CO oxidation on AuCu/MgO(100): Role of support vacancies

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A comprehensive theoretical study of $Au_{15}Cu_{15}$ clusters on MgO(100) support and their catalytic activity for CO oxidation has been performed based on density functional theory calculations and microkinetic modelling analysis. Different reaction paths based on the Langmuir−Hinshelwood (LH) and Eley−Rideal (ER) mechanisms have been explored by tuning the location of vacancies in MgO(100). The charge states of the $Au_{15}Cu_{15}$ clusters are negative on all supports, defect free, O-vacancy (F-center) and Mg-vacancy, and the effect is significantly amplified on the F-center. In each case, the O_2 molecule can be effectively activated upon adsorption and dissociated to 2×O atoms easily, and the reaction modelling takes into account reaction paths with adsorbed O atoms. Overall, the CO oxidation reaction has lower reaction barriers on the F-center. The microkinetic modelling analysis reveals that CO oxidation on the AuCu/MgO(100) cluster is very sensitive to the CO partial pressure, as the relative strong CO binding leads easily to CO poisoning of the cluster surface sites and hinders CO_2 formation. For low CO partial pressures, the catalytic reaction takes place already at 150 K for the cluster on F-center. The CO_2 production rates are much lower for the defect free and Mg-vacancy supports which display similar activity at elevated temperatures. Correspondingly, the combination of CO and O_2 partial pressures is instrumental for CO_2 production.

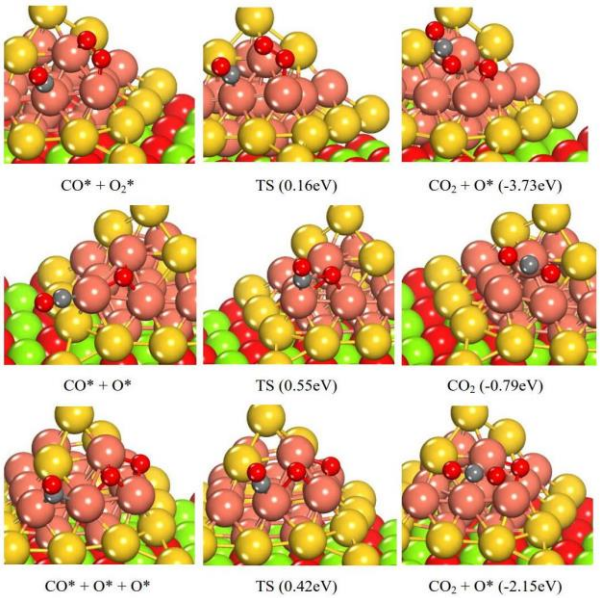

Figure 1: Structures of the initial state (IS), transition state (TS), and final state (FS) for the catalytic CO oxidation on $Au_{15}Cu_{15}$/MgO(100) with O-vacancy surfaces by LH mechanism and the energy changes with respect to the IS. The symbol '*' refers to the atom or molecule being adsorbed on the $Au_{15}Cu_{15}$ cluster.