



# Effect of ZrO<sub>2</sub> addition method on the activity of Al<sub>2</sub>O<sub>3</sub>-supported CuO for NO reduction with CO: Impregnation vs. coprecipitation

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## ABSTRACT

Supported copper oxide catalysts (CuO/Al<sub>2</sub>O<sub>3</sub>, CuO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, CuO/ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>) were prepared from different procedures and tested in the catalytic reduction of NO with CO to investigate the effect of ZrO<sub>2</sub> addition method. The catalysts were characterized by means of ICP, BET, XRD, Raman, H<sub>2</sub>-TPR, XPS, FTIR of NO or/and CO adsorption. Activity results demonstrated that the addition of ZrO<sub>2</sub> could improve catalytic performance, which is dependent on the addition method. The sequence of activity is CuO/ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> > CuO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> > CuO/Al<sub>2</sub>O<sub>3</sub>. Based on the results of composition and texture, CuO/ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> sample shows more surface zirconia species and larger surface area than CuO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. XRD and Raman results suggest amorphous ZrO<sub>2</sub> and highly dispersed copper oxide species are mainly present in the ZrO<sub>2</sub>-added catalysts except for a few CuO crystallites in CuO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. Highly dispersed copper oxide species strongly interacting with amorphous zirconia (Cu–O–Zr species) was observed in H<sub>2</sub>-TPR and XPS, which was considered as the origin of the enhanced activity. In addition, the adsorption type and configuration of NO was similar over these catalysts. However, CuO/ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> sample shows the greater capacity to activate the adsorbed NO species than CuO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>.

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## 1. Introduction

Catalytic reduction of NO with CO is one of the central reactions occurring in three-way catalytic converters where both reactants are undesirable pollutants. Many efforts have been spent on investigating the mechanistic detail and performance of this model reaction over various supported noble metal catalysts, such as Pd/Al<sub>2</sub>O<sub>3</sub>, Rh/Al<sub>2</sub>O<sub>3</sub>, Pt/WO<sub>3</sub>/CeO<sub>2</sub>/ZrO<sub>2</sub>, Au/CeO<sub>2</sub>–M<sub>2</sub>O<sub>3</sub> (M = Al, La), Ir/WO<sub>3</sub>–SiO<sub>2</sub> [1–7]. Because of the scarcity and high cost of noble metal, developing highly efficient non-precious metal catalyst for automobile exhaust purification is one of the focuses in the field of deNO<sub>x</sub> research.

Besides those reported noble metal catalysts, copper-containing catalysts as potential substitutes have attracted considerable interests due to unique redox properties and promising activities toward NO + CO or NO + CO + O<sub>2</sub> reaction, which are closely associated with strong interaction between copper species and support [8–15]. It is of importance to tune this interaction from the perspective of active

phase and support, respectively. For instance, Yamamoto et al. [11] found that CuO/Al<sub>2</sub>O<sub>3</sub> system containing highly dispersed Cu<sup>2+</sup> as active species was active for NO + CO reaction in the presence of O<sub>2</sub>, and the appearance of aggregated copper species would lead to the loss of catalytic activity. Sagar et al. [16] studied the dispersion of copper species on Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> mixed oxide and revealed two types of copper species including isolated and clustered on the support, depending on the copper oxide loading. These results reveal that high dispersion of copper species is responsible for catalytic activity. Besides this point, it is well known that the coordination environment of active species was related to support surface structure, which also altered the interaction of dispersed copper species with support. Our previous work [15d] demonstrated that dispersed copper species supported on several oxide supports (Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, and Ce<sub>1–x</sub>Zr<sub>x</sub>O<sub>2</sub> solid solution) with different surface structures showed different catalytic activities.

The addition of modifier into supported mono-active component catalyst is an alternative strategy to change the interaction between them. Although many studies focusing on the introduction of Ti [17], Fe [18a], Mn [18b], Ce [19], and Zn oxides [20] into CuO/Al<sub>2</sub>O<sub>3</sub> system in order to compare the activity and explore the interactions, there is still a lack of general agreement on the intrinsic interaction among the components due to the complexity of supported multicomponent catalysts. However, in fact, the

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