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Effect of titania surface modification of mesoporous silica SBA-15 supported Au catalysts: Activity and stability in the CO oxidation reaction

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ABSTRACT

As part of an ongoing effort to understand the deactivation and improve the stability of metal oxide-supported Au catalysts in the low-temperature CO oxidation reaction while maintaining their high activity, we have investigated the influence of a mesoporous silica SBA-15 substrate on the activity and stability of Au/TiO_2 catalysts, which consist of a SBA-15 support surface modified by a monolayer of TiO_x with Au nanoparticles on top. The extent of the TiO_x surface modification was systematically increased, while the Au loading and the Au particle sizes were largely kept constant. Employing kinetic measurements at three different temperatures (30 °C, 80 °C, 180 °C) and a number of *ex situ* methods as well as *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) for catalyst characterization, we found that the activity of these catalysts increases significantly with the Ti concentration and with reaction temperature. The tendency for deactivation remains essentially unchanged. Detailed *in situ* DRIFTS measurements reveal that the Au nanoparticles are largely formed on the TiO_x surface-modified areas of the SBA-15 support and that the tendency for surface carbonate formation is very low. The observed deactivation may at least partly be related to the accumulation of molecularly adsorbed H_2O species, in particular at low temperatures (30 °C). These are likely to be formed from surface hydroxyl groups, they may affect the reaction either by blocking of active sites or by blocking the adsorption of reactants on the substrate. Other effects, such as reaction induced changes in the titania layer, must however, play a role as well, both at 80 °C and in particular at 180 °C, where accumulation of adsorbed species is negligible. The mechanistic ideas are supported by reactivation tests subsequent to calcination at 400 °C, which were found to fully restore the initial activity.

1. Introduction

Gold catalysts consisting of gold nanoparticles (NPs) supported on various metal oxides have attracted significant attention due to their remarkable catalytic properties in numerous important chemical reactions such as acrolein hydrogenation, H_2O_2 production, water gas shift reaction, propene epoxidation and CO oxidation [1–6]. In particular, the CO oxidation reaction continues to be in the focus of ongoing research, mainly from a fundamental interest, since it is considered as an apparently simple model reaction, but also due to its potential application, *e.g.*, for the removal of CO from H_2-rich feed gases in polymer electrolyte membrane fuel cells (PEM FCs) [7–9]. The commercial introduction is hindered, however, by the pronounced tendency of these Au catalysts to deactivate during time on stream, *e.g.*, by up to about 70% over 1000 min on stream for CO oxidation reaction over a standard Au/TiO_2 (P25) catalyst [10].

The mechanisms responsible for the deactivation are not yet resolved and discussed controversially, and they may depend significantly also on the support material and the reaction conditions. Specifically for Au/TiO_2 catalysts it was proposed, based on *in situ* infrared measurements, that during the CO oxidation reaction surface carbonate species accumulate on the support and at the perimeter sites at the interface between Au nanoparticles and support [11–13]. This could lead to poisoning of the active sites. Other proposals suggest irreversible agglomeration/sintering of the Au nanoparticles [11,14] or consumption of surface OH groups during the reaction [15,16]. For other supports, also a change of the gold

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oxidation state during the exposure to the reaction gas mixture was proposed to play a role [15].

In all cases, the surface chemistry of the support plays a decisive role for the deactivation, either by favoring/disfavoring the formation or consumption of surface species that may affect the reaction, or by stabilizing the Au nanoparticles. We therefore started to explore the possibility of modifying the surface chemistry of oxide-supported Au catalysts, specifically of Au/TiO_2 catalysts. We followed different routes, using, *e.g.*, either mesoporous TiO_2 supports with significantly larger surface areas than the standard TiO_2 (P25) support [17] or modifying the surface composition by using mesoporous mixed $Ti_xSi_{1-x}O_2$ oxides with varied composition as support material [18]. The mixed oxides were obtained by introducing Si atoms into the framework of the TiO_2 during the sol-gel synthesis [18]. In the latter case we hoped to reduce the tendency for deactivation by modifying the acidic character of the support material surface, which should reduce the tendency for forming reaction inhibiting carbonate species. Although we observed clear improvements in the activity of these catalysts, the level of deactivation remained principally unchanged [18].

Here we describe results of a different approach to modify the surface chemistry of the TiO_2 surface layer by using mesoporous silica (SBA-15) as an underlying substrate material, which was subsequently surface modified by grafting of different amounts of TiO_x. All TiO_x loadings were below monolayer coverage (crystallization limit) as reported by Gao et al. [19]. We systematically studied the CO oxidation activity and deactivation behavior of these Au catalysts at different reaction temperatures (30 °C, 80 °C, 180 °C) and its variation with the amount of deposited TiO_x. The high reaction temperature of 180 °C was chosen to obtain information on thermal effects in the deactivation process, *e.g.*, by decomposition of surface species causing deactivation. The activity and deactivation were followed both by kinetic measurements performed under differential reaction conditions and *in situ* IR spectroscopy (Diffuse Reflection FTIR – DRIFTS). In addition to elucidating the role of the TiO_x surface layer on the above properties, we also wanted to identify possible changes in the chemical surface properties of the Au NPs upon increasing the Ti surface concentration. This question was investigated by a detailed DRIFTS analysis of adsorbed CO during the reaction, *i.e.*, by using adsorbed CO as probe molecule and the Au – CO_{ad} interactions, as indicated by the CO vibrational characteristics. Finally, in response to our finding in this study that significant amounts of adsorbed water are formed during the reaction, we performed additional experiments where the catalyst was first exposed to an inert gas (N_2) under reaction conditions (80 °C) over 1000 min before switching to the actual reaction gas mixture to learn more on the role of water in the reaction.

Previous studies on the CO oxidation reaction over TiO_x-modified Au/SBA-15 (Au/SBA-15-xTi) catalysts, where the SBA-15 support was surface modified with TiO_x either by impregnation [20,21] or by grafting methods [20–23], focused mainly on the activity of these catalysts. More detailed information on the deactivation of both the Au/SBA-15 and the Au/SBA-15-xTi catalysts during time on stream or on the interaction of CO with the catalysts is largely missing. Yang et al. reported a strong deactivation of Au/SBA-15 catalysts with time on stream during the CO oxidation reaction, which they explained by an agglomeration of the Au NPs [24], supported by TEM observations. But to the best of our knowledge there are no data on the deactivation behavior of TiO_x surface-modified Au/SBA-15-xTi catalysts.

In the present contribution, we first describe the procedure used for surface modification of the SBA-15 support material and the synthesis of the respective Au catalysts (Section 3.1). Support materials and catalysts were characterized with respect to Au particle size, Au and Ti loading, and surface composition by transmission electron microscopy (TEM), inductively coupled plasma – optical emission spectroscopy (ICP-OES), and X-ray photoelectron spectroscopy (XPS), respectively. Subsequently, we present data on the reaction behavior, which was characterized by kinetic measurements performed under differential reaction conditions, monitoring the activity with time on stream at three different temperatures (30 °C, 80 °C, 180 °C) and for different TiO_x surface contents (Section 3.2). Next, we present a detailed *in situ* DRIFTS analysis, with focus on the different CO_{ad} species present during the reaction, but covering also the evolution of other surface species during time on stream (Section 3.3). In the last section (Section 3.4), we present and discuss additional experiments performed to better understand the role of surface OH species and adsorbed water during the reaction.

2. Experimental

2.1. Support preparation

The SBA-15 material was prepared following the procedure given in Ref. [25]. TiO_x was dispersed on the surface of SBA-15 using a grafting procedure, which was also described previously [26]. In short, the solution of the precursor $Ti(OiPr)_4$ in 50 ml of dry toluene was added to 2 g of dried SBA-15 (dried at 120 °C, overnight) at room temperature and stirred for 4 h. The concentration of the $Ti(OiPr)_4$ precursor was chosen to nominally yield a coverage of 1.5 Ti atoms nm^{-2}, which resulted in $\sim$1 to 1.2 Ti atoms nm^{-2} deposited on the SBA-15 in a first grafting procedure. For higher loadings, this grafting procedure was repeated multiple times, where each time less additional titania was deposited. The complete grafting procedure was performed under inert atmosphere to keep the water content as low as possible level. Hydrolysis of the Ti precursor in solution needed to be prevented, otherwise, non-specifically deposited TiO_x agglomerates might have been formed. After sedimentation and removal of the solution using a capillary, the samples were washed three times with dry toluene ($\sim$30 ml), separated by sedimentation, and dried under vacuum after the third washing step. Subsequently, the support material was calcined in two steps. In the first step, the sample was heated in a stream of N_2 (100 ml/min, 300 °C, 2 °C/min) for 1 h, in the second step N_2 was substituted by synthetic air and the sample was heated to 500 °C (2 °C/min) and kept at this temperature for 4 h. Mei et al. recently reported UV–VIS and X-ray absorption near-edge structure (XANES) spectroscopy measurements on SBA-15-xTi samples, which were synthesized in the same way as here. They showed that with higher TiO_2 loading more agglomerated TiO_x species/larger agglomerates of TiO_x are formed [26].

The TiO_x loading was determined by ICP-OES. The specific surface areas of the supporting materials and of the Au/SBA-15 catalyst were determined *via* nitrogen physisorption using a gas sorption analyzer (Quantachrome Autosorb-1) *via* the single point BET method. The samples are named according to the actual Ti concentration in wt.%, *i.e.*, the sample loaded with 7.2 wt-% Ti is labelled SBA-15-7Ti.

2.2. Catalyst preparation

The Au/SBA-15-xTi catalysts (x = 0, 7, 12, 15, 17) were prepared by a deposition-precipitation method, using two different Au precursors. For the silica-supported Au/SBA-15 catalyst the conventional DP procedure using $AuHCl_4{\cdot}3\ H_2O$ for Au nanoparticle deposition is not possible because of the low isoelectronic point (IEP $\sim$ 2) of SiO_2. Therefore, we used the cationic complex [Au