The role of electronic metal-support interactions and its temperature dependence: CO adsorption and CO oxidation on Au/TiO₂ catalysts in the presence of TiO₂ bulk defects

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Abstract

Despite numerous studies on the role of surface oxygen vacancies in oxidation reactions on metal-oxide supported Au catalysts, little is known on how bulk defects in the support material affect their catalytic performance. Here we report results of a comprehensive study on the effect of bulk defects on the CO oxidation reaction on Au/TiO₂ catalysts, combining quantitative information on the amount of surface and bulk defects from in-situ non-contact electrical conductivity measurements after pretreatment and during reaction with information on the electronic / chemical state of the Au nanoparticles (NPs) provided by in situ IR spectroscopy using CO as probe molecule, and kinetic measurements. Treating the catalyst in strongly reducing atmosphere (10% CO / 90% N₂) at 400 °C results in a distinct increase in electrical conductivity, indicative of the formation of defects (oxygen vacancies), which are stable at 80 °C in N₂. Long-term reaction measurements performed at 80 °C show a distinctly lower activity of the bulk reduced catalyst, which increases slowly with time on stream, which is directly correlated with the decreasing abundance of bulk defects. Furthermore, they allow to distinguish between bulk and surface defects. The detrimental effect of bulk defects on the CO oxidation activity is shown to originate from the lowered CO adsorption strength and hence very low CO_{ad} coverage on the Au NPs due to electronic metal-support interactions (EMSI) induced by the presence of TiO₂ bulk defects, in good agreement with our recent proposal (Wang et al., ACS Catal. 7, 2339 (2016)). These conclusions are further supported by results of CO adsorption measurements performed at -20 °C. For reaction at -20 °C EMSIs lead to a promoting effect on the CO oxidation, pointing to a change in the dominant reaction mechanism, away from the Au-assisted Mars-van Krevelen mechanism dominant at 80 °C. The role of EMSIs in the CO oxidation reaction and its temperature dependence is discussed in detail.

Keywords: Au/TiO₂, CO oxidation, CO adsorption, electrical conductivity, bulk defects, electronic metal-support interactions (EMSI), kinetic measurements, IR

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