Deactivation of Au/CeO$_2$ catalysts during CO oxidation: Influence of pretreatment and reaction conditions

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ABSTRACT

The influence of the pretreatment on the activity and deactivation behavior of a high surface area 4.5 wt.% Au/CeO$_2$ catalyst during low temperature CO oxidation reaction (T_{react} = 80 °C) was studied in a multi-technique approach. Furthermore, the influence of changing from a close-to-stoichiometric (1% CO, 1% O$_2$ rest N$_2$), to O$_2$-rich (1% CO, 5% O$_2$ rest N$_2$) and CO-rich (5% CO, 1% O$_2$ rest N$_2$) gas mixtures was investigated. Findings from kinetic and deactivation measurements are correlated with experimental data on the Au particle size, Au and Ce oxidation state, and on the nature of adsorbed species after the different pretreatments and during/after subsequent reaction, which were obtained by *operando* and *in situ* methods such as *operando* X-ray absorption spectroscopy and IR spectroscopy, as well as *ex situ* X-ray photo-electron spectroscopy, X-ray diffraction and transmission electron microscopy. These data revealed that the pretreatment significantly affects catalyst structure, surface composition and activity in the initial stages of the reaction. During reaction, however, the catalyst surface composition approaches a dynamic equilibrium state, which is largely reached already after 10 min time on stream and which is independent of the pretreatment. Consequently, under present reaction conditions, longer-term deactivation is not dominated by the buildup of site blocking adsorbed species such as surface carbonates, but by slow processes such as reduction/re-oxidation of the bulk support during the reaction in combination with a modest irreversible Au NP growth.

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1. Introduction

Despite the enormous interest in Au based catalysts, and specifically in (metal) oxide supported Au nanoparticle catalysts [1–3], fundamental aspects of these catalysts and their working principle are still debated intensely and are essentially unresolved. This includes topics such as the nature of the active Au species, the molecular scale reaction mechanism including possible reaction intermediates, or the physical origin of the pronounced deactivation which had been observed in many reactions. The catalyst stability is a decisive aspect for commercial applications, and the rapid deactivation of these catalysts is one of, if not the main, reasons for the very slow commercial application [4–9].

The systematic understanding of Au catalysis/Au catalysts, including their stability and deactivation behavior, is hindered by the wide variation in experimental findings, which resulted in different and partly contradictory proposals on these topics. This is true even when considering a single reaction only, such as the oxidation of CO, which is generally considered as a prototype reaction [5,8–15]. Among others, the deactivation of Au catalysts during CO oxidation had been proposed to mainly originate from (i) effects associated with changes of the formal oxidation state of Au [5,8,10], (ii) the buildup of surface poisoning carbon containing species at the perimeter of the Au-support interface [9,11,12,15], (iii) irreversible agglomeration/sintering of the Au nanoparticles during reaction [8,11,13,14] and/or (iv) consumption of surface OH groups during the reaction [10,16].

To our belief, the considerable discrepancy in the data and, as a consequence, in the resulting interpretation, is largely due to the distinct differences between (support) materials, the preparation procedures, the pretreatments employed for catalyst activation, and finally the exact reaction conditions. Even for the same reaction, these parameters may sensitively affect the reaction

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characteristics. Therefore, comparison between studies performed under different reaction conditions or employing different preparation and pretreatments may result in strongly misleading conclusions. A more general fundamental understanding of the reaction and deactivation processes can hardly be derived from such data. Instead, it requires systematic studies where at best only a single parameter is changed, while all others are kept constant.

In the present paper we report results of a systematic study on the influence of the pretreatment on the activity and in particular on the deactivation behavior of a high surface area Au/CeO_2 catalyst during CO oxidation, aiming at a molecular scale understanding of the physical reasons for the observed differences in the reaction and deactivation characteristics. Pretreatments involve treatment in oxidative (10% O_2 in N_2), reductive (10% H_2 in N_2, 10% CO in N_2) or inert (N_2) atmosphere for 30 min at 400 °C. Furthermore we explored the influence of the reaction atmosphere using an excess of oxygen or CO for O_2/N_2 and H_2/N_2 pretreated catalysts. In addition to the following and elucidating the activity and deactivation of the differently pretreated catalysts or in the different reaction atmospheres, this involves a detailed characterization of the structure and chemical composition of the Au/CeO_2 catalysts after pretreatment and during/after subsequent CO oxidation, employing X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge spectroscopy (XANES) for *ex situ* and *operando* characterization of the oxidation state of the catalyst, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) for characterization of the adsorbed species after pretreatment and during reaction, and extended X-ray absorption fine structure (EXAFS) spectroscopy for characterization of the Au nanoparticle (NP) size after pretreatment and during reaction. Additional information on the Au NP size/size distribution is obtained from X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis before/after the reaction.

Before presenting and discussing the results, we will briefly summarize previous results relevant for this topic, focusing specifically on Au/CeO_2 catalysts. A literature review indicates that the deactivation of Au/CeO_2 catalysts during CO oxidation depends among others on the gold loading [9], the gold particle size [9], the composition of the reaction mixture [17], and on the reaction conditions (gas flow rate) [13]. In these studies, the deactivation of Au/CeO_2 catalyst during the CO oxidation was ascribed to the agglomeration of Au NPs during the reaction [8,13], formation of carbon containing adsorbed species [9,18] in combination with the reduction of the ceria surface during the reaction [8,18], or reduction of Au cationic species [5,8]. Recently, Hernández et al. reported on the deactivation behavior of Au/CeO_2 with different Au concentrations in the preferential CO oxidation, i.e., in the presence of H_2 and related to the deactivation to a reduction of both, of cationic Au species and of the CeO_2 support surface during reaction, together with an agglomeration of the Au NPs [8]. Based on the results of extensive DRIFTS measurements, Chen et al. proposed that the formation of carbonate species on the surface of the Au/CeO_2 catalyst will block active sites only for very small Au NPs (<2 nm), while over catalysts with larger Au NPs the reaction was supposed to proceed also by continuous formation and decomposition of adsorbed carbonate species, which would result in a different deactivation behavior of these catalysts [9]. On the other hand, several studies reported that Au/CeO_2 catalysts do not deactivate during CO oxidation [17,19–22]. Overall, the differences in Au/CeO_2 catalysts (Au content, CeO_2 support) and in the reaction conditions (reaction gas mixture composition, pretreatment) during long-time tests [8,13,17,23] are so pronounced that a direct comparison of the results reported in the above studies for a more comprehensive understanding is hardly possible. For instance, in most of the studies where Au/CeO_2 catalysts were

found to be stable (no deactivation), the reaction was performed in a pronounced excess of oxygen [17,19–22].

In the following we will, after a brief description of the experimental set-up and procedures (Section 2), first describe results of activity measurements performed with the differently pretreated catalysts (Section 3.1), followed by results of different spectroscopy and microscopy measurements on the Au nanoparticle size and catalyst surface composition after pretreatment (Section 3.2). Changes in these properties during CO oxidation are topic of Section 3.3. In next two sections we focus on the nature of the adsorbed species on these catalysts after pretreatment (Section 3.4) and reaction induced changes therein (Section 3.5). The influence of the gas phase composition, specifically of the $CO:O_2$ ratio, on the reaction characteristics is topic of Section 3.6. Finally, the main conclusions from this work are presented in Section 4.

2. Experimental

2.1. Catalyst preparation and characterization

The Au/CeO_2 catalysts were prepared by a deposition–precipitation procedure which had been described in detail earlier [24]. In brief, the supporting CeO_2 material (HSA 15, Rhodia, calcined in air at 400 °C for 4 h) was dispersed in water at 60 °C. Subsequently, a gold precursor ($HAuCl_4 \cdot 3H_2O$, 99.5%, Merck) was added dropwise, while adjusting the pH to ~6 by addition of 0.16 M Na_2CO_3 (Aldrich) solution. Then the as prepared Au/CeO_2 catalyst was filtered, washed three times with deionized water and dried at room temperature overnight. After drying the catalyst was stored in a fridge to reduce aging effects.

The Au metal loading of 4.5 wt.% was determined *via* inductively coupled plasma atom emission spectroscopy (ICP-AES) (Spectro ICP Modula S). The BET surface area of the catalyst, as determined by N_2 adsorption, was 188 $m^2 g^{-1}$ (Porotec Sorptomatic 1990 system).

2.2. Catalytic activity measurements

Kinetic CO oxidation measurements were performed at 80 °C at atmospheric pressure in a quartz tube micro reactor (i.d. 4 mm). This reaction temperature was chosen considering possible applications of Au catalysts for removal of CO from feed gases for low temperature fuel cells, which typically operate at these temperatures. In order to work under differential reaction conditions (conversion below 15%), the catalyst was diluted with α-Al_2O_3, which is inactive for CO oxidation under present reaction conditions. About 70 mg diluted catalyst powder was used, which resulted in a catalyst bed length of 1 cm. Prior to the CO oxidation measurements the diluted catalyst was pretreated *in situ*. This involved first heating the catalyst in a flow of 20 N ml min^{-1} N_2 to 400 °C (10 K min^{-1}). Afterward, N_2 was replaced by the respective pretreatment gas mixtures (20 N ml min^{-1}) for 30 min at 400 °C. Pretreatment was performed either in an oxidative atmosphere (10% O_2/N_2 - *O400*), in inert N_2 atmosphere (*N400*), or in a reductive atmosphere (10% H_2/N_2 - *H400* or 2% CO/N_2 - *CO400*). After the respective pretreatment, the catalyst was cooled down from 400 °C to the reaction temperature of 80 °C in a stream of 20 N ml min^{-1} N_2.

The CO oxidation gas mixture was introduced with a total flow rate of 60 N ml min^{-1}. It mostly consisted of 1% O_2, 1% CO and 98% N_2 (close-to-stoichiometric CO reaction gas mixture); in addition, we also used an *O_2-rich* gas mixture (1% CO, 5% O_2, and 94% N_2) and a *CO-rich* gas mixture (5% CO, 1% O_2, and 94% N_2). The reaction gases were prepared from high-purity gases (CO 4.7, O_2 5.0, H_2 5.0,