

# The correlation of poisoning effect of P and the redox properties for NH<sub>3</sub> and NO oxidation over CeO<sub>2</sub>-MoO<sub>3</sub> catalyst for DeNO<sub>x</sub>

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## Introduction

Phosphorus exists in fossil fuel and especially in biomass fuel. Co-combustion of coal and biomass fuels increases the content of phosphorus in produced fine particles and flue gas. The deactivation effect of phosphorus compounds on the selective catalytic reduction (SCR) DeNO<sub>x</sub> catalysts from flue gas has been identified previously.<sup>1</sup> Formation of vanadyl phosphate, pore blocking by phosphoric acid or phosphorus (V) oxide are supposed as the main causes of V-based catalyst deactivation. Over the lifetime of a heavy-duty diesel vehicle equipped with a SCR system, phosphorus compounds deposited on the surface of the V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub> catalyst also affect its activity and selectivity. Up to now, there's no effective way to avoid P-poisoning of V-based catalyst yet.<sup>2</sup>

Li et al.<sup>3</sup> reported that CeO<sub>2</sub> catalyst with addition of phosphorus showed excellent NH<sub>3</sub>-SCR activity in a wide temperature range. However, other researchers found that incorporation of P caused a significant decline in the concentration of labile active (OSC) and total (OSCC) oxygen species, and resulted in deactivation of Ce-based catalyst.<sup>4</sup> In this study, the SCR activity and influence of phosphorus on CeO<sub>2</sub>, CeO<sub>2</sub>-MoO<sub>3</sub> and VMo/Ti catalysts were studied. An extensive investigation has been undertaken in our laboratories, aiming at a better understanding of the P-poisoning effect and chemico-physical properties of Ce-Mo-O catalytic system.

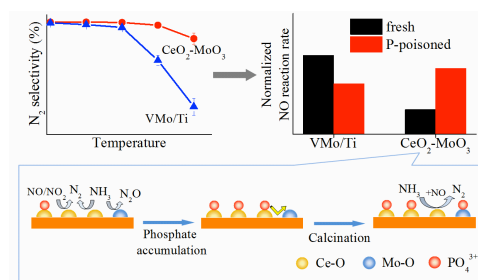
## Materials and Methods

The Ce-Mo-O composite oxide catalysts were prepared by a co-precipitation method, where Ce(NO<sub>3</sub>)<sub>3</sub> and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> used as the catalyst precursors and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> as precipitator. The samples are expressed as Ce-Mo(*x*)-O, where *x* denotes the molar ratio of Mo/Ce, e.g. Ce-Mo(0.5)-O. The P-poisoned catalysts were prepared by impregnation of samples in aqueous solution of corresponding amount of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, followed by drying and calcination at 500 °C for 4 h. These P-contaminated loadings are within the range detected in aged commercial catalyst.<sup>4</sup> The catalysts were characterized by BET, DRIFTS, and NH<sub>3</sub>-TPD, and their NH<sub>3</sub>-SCR activity was measured in a flow reactor.

## Results and Discussion

A series of Ce-based catalysts were synthesized by addition of Mo and the sample with a molar ratio of Mo/Ce=0.5 (Ce-Mo(0.5)-O) exhibited the best SCR activity. Meanwhile, it showed much better N<sub>2</sub> selectivity at high temperatures comparing with traditional VMo/Ti catalyst. For NH<sub>3</sub> oxidation, the N<sub>2</sub> selectivity was kept at >91 % below 400 °C and decreased at high temperatures due to the formation of N<sub>2</sub>O over Ce-Mo(0.5)-O catalyst; whereas, larger amount of N<sub>2</sub>O and NO formed over VMo/Ti catalyst, which can be attributed to the occurrence of the NH<sub>3</sub> oxidation on Mo.<sup>5</sup> The decrease of N<sub>2</sub> selectivity of both NH<sub>3</sub>-SCR and NH<sub>3</sub>-SCO (selective catalytic oxidation of NH<sub>3</sub>) contributed to the formation of nitrous oxide.

The effects of phosphorus over three catalysts (CeO<sub>2</sub>, CeO<sub>2</sub>-MoO<sub>3</sub> and VMo/Ti) for NH<sub>3</sub>-SCR were studied. With addition of 1.3 wt% P, the SCR activity of VMo/Ti decreased dramatically at low temperature due to the impairment of redox property for NO oxidation; meanwhile, the activity over CeO<sub>2</sub> and CeO<sub>2</sub>-MoO<sub>3</sub> catalysts was improved. The superior NO oxidation activity contributes to the activity over P-poisoned CeO<sub>2</sub> catalyst. The increased surface area and abundant Brønsted acid sites (by DRIFTS) account for the excellent activity over P-poisoned CeO<sub>2</sub>-MoO<sub>3</sub> catalyst. As the content of P increased to 3.9 wt%, the redox cycle over CeO<sub>2</sub> catalyst (2CeO<sub>2</sub> ↔ Ce<sub>2</sub>O<sub>3</sub> + O\*) was destroyed as phosphate accumulated (no activity in NH<sub>3</sub> oxidation at T < 400 °C), which led to the decline of SCR activity. However, more than 80% NO<sub>x</sub> conversion and superior N<sub>2</sub> selectivity were obtained over CeO<sub>2</sub>-MoO<sub>3</sub> at T > 300 °C. The effect of phosphorus was correlated with the redox properties of SCR catalyst for NH<sub>3</sub> and NO oxidation. A spillover effect, in which phosphate transfers from Ce to Mo during calcination, was proposed. Moreover, CeO<sub>2</sub>-MoO<sub>3</sub> catalyst exhibited good resistance to H<sub>2</sub>O and SO<sub>2</sub>, indicating that the Ce-Mo-O catalyst was an ideal alternative for NO<sub>x</sub> abatement from industrial flue gas, especially for the flue gas containing high content of phosphorus.



**Figure 1.** The comparison of N<sub>2</sub> selectivity and effects of P on VMo/Ti and CeO<sub>2</sub>-MoO<sub>3</sub> catalysts; and the spillover effect of phosphate on CeO<sub>2</sub>-MoO<sub>3</sub> catalyst.

## Significance

A novel CeO<sub>2</sub>-MoO<sub>3</sub> catalyst showed much better catalytic behavior and superior N<sub>2</sub> selectivity with respect to resistance to P up compared with traditional SCR catalyst (i.e., VMo/Ti). A spillover effect that phosphate transfers from Ce to Mo was proposed. The poisoning effect of P was correlated with the redox properties of SCR catalyst for NH<sub>3</sub> and NO oxidation.

## References

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