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Priority Communication

On the origin of the selectivity in the preferential CO oxidation on Au/TiO_2 – Nature of the active oxygen species for H_2 oxidation

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ABSTRACT

The reaction of stable adsorbed, active surface oxygen (O_{act}) with H_2 on Au/TiO_2 catalysts with the same Au loading, but varying Au particle size was studied by quantitative Temporal Analysis of Products reactor measurements between 80 °C and 400 °C and compared to the O_{act} removal by CO. The absolute amount of O_{act} for H_2 oxidation is identical to that in CO oxidation, and it also occurs at the Au–TiO_2 interface perimeter, indicating that the O_{act} species for this reaction is identical to that for CO oxidation. Implications on the mechanism of the H_2 oxidation and the origin of the selectivity during the preferential CO oxidation (PROX) are discussed.

1. Introduction

Highly dispersed gold catalysts supported on various metal oxides such as Au/TiO_2, Au/CeO_2 and Au/Fe_2O_3 have attracted considerable attention over the past three decades because of their high catalytic activity for a multitude of oxidation and reduction reactions at low temperatures [1–3]. One of the most often named possible applications of these catalysts is their use in fuel gas processing, for the selective removal of CO from H_2-rich feed gases for low-temperature fuel cells, by the preferential oxidation of CO (PROX) [4,5]. Good catalysts, however, should selectively oxidize only CO, ideally without or with only little oxidation of H_2 to water, which represents an undesirable side reaction of the CO oxidation in H_2-rich reformates [6]. Recent studies demonstrated that at low temperatures (below 100 °C) TiO_2 supported Au catalysts are the most promising candidates for this reaction. At typical reaction conditions (80 °C, 1–2% CO, excess H_2) they not only show a high activity for the CO oxidation reaction, but also a rather high selectivity of about 50%, despite the large excess of H_2 [7,8]. The selectivity decreases, however, with (i) increasing reaction temperature and (ii) decreasing CO content in the reaction atmosphere [7,8]. Since the CO content in H_2-rich feed gases has to be lowered to values below 10 ppm for practical applications, e.g., for polymer electrolyte membrane (PEM) fuel cells, it is still an issue to improve the selectivity of these systems. A fundamental understanding of the main factors affecting selectivity is a first step toward this goal. This requires detailed understanding of the reaction mechanism for both reactions on a molecular scale.

For the CO oxidation reaction, which is the most often investigated reaction on supported Au catalysts, it is well known that under catalytically relevant reaction conditions, at room temperature and above, CO adsorbs mainly on the surface of the Au nanoparticles. The formation and nature of the catalytically active oxygen species and the active site for its reaction with CO, however, have long been controversially discussed. In the meantime, however, there is agreement that CO adsorbed on the Au NPs reacts with active oxygen species located at perimeter sites of the Au–TiO_2 interface [9,10]. Moreover, we could recently demonstrate that the active oxygen species (O_{act}) for CO oxidation on Au/TiO_2 catalysts under practical reaction conditions, for $T \geqslant 80$ °C, is TiO_2 surface lattice oxygen located at the perimeter of the interface between Au nanoparticles and TiO_2 support, resulting in a Au-assisted Mars-van Krevelen mechanism for the CO oxidation on Au/TiO_2 [11,12]. It was also demonstrated that, in contrast to many earlier proposals, the reactive removal of active oxygen by CO is the activated process during CO oxidation, rather than the formation of active oxygen species due to O_2 dissociation, which is facile and only a little activated [11].

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Regarding the mechanism of the H_2 oxidation on supported Au NPs, previous studies focused mainly on the interaction of H_2 with these catalysts. Here it could be demonstrated that supported Au NPs are able to dissociatively adsorb H_2, resulting in an atomically adsorbed hydrogen species, which is active for the H_2 oxidation reaction as well as for hydrogenation reactions [13]. On extended smooth Au surfaces, in contrast, dissociative H_2 adsorption is inhibited [14,15]. The active sites for H_2 dissociation on highly dispersed Au/TiO_2 catalysts have been proposed to be either low coordinated neutral Au atoms [16] or perimeter sites at the Au–TiO_2 interface [15,17]. There are, however, almost no studies on the nature of the O_{act} species for the H_2 oxidation. Hence, information on this topic is scarce. It is, for example, still not clear whether H_2 and CO are oxidized by the same O_{act} species. One may envision that H_2 and CO compete for this species when present simultaneously. Hence, this information can give valuable knowledge about the origin of selectivity during the PROX reaction.

Another aspect that should be considered during the PROX reaction is the presence of hydroxyl groups and adsorbed water on the catalyst surface, which are inevitably formed under PROX reaction conditions, due to H_2 oxidation [18]. It is well known that the presence of small quantities of adsorbed H_2O and/or hydroxyl groups increases the CO oxidation activity [19,20], e.g., by the formation of hydroxycarbonyl species at active sites including hydroxyl species [21], by promotion of molecular oxygen activation [22], or by H_2O induced decomposition of reaction inhibiting surface species, such as surface carbonates [23,24]. Preliminary results from our laboratory have shown that the total amount of O_{act} available for CO oxidation on Au/TiO_2 catalysts at 80 °C depends sensitively on the amount of adsorbed H_2O_{ad}/OH_{ad} present on the catalyst surface: with increasing water content this also increases. How exactly H_2O_{ad}/OH_{ad} promotes the formation of the O_{act} species for the CO oxidation, however, is not yet clear.

In the present contribution we focus on the nature of stable adsorbed, but nevertheless active oxygen species for the H_2 oxidation and its role in the reaction mechanism. Applying Temporal Analysis of Products (TAP) techniques, multi-pulse experiments with alternating sequences of H_2/Ar pulses and O_2/Ar pulses were used in order to determine the total amount of O_{act} species which can be removed and replenished from the catalyst surface, respectively. These measurements were performed on four different Au/TiO_2 catalysts with same Au loading but different mean Au particle size at low (80 °C) and high (400 °C) temperatures in order to identify the nature and the location of the active oxygen species for H_2 oxidation. The total amount of O_{act} for the CO oxidation over the same catalysts was also determined (oxygen storage capacity; OSC). This enables a direct comparison between the total amounts of O_{act} available for H_2 and CO oxidation and, hence, elucidates whether the same oxygen species acts as O_{act} species for both reactions.

2. Experimental

2.1. Au/TiO_2 catalyst preparation and characterization

The Au/TiO_2 catalyst with a Au loading of 2.6 wt.% Au (ICP-OES) was prepared via a deposition–precipitation method using commercial, non-porous TiO_2 (P25, Degussa) as support material (surface area 56 $m^2\ g^{-1}$). Prior to the TAP reactor measurements, the raw catalyst was dried at 100 °C for 15 h in a flow of Ar and subsequently pre-treated *in-situ* by calcination in a continuous flow of 10% O_2/N_2 at atmospheric pressure for 30 min. In order to obtain Au catalysts with constant Au loading, but different Au particle size, the raw catalyst was calcined at temperatures of 400 °C, 500 °C, 600 °C, and 700 °C, resulting in Au/TiO_2 samples denoted O400, O500, O600 and O700, respectively. The Au particle size distributions of these samples were determined by transmission electron microscopy (TEM).

2.2. Pulse experiments

Pulse experiments were performed in a home-built TAP reactor [25], which is largely based on the TAP-2 approach of Gleaves et al. [26]. It consists of a gas mixing unit, two independently working piezo-electrically driven pulse valves and a tubular quartz glass microreactor (90 mm long, 4.0 mm i.d., 6.0 mm o.d.), which is connected to an ultra high vacuum system (analysis chamber) via a differentially pumped gate valve. Here the catalyst can first be pre-treated *in situ*, under continuous flow conditions at atmospheric pressure, before the microreactor is evacuated and directly connected to the analysis chamber. By use of the piezo-electric pulse valves, gas pulses of typically 1×10^{16} molecules per pulse were generated. These were directed into the microreactor, in which the catalyst bed was fixed by stainless-steel sieves. After passing through the catalyst bed the effluent gases were analyzed by a mass spectrometer located in the analysis chamber. For the experiments described here, 10 mg (for the Au/TiO_2 sample calcined at 400 °C; O400), 16 mg (O500 and O600), or 30 mg of the catalyst (O700) were diluted 1:1 with SiO_2 and packed between two layers of SiO_2, resulting in a catalyst bed with a total amount of 150 mg and a total length of about 8 mm for all samples. SiO_2 as well as the metal sieves were checked to be inactive for the oxidation of H_2 and CO under present reaction conditions.

In order to quantify the amount of stable adsorbed, active oxygen which can be reversibly stored and reactively removed on the catalyst surface, multi-pulse experiments were performed at 80 °C and 400 °C, exposing the catalyst alternately to sequences of at least 100 O_2/Ar pulses ($O_2/Ar = 1/1$, separation time 5 s) and either 200 CO/Ar pulses (CO/Ar = 1/1, separation time 5 s) or 800 H_2/Ar pulses ($H_2/Ar = 3/1$, separation time 1 s), respectively. This procedure was repeated at least three times on all samples in order to check for reversibility of the oxygen storage/removal. The amount of CO and O_2 consumed within each pulse, respectively, can be calculated by the missing intensity measured by the mass spectrometer compared to the measured intensity after saturation, at the end of each sequence. Adding up the oxygen uptake in all pulses during a sequence of O_2/Ar pulses gives the total amount of O_{act} which can be removed by CO (OSC) or H_2, respectively. In order to exclude further formation and accumulation of H_2O_{ad}/OH_{ad} during H_2 pulses, which may alter the catalyst oxygen storage capacity (see above), the freshly calcined catalysts were first exposed to several cycles of alternating sequences of H_2/Ar and O_2/Ar pulses, until there is no further accumulation of H_2O_{ad}/OH_{ad} on the catalyst surface during the H_2/Ar pulses (see Supporting Information). This way, changes in the total amount of O_{act} for CO or H_2 oxidation by coadsorbed H_2O_{ad}/OH_{ad} can be excluded, and the oxygen uptake after multiple CO and H_2 pulses can be compared directly. Moreover, the catalyst situation in this case is much closer to the real conditions during PROX reaction as compared to freshly dried catalysts.

3. Results and discussion

TEM images of the Au/TiO_2 catalysts after the different pretreatment procedures and their evaluation clearly demonstrate the increase of the Au particle size with increasing calcination temperature, from 400 °C to 700 °C (TEM images and particle size distributions are included in the Supporting Information). The mean diameter of the Au particles increased in the following order: 3.0 ± 0.8, 4.0 ± 1.1, 6.8 ± 1.7, and 12.4 ± 4.0 nm for O400, O500,