CO oxidation with Au/TiO2 aggregates encapsulated in the mesopores of MCM-48: Model studies on activation, deactivation and metal–support interaction

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ABSTRACT

The activation of Au/TiO2 clusters encapsulated in MCM-48 and related poisoning phenomena were studied. With these catalysts, which contain extremely disperse Au particles (average size below 1 nm still after exposure to 473 K according to EXAFS), light-off temperatures of 250–280 K were obtained upon activation by precursor reduction in a net oxidizing CO/O2 feed, which is well comparable with state of the art Au/TiO2 catalysts. This activation was, however, found to be superimposed by parallel poisoning. In an operando XAFS study with catalyst batches containing Au(II) precursor species of different reducibility for unknown reasons, it was observed that the final activity was strongly influenced by the precursor reduction. Apparently, high activities were achieved by Au particles formed at low temperatures making contact with the clean support surface. Delayed Au(III) reduction produced particles of similar size but much lower activity, probably due to predominant contact with poisoned support species. The catalysts were most active right after an initial incomplete reduction of the Au(III) precursor and deactivated at higher temperature despite further Au(0) formation. However, as complete reduction of Au ions did not cause breakdown of CO oxidation activity, Au ions do not seem to be a part of the active site. The poisoning could be effectively removed by an inert gas treatment at temperatures up to 673 K, which resulted in light-off temperatures down to 225 K. Turnover frequencies derived for this state agree with data published recently for sub-nanometer bilayered Au particles, which supports the importance of sub-nanometer particles for CO oxidation over Au catalysts. From the absence of significant contributions from support oxygen in the Au L3 EXAFS spectra and of Au-derived signals in Ti K EXAFS spectra of reduced catalysts, it was concluded that there was no ordered relation between metal clusters and support surface, which appears therefore to be irrelevant for CO oxidation.

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1. Introduction

Among the many reactions that can be catalyzed by supported Au particles, CO oxidation is certainly one of the simplest. However, even for this reaction there is no agreement about the reasons which make the inert gold a tremendously active catalytic component, despite many contributions to the elucidation of structure–function relationships [1]. Questions under debate include the oxidation state of gold in the active sites and the particle size dependence of the activity, the mechanism of particle stabilization by the support and the role of both metal and support in the catalytic reaction mechanism.

Although many authors favor metallic gold as the active site for CO oxidation [2–9], other groups advocate a cooperation between cationic and metallic gold [10–13]. While results of Haruta et al. suggested a monotonous increase of the catalytic activity with decreasing particle size [14,15], a maximum at a particle size of ca. 3 nm was observed in other studies [3,6,16]. The importance of the support to keep gold in high dispersion is beyond doubt. In model catalysts, gold was shown to wet the TiO2 support forming predominantly raft-like structures, and defects in the TiO2 surface were suggested to be important for particle nucleation [6]. Bilayered Au rafts were proposed to be the most efficient in offering active sites [17] and while these structures were extended in the nm range in model catalysts [6], extremely small entities (ca. 0.5 nm size) were suggested to be responsible for the particular activity.