

A Comprehensive Study to Enhance CO Oxidation Activity by Using Doped CeO₂

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Ceria (CeO₂) has been an attractive catalyst due to its unique properties such as facile redoxability and high stability [1]. One way to enhance or control the catalytic activity of CO oxidation is doping a transition metal (TM) or rare-earth (RE) metal onto CeO₂. However, the comprehensive studies through both theoretical and experimental approaches to elucidate the effect of dopant on the chemical reactivity of doped CeO₂ have been rare.

In this study, we carefully examined the catalytic activity of CO oxidation on RE (RE = Pr, Nd, and Sm)-doped CeO₂ nanoparticles (NPs) synthesized by EDTA-citrate complexing method, which is capable of producing highly pure and homogeneous nanoparticles. Our experimental results show that the catalytic activities of RE-doped ceria NPs are in order of PDC > NDC > SDC > CeO₂. We also found that the catalytic activity of CO oxidation has a linear relationship with the surface area of NP whose size depends on the RE dopant. The dependence may be attributed to the different degree of interaction between RE cation and oxygen ion.

To investigate the intrinsic effect of RE dopant on the catalytic activity of CO oxidation, we performed density functional theory (DFT) calculations in collaboration with well-designed experiments where well-controlled particle size and surface area of RE-doped ceria NPs were used to examine the catalytic activity. In the light of Mars-van Krevelen (MvK) mechanism (Fig. 1), we extensively explored the entire reaction mechanism over a wide range of RE-doped CeO₂ with identifying the rate determining step and successfully described our experimental results of CO oxidation.

On the basis of our careful mechanistic study, we found that ionic radius of RE metals (R_{ion})

can act as a simple descriptor to predict the activity of CO oxidation on RE-doped CeO₂(111) (Fig. 2) [2].

Separately, we explored the effect of co-doping of TMs on the catalytic activity of CO oxidation by investigating the entire reaction profile of CO oxidation *via* the MvK mechanism on Fe-, Mn- and (Mn,Fe)-doped CeO₂(111) [3]. Our results demonstrated that oxygen vacancy formation energy can be used as a screener to predict the catalytic activity on co-doped oxide system and (Mn,Fe) co-doped CeO₂ is promising rather than Mn- or Fe-single doped CeO₂ for CO oxidation.

We believe that the comprehensive results in this study will provide useful insight to develop the enhanced CO oxidation activity on various types of oxide catalysts.

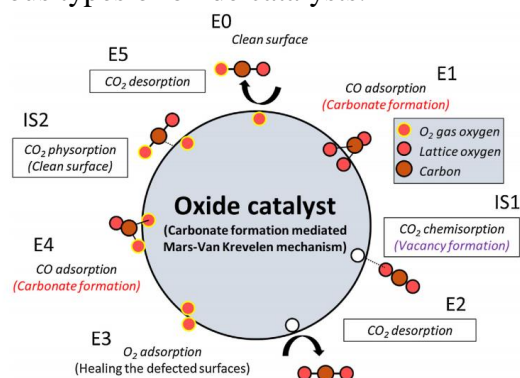


Fig. 1 Schematic illustration of the consecutive CO oxidation cycle on CeO₂(111) *via* MvK mechanism.

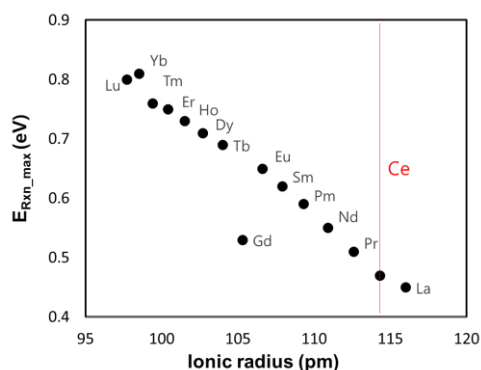


Fig. 2 Linear relationships between E_{Rxn_max} and the ionic radius of dopants on RE-doped CeO₂(111).

REFERENCES

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