x</sub>-CeO<sub>2</sub> catalyst. Additionally the Mn-Mn coordination number (not shown in Table 1) was lower for the 3.4% than the 30.7% catalyst. The XPS and EXAFS results point to the presence of small MnO<sub>2</sub> clusters in close contact with the CeO<sub>2</sub> and that the cluster size increases with MnO<sub>x</sub> loading. DFT calculations show that the NO<sub>2</sub> formation and desorption on MnO<sub>2</sub> cluster

supported on the CeO<sub>2</sub> (MnO<sub>2</sub>/CeO<sub>2</sub>) are significantly facilitated by the interfacial Mn—O—Ce sites, compared to the pure CeO<sub>2</sub>. In addition, DFT results also suggest that the oxygen vacancies generated by the NO<sub>2</sub> desorption are more easily replenished on the MnO<sub>2-x</sub>/CeO<sub>2</sub> compared to the either CeO<sub>2-x</sub> or MnO<sub>2-x</sub>. The proposed active sites will be justified on the bases of the DFT along with IR results.



**Figure 1.** Temperature programmed reduction (left) and Mn2pXPS spectra for the MnO<sub>x</sub>-CeO<sub>2</sub> catalysts after oxidation at 500 °C.

	BET (m <sup>2</sup> /g)	Mn/Ce (XPS)	Conversion (%)	TOF (min <sup>-1</sup> )*	Mn—O (Å)	Mn—Mn (Å)
3.4%	132	0.2	11.2	476	1.84	2.80
14.7%	115	0.64	13.9	212		
30.7%	87	0.69	18.8	348	1.86	2.86
MnO <sub>x</sub>	14.7	-	7.2	541	1.90	3.16

**Table 1.** BET surface area, Mn/Ce ratio from XPS, NO conversion to NO<sub>2</sub> at 200 °C, reaction rate normalized to Mn on the surface (TOF), Mn—O and Mn—Mn bond lengths from EXAFS. \*using Mn/Ce from XPS and a surface density of ~ 11.2 atom/nm<sup>2</sup>.

## Significance

We identified the active phase and the plausible mechanism for NO oxidation on MnO<sub>x</sub>-CeO<sub>2</sub>. We showed that small MnO<sub>2</sub> clusters supported on ceria show high activity for NO oxidation. The findings will help in the design of Pt-free catalysts for LNT and DOC.

## References

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- 2 C. H. Kim, G. S. Qi, K. Dahlberg, and W. Li, Science 327, 1624 (2010).