## Oxygen vacancies evolution in MnOx(0.4)-CeO<sub>2</sub> catalysts mixed with soot with in situ Raman analyses

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## Introduction

Raman technique <sup>[1-2]</sup> has been utilized to study the oxygen vacancies in ceriabased oxides. In our previous work <sup>[3]</sup>, Raman technique combined with XPS and XRD has confirmed the modification effect of Mn on the activity of MnOx(0.4)-CeO<sub>2</sub> compared to CeO<sub>2</sub> or MnOx. However, few works have been reported on the evolution of the oxygen vacancies.

Herein, in situ Raman is used to exam the microstructure of and oxygen vacancies in MnOx(0.4)-CeO<sub>2</sub> catalysts with model soot present in Ar or O<sub>2</sub>(10%)+Ar(balance). Specifically, the Raman measurement cycles under increasing and decreasing temperatures are performed, to provide an insight into the evolution of oxygen vacancies in MnOx(0.4)-CeO<sub>2</sub>. **Materials and Methods** 

Details of catalyst preparation referred to previous work <sup>[3]</sup>. The in situ Raman spectra of catalyst/model soot (Printex-U, Degussa) mixture were obtained in Ar or  $O_2(10\%)$ +Ar(balance) with a LabRAM HR Evolution at excitation laser line of 532 nm.

## **Results and Discussion**

For Ar atmosphere (Figure 1),  $A_{640}/A_{445}$ , the ratio of the peak areas of the bands at around 640(oxygen vacancies <sup>[4]</sup> in defective structure due to the incorporation of Mn ions into the CeO<sub>2</sub> lattice) and 445 cm<sup>-1</sup>(symmetric breathing mode of oxygen atoms around cerium ions <sup>[4]</sup>), reflects the oxygen vacancies concentration in the ceria lattice. The  $A_{640}/A_{445}$  ratio decreases with increasing temperature, suggesting that more oxygen vacancies take part in soot oxidation. Therefore, the recovery of oxygen vacancies draws further attention, which leads to the following Raman measurement cycles (Figure 2).



Figure 1. In situ Raman spectra of MnOx(0.4)-CeO<sub>2</sub> soot mixture under Ar atmosphere.

For the first cycle (Figure 2), the attribution and changing trends of Raman spectra with temperature rising under such oxidizing atmosphere (Fig. 2 a) and Ar (Fig. 1) are similar. When the sample is cooled down to room temperature (Fig. 2 b), a recovery of oxygen vacancies is observed, however,  $A_{640}/A_{445}$  ratio decreases compared to that in the case of rising temperature experiments (Fig. 2 a). We hypothesize that there are some oxygen vacancies,

disposable or not active, for soot oxidation. The latter can be called as spectators <sup>[5]</sup>, for that <sup>[6]</sup> only parts of vacancies can contribute to the amount of charge carriers in ceria-based oxides.

For the second and third cycles (Figure 2), the position and intensity of the bands due to oxygen vacancies revert completely after temperatures rising and dropping, as well as the  $A_{640}/A_{445}$  ratio. This suggests that the oxygen vacancies in this solid solution can keep at a relatively stable level even after 2-3 cycles under increasing and decreasing temperatures.



Figure 2. In situ Raman spectra of MnOx(0.4)-CeO<sub>2</sub> soot mixture in O<sub>2</sub>(10%)+ Ar(balance). Significance

In MnOx(0.4)-CeO<sub>2</sub>, some oxygen vacancies are hypothesized as disposable or spectators for soot oxidation. And this catalyst system presents great potential for practical applications. Acknowledgement

This work is financially supported by National Natural Science Foundation of China (51108187, 50978103, 21207039, U1201231), Guangdong High Education Engineering Technology Research Center for Air Pollution Control Program (GCZX-A0903) and the Guangdong Natural Science Foundation, China (Grant No. S2011010000737). **References** 

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