

# A combined experimental and theoretical study on the mechanism of CO–NO reaction over Cr–Cu embedded CeO<sub>2</sub>

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**Abstract:** The mechanism of CO–NO reaction on a CeO<sub>2</sub> surface embedding Cr–Cu was investigated by experimental and theoretical approaches. The reaction between CO and the oxygen atoms exposed at the surface increased the amounts of oxygen vacancy (V<sub>O</sub>). This affects the spin density on the surface Ce, which in turn enhances NO adsorption onto Ce. Nudged elastic band (NEB) calculations indicate that one adsorbed NO can approach a second adsorbed NO molecule to form a dimer (NO)<sub>2</sub> carrying an N–N bond. Two O atoms of the dimer are then released to be incorporated into the V<sub>O</sub> sites, leading to the N<sub>2</sub> formation and the regeneration of catalyst surface.

**Keywords:** CeO<sub>2</sub>, CO–NO reaction, reaction mechanism.

## 1. Introduction

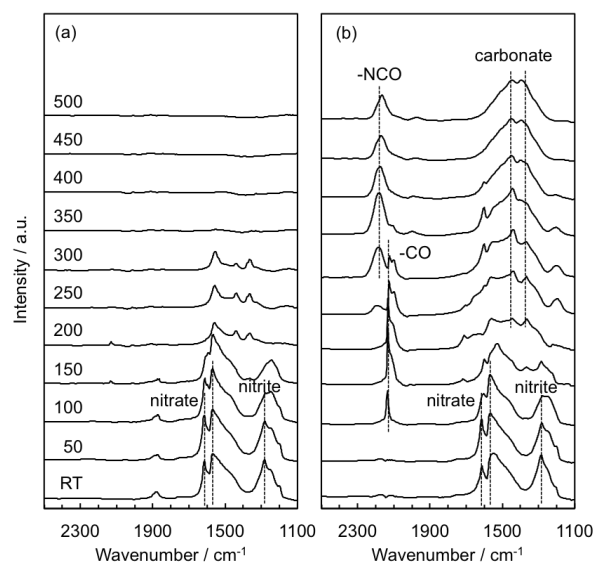
Noble metals are widely used in current automotive emission control, despite their limited availability. Development of cheaper and more abundant catalytic elements has therefore become a primary issue. Recently, we reported that thermally aged Cr–Cu embedded CeO<sub>2</sub> with extremely small metal loadings possess high activity for CO–O<sub>2</sub> and CO–NO reactions, namely better or at least comparable to those of Pt-group catalysts.<sup>1,2</sup> Surface-embedded Cr–Cu enhances CO adsorption and accelerates the reaction with surface O atoms for CO–O<sub>2</sub> reactions. Yet, the detailed mechanism of CO–NO reaction is still unclear. The present study aims at elucidating the mechanism of the CO–NO reaction on a Cr–Cu/CeO<sub>2</sub> surface using *in situ* experimental techniques and first principles calculations.

## 2. Experimental

Cr–Cu/CeO<sub>2</sub> was prepared by co-impregnation using pure CeO<sub>2</sub> (169 m<sup>2</sup> g<sup>-1</sup>) without any treatment, and the sample was thermally aged at 900 °C in 10% H<sub>2</sub>O/air for 25 h. *In situ* FTIR spectra were obtained after exposure to 1% NO/He, and the gas feed was changed to 1% CO/He. Isotopic reactions, chemisorption, and ESR experiments were also performed. An optimized Cr–Cu/CeO<sub>2</sub> surface was obtained by a spin-unrestricted density functional theory (DFT) based calculations and reaction pathway sampled by NEB technique.<sup>3</sup>

## 3. Results and discussion

The chemisorption of NO and CO on Cr–Cu/CeO<sub>2</sub> was observed by *in situ* FTIR (Fig.1) at different temperatures. On exposure to 1% NO/He at ≤150 °C, the observed bands can be assigned to nitrate (1590 and 1544 cm<sup>-1</sup>) and nitrite (1268 cm<sup>-1</sup>) on CeO<sub>2</sub>. The peaks were less-intensified at elevated



**Figure 1.** *In situ* FTIR spectra of adsorbed species on Cr–Cu/CeO<sub>2</sub> (a) in 1% NO and (b) after subsequent exposure to 1% CO at different temperatures.

The peaks were less-intensified at elevated

temperatures and disappeared at  $\geq 350$  °C. Subsequent admission of CO to NO-adsorbed surface yielded a new band at  $2167\text{ cm}^{-1}$  that can be assigned to isocyanate (NCO) (Fig. 1b). Although NCO seemed to act only as a spectator, this clearly suggested the presence of hidden adsorbed species containing N after NO admission even at  $\geq 350$  °C.

The reaction between CO adsorbed and substrate O atoms to form  $V_O$  is the first step of the CO–NO reaction onto Cr–Cu/CeO<sub>2</sub>. Simulations were performed to get optimized Cr–Cu/CeO<sub>2</sub> surfaces with different  $V_O$  amounts. Related projected density of states (PDOS) are shown in Fig. 2. For the model with two  $V_O$ , the up-spin peaks of O do not match the down-spin ones (a), whereas these peaks are well aligned in the five  $V_O$  model (b). In the latter case, an increase of the Ce PDOS near the Fermi-level is observed. These results indicate that the spin density is displaced from O to Ce with increasing formation of  $V_O$ . The increased spin density on Ce enhances the NO adsorption, due to an increase in the NO adsorption energy on Ce1 (Fig. 2) from 0.10 to 1.53 eV. Simulations are consistent with ESR and chemisorption experiments.

Viable reduction mechanisms of NO adsorbed on Ce were inspected via NEB (Fig. 3). Direct dissociation of adsorbed NO is unlikely to occur due to its very high energy barrier ( $108\text{ kcal mol}^{-1}$ ) (a). Conversely, the adsorbed NO can easily rotate to allow the oxygen atoms of the NO moiety to be trapped by a neighboring  $V_O$ . Such a structure enables a barrierless pathway to the formation of a (NO)<sub>2</sub> dimer with a N–N bond (b). Finally, the two O of the dimer are released to fill  $V_O$  with a low barrier. This is accompanied by N<sub>2</sub> desorption and regeneration of the catalyst surface.

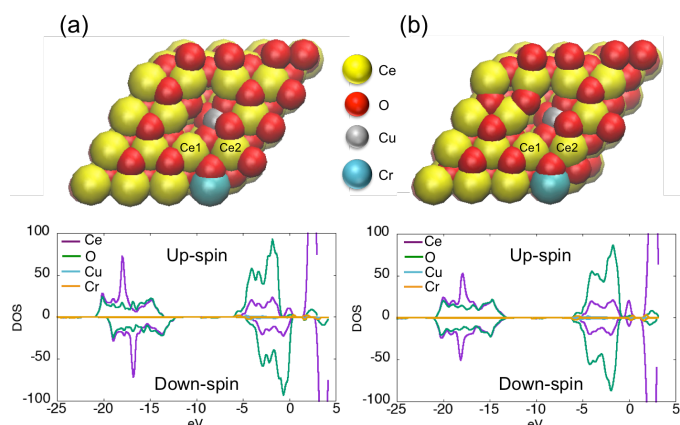
#### 4. Conclusions

A combined experimental and theoretical study evidenced a viable reaction pathway for the CO–NO reaction on a Cr–Cu/CeO<sub>2</sub> surface. Our results show that CO oxidation by surface O atoms, in the presence of a high concentration of  $V_O$  on the outermost surface, plays a key role in enhancing the spin density on Ce sites and thus NO adsorption thereon. The adsorbed NO can easily form (NO)<sub>2</sub> dimers, the O atoms of which are incorporated into the  $V_O$  site to facilitate the desorption of N<sub>2</sub>.

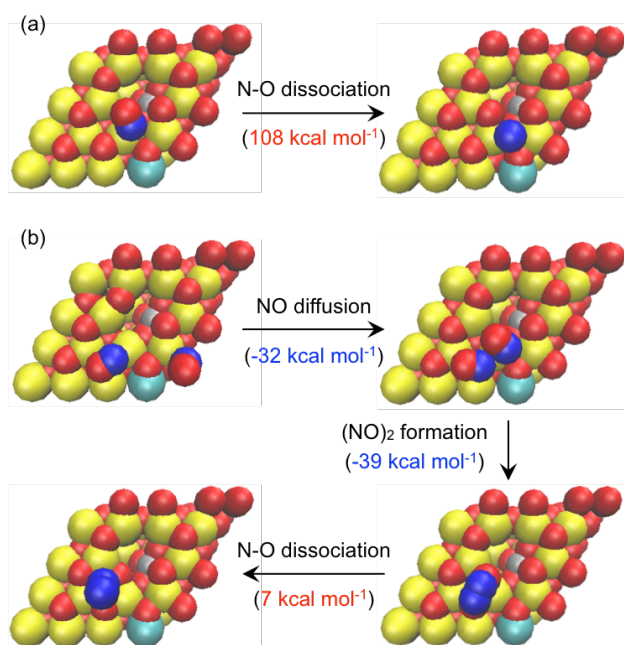
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**Figure 2.** Top view of optimized surface structure and PDOS computed from the configuration for up-spin and down-spin for Cr–Cu/CeO<sub>2</sub> with  $V_O$  numbers of (a) two and (b) five.



**Figure 3** Structure models and energy changes for (a) direct NO dissociation and (b) indirect NO dissociation via (NO)<sub>2</sub> formation from two NO adsorbed on Ce.