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The role of electronic metal-support interactions and its temperature dependence: CO adsorption and CO oxidation on Au/TiO_2 catalysts in the presence of TiO_2 bulk defects

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ABSTRACT

We report results of a comprehensive study on the effect of bulk defects on the catalytic behavior of Au/TiO_2 catalysts in the CO oxidation reaction, 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. Treating the catalyst in strongly reducing atmosphere (10% CO/90% N_2) 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 N_2. Long-term kinetic measurements performed at 80 °C show a distinctly lower activity of the bulk reduced catalyst, which increases slowly with time on stream, directly correlated with the decreasing abundance of bulk 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 (EMSIs) induced by the presence of TiO_2 bulk defects, in good agreement with our recent proposal (Wang et al., ACS Catal. 7 (2017) 2339). 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.

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1. Introduction

Metal – support interactions are well known to play an important and often decisive role for the catalytic performance of supported metal catalysts, in particular for catalysts supported on reducible (oxide) supports [1–6]. Tauster introduced the term *strong metal – support interactions (SMSIs)* [7], which according to his definition refers to a specific strongly bonding interaction between support and metal nanoparticles (NPs) that is created upon treating the catalyst in a reducing atmosphere. These interactions may result in a variety of effects such as masking parts of the metal surface, by overgrowth of the metal surface with the reduced oxide, the formation of specific contact zones with enhanced catalytic performance or spreading of the metal [1]. They were attributed to the formation of less positively charged cations, such as Ti^{3+} in the case of TiO_2, at the surface of the support upon reducing treatment and their specific interactions with the metal NPs. Recently, electronic interactions involving a distinct modification of the electronic properties of the metal NPs, in this case for Pt NPs on CeO_2, were introduced as yet another type of SMSIs [5,8]. These electronic metal-support interactions (EMSIs) were demonstrated to significantly improve, e.g., the ability of a Pt/CeO_2 catalyst to dissociate the O-H bonds in water in the water gas shift reaction to produce H_2.

While these examples refer to the direct bonding interaction at the interface, one may also envision that deeper lying defects, e.g., bulk vacancies in oxide supports, may affect the catalytic performance of a catalyst via electronic interactions. Freund and coworkers had shown, e.g., that the CO adsorption properties of very small Au NPs on a MgO film, depended sensitively on the thickness of the oxide film [9–11]. They explained this by an increasing probability for electron transfer from the metal oxide support to the electronegative Au NPs with decreasing film thickness, the size of the

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Au NPs [9,10] and increasing film conductivity due to defects/doping [10,12,13]. The influence of charging on the catalytic activity of small supported metal clusters was convincingly demonstrated in previous studies on surface deposited mass selected metal clusters [14].

The possible influence of deeper lying bulk defects on the catalytic performance of supported metal catalysts, mediated via electronic metal – support interactions, is topic of an ongoing study in our laboratory, in which we aim at a fundamental understanding of such effects using oxide supported Au catalysts as model system. Here we report results of a comprehensive study on the influence of bulk defects in the CO oxidation reaction on Au/TiO_2 catalysts, combining kinetic measurements with *in situ* IR spectroscopy and electrical conductivity measurements. The influence of bulk defects is identified by comparing the CO adsorption and reaction properties of a Au/TiO_2 catalyst in the presence and absence of oxygen bulk vacancies, which were annihilated or created by pretreatment in a strongly oxidizing (O400, 10% O_2/90% N_2) or strongly reducing (CO400, 10% CO/90% N_2) atmosphere at 400 °C, respectively. To distinguish between bulk defects and surface vacancies and their re-oxidation, adsorption/reaction measurements were performed at two different temperatures, 80 °C and −20 °C, where re-oxidation of bulk vacancies is slow but possible (80 °C) or essentially inhibited (−20 °C). First preliminary results of this study were reported recently [15].

Before presenting and discussing the results of our study, we will briefly summarize previous findings relevant for the understanding of this study. From their similarity with reducible oxides supported platinum group metal (PGM) catalysts, SMSI effects would be observed also for the corresponding supported Au catalysts such as Au/TiO_2. Previous studies found no indications for encapsulation of the Au NPs by a reduced oxide layer upon high temperature annealing in vacuum or under reducing atmospheres [3,16]. It was proposed that the lack of such an encapsulation of the Au NPs in Au/TiO_2 catalysts is due to the weaker interaction of Au with reduced TiO_{2-x} compared to that of Pt. On the other hand, Tang et al. reported the observation of partial encapsulation of Au nanoparticles the support during oxidative pretreatment and a pronounced stabilization of the metal nanoparticles against sintering for a Au nanoparticle catalyst supported on hydroxyapatite (HAP) [17].

While little is known about the role of bulk oxygen vacancies, much more attention has been devoted to surface vacancies, whose role in the CO oxidation reaction was studied in detail. In a series of temporal analysis of products (TAP) reactor studies we provided convincing evidence that they participate in the CO oxidation reaction via a Au-assisted Mars – van Krevelen mechanism, involving the Au-assisted formation of surface lattice oxygen vacancies at the perimeter sites of the Au-TiO_2 interface by reaction with adsorbed CO and the subsequent replenishment of these vacancies by reaction with molecular oxygen [18,19]. This mechanism was proposed as dominant mechanism for CO oxidation on Au catalysts supported on reducible oxides at ambient temperature and above [18–23].

Maeda et al. followed the electrical conductivity during CO oxidation on a Au/TiO_2 catalyst pretreated in an oxidizing atmosphere [24]. They observed a distinct increase in conductivity of the catalyst upon exposure to the reaction gas mixture (CO:O_2 = 2:1, 50 mbar, 200 °C). A significantly higher increase was observed upon exposure to CO at 200 °C. In both cases, however, the authors claimed that vacancy formation was limited to the creation of surface vacancies. Based on these results they concluded that surface vacancies generated during the CO oxidation stabilize adsorbed O_2 and thus activate O_2 for the reaction [24].

A number of model studies performed on single crystal TiO_2 or ultrathin TiO_2 films decorated with Au nanoparticles reported that surface defects act as preferential nucleation sites for Au NP growth and stabilize them against sintering [25–30]. Furthermore, from the red-shift of Au-CO_{ad} IR band absorption frequency and based on theoretical calculations they proposed an electron transfer from surface defect sites on reduced TiO_{2-x} to the Au NPs, resulting in electron rich and often more active Au species [27–30]. Furthermore, Goodman concluded that by re-oxidizing previously reduced TiO_{2-x} thin film substrates or highly disperse supports in oxidizing atmospheres, the metal – support interaction can be reversed back to the original state after oxidizing pretreatment [31].

In the following we will, after a brief description of the Au/TiO_2 catalyst and its pretreatment as well as the experimental set-ups and procedures, first describe results of *ex situ* catalyst characterization before and after reaction by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Next we will present results of kinetic, *in situ* electrical conductivity and *in situ* IR spectroscopy measurements on the influence of bulk defects on the CO oxidation and CO adsorption characteristics, which was identified by comparing the adsorption/reaction characteristics of two catalyst samples from the same batch. The two catalysts were pretreated differently, one in oxidizing and one in reducing atmosphere at elevated temperature. Overall, these results are expected to provide detailed insight in the role of bulk oxygen vacancies in the CO oxidation reaction on supported Au catalysts, and also into the nature of the reaction mechanism for CO oxidation on Au/TiO_2 catalysts at temperatures below 0 °C, which was proposed [19,32] to differ from the Au-assisted Mars-van Krevelen mechanism dominant for Au catalysts supported on reducible oxides above room temperature [18,20–23]. The main conclusions derived from these results will finally be summarized.

2. Experimental section

2.1. Au/TiO_2 catalyst and pretreatment

For the experiments we used a commercially available Au/TiO_2 catalyst (AURO*lite*™, supplied by STREM Chemicals) prepared via deposition precipitation, with a Au loading of 1.0 wt%. P25 (Degussa AG) was used as TiO_2 support. The overall concentration of Na^+ and Cl^- in the catalyst is below 1500 ppm according to the supplier. Although the catalyst was already calcined before by the supplier, we pretreated it additionally *in situ* prior to all measurements in order to remove the majority of residual surface species such as hydrocarbons, moisture etc., which may have originated from exposure to air. For that reason the Au/TiO_2 catalyst was first dried *in situ* in a flow of 20 Nml·min^{-1} N_2 at 100 °C overnight (ca. 17 h) in order to obtain a low and constant level of adsorbed water and OH-groups on the catalyst surface, followed by *in situ* pretreatment at 400 °C for 30 min in either oxidizing (O400, 10% O_2/90% N_2, 20 Nml·min^{-1}) or reducing (CO400, 10% CO/90% N_2, 20 Nml·min^{-1}) atmosphere. After the respective pretreatment, the catalyst was cooled down to the desired reaction temperature in a flow of 20 Nml·min^{-1} N_2. For pretreatment as well as for subsequent reaction high purity gases from Westfalen AG were used (CO 4.7, O_2 5.0, N_2 6.0). Additionally, all gases were passed through an in-line water filter (Agilent, CP17971) before entering the reactor to prevent further insertion of water, and thus adsorption and accumulation of water on the catalyst surface during pretreatment and/or reaction.

2.2. Catalyst characterization

The mean Au NP size and the Au particle size distribution after both pretreatments and after reaction were evaluated from trans-

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