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Combining XPS and ToF-SIMS for assessing the CO oxidation activity of Au/TiO_2 catalysts

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ABSTRACT

Au/TiO_2 catalysts were produced by deposition-precipitation using different preparation conditions. Emphasis was laid on producing TiO_2 supports via oxalate precursors in the presence or absence of alkali and/or alkali-earth elements to vary on purpose the catalysts' morphological state, surface composition and electronic structure. The home-made catalysts and a commercial Au/TiO_2 were analyzed in a comparative manner by mainly X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) to identify the key parameters responsible for their high activity in the CO oxidation at room temperature. Among these parameters, which were strongly influenced by the catalyst preparation conditions, the abundance of reduced Ti^{3+} species was ascertained to be overarching along with the availability of negatively charged Au nanoparticles. The abundance of O 2p bonding orbitals in the valence band of TiO_2, which was modified by the presence of Au particles, and the extent of the support hydroxylation were also found to have a positive effect on the reaction rate. We further demonstrate that it is the specific area occupied by gold particles on the support surface that has to be taken into account to establish a reliable dependence of the reaction rate on the XPS-derived Au/Ti atomic ratio. All these factors have to be considered when assessing the activity performance of Au/TiO_2 catalysts prepared and activated according to different recipes. After-reaction studies, which were also performed with a selected home-made catalyst, show that a slight decrease in its catalytic activity with time-on-stream can be mainly attributed to an appreciable accumulation of various carbon-containing species on the support surface along with a loss of OH groups. In summary, we show that combined XPS/ToF-SIMS studies provide a reliable guide for tailoring the preparation of high-performance Au-supported catalysts.

1. Introduction

Supported gold nanoclusters have been receiving considerable attention for their high catalytic activity and selectivity in various types of industrially important reactions [1]. In particular, titania-supported gold catalysts have shown excellent performance in the low-temperature CO oxidation. Numerous studies of supported gold catalysts over the past two decades elaborated on the influence of the preparation and activation procedures. Accordingly, some general trends were established. For instance, the effect of preparation method, reduction temperature, calcination temperature and Au loading on the catalytic activity in CO oxidation over Au/TiO_2 catalysts was demonstrated [2–4]. Moreover, the non-monotonic dependence of the catalytic performance on the pH value of the precipitation solution [5] and the calcination temperature [2,5,6] were reported for low-temperature CO oxidation over Au/FeO_x/Al_2O_3, Au/TiO_2 and Au/ZrO_2 catalysts. The influence of impurities introduced either during catalyst preparation (such as chlorine [7]) or deliberately added to the Au/TiO_2 catalyst (such as Na or K [8]) was likewise examined.

The intrinsic CO oxidation activity of gold metal was found to be structure-sensitive and dependent on the Au particle shape, morphology and size. Correlations between the Au particle mean diameter and the CO oxidation activity were reported for Au/TiO_2 catalysts [1,2,4,9,10]. The low-coordination number of Au atoms which is directly related to the size of the Au particles was suggested [11] to be the dominant factor determining the exceptional catalytic activity of nanometer-sized gold particles. Even for

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sub-nanometer sizes, as shown [12] for clusters of Au_n (n = 1 – 7) deposited on TiO_2(1 1 0), the activity for the CO oxidation varies strongly with the number of gold atoms in a cluster, with significant activity appearing for Au_3.

Establishing relationships between the catalytic activity and the physico-chemical surface properties of materials as a function of preparation, activation or catalytic run-in procedures and the change of these properties due to reactive conditions is an essential prerequisite for elucidating the nature of the catalytically active sites and the optimization of the catalytic performance. Ultimately, the mechanism of the catalytic process can be demonstrated. In a recent review [13], we have investigated respective achievements by referring to a number of research works performed by using surface-sensitive techniques, mainly time-of-flight secondary ion mass spectrometry (ToF-SIMS) and low energy ion scattering (LEIS), which, in combination with X-ray photoelectron spectroscopy (XPS), provide straightforward correlations between parameters of the surface physico-chemical state and the reactivity/catalytic activity of divers materials in various reactions. For supported gold catalysts, however, reports on such correlations are scarce and have mainly relevance to ascertaining the existence of major catalytically active species and their oxidation state. From the direct correlation between the activity and the surface content of Au^{1+} species in Au/MgO [14] and Au/(TiO_2 + ZrO_2) [15] catalysts, cationic gold was claimed to play a crucial role in catalyzing CO oxidation at low temperatures. On the other hand, clear correlations between the catalytic activity and the fraction of metallic gold in Au/TiO_2 catalysts [2,16] support the idea that Au^0 is the active species [1] and that metallic Au is necessary for low-temperature CO oxidation activity.

In view of the achievements mentioned above, it seems that while much information has been acquired about size effects of Au nanoparticles or possible oxidation states, considerably less is known about the influence of the support as a result of varying preparation conditions. The present paper is aimed at filling this gap in knowledge. A research strategy on the basis of a rigorous surface chemical analysis by XPS and ToF-SIMS has been developed to identify relevant parameters and to establish useful correlations between the reaction rate and the surface chemical and electronic properties of Au/TiO_2 catalysts. Rather than focussing on developing catalysts with improved catalytic performance, we synthesized catalysts by varying the nature of precursor materials, chemical environments during the preparation and pre-treatment conditions. For a series of catalysts with seemingly identical nominal Au/TiO_2 stoichiometry, we have established correlations between the measured surface physico-chemical characteristics and the activity of these catalysts in room temperature CO oxidation.

2. Experimental

2.1. Catalysts and procedures

Three Au/TiO_2 gold catalysts (GC1, GC2, GC3) were prepared by deposition-precipitation (DP), using different chemical procedures and calcination conditions. A detailed description of the catalysts is given in the Supplementary Material. Briefly, the TiO_2 support was prepared from a titanyl oxalate complex. Oxygen-assisted thermal decomposition at 525–560 °C transformed the titanyl complex into titania with anatase structure, as verified by X-ray diffraction (Fig. S1). DP of Au nanoparticles onto the as-prepared TiO_2 was accomplished using an aqueous solution of $HAuCl_4$ and either 0.1 M NaOH at pH ≈ 7 (GC1) or urea $CO(NH_2)_2$ at pH ≈ 7 (GC2, GC3) as precipitating agent. For all the samples, the amount of gold in the solution was adjusted to provide a loading of 1.5 wt% Au. Filtration and drying of the Au/TiO_2 precipitate at 120 °C overnight was followed by calcination either in air at 400 °C for 2 h (GC1) or in 10% O_2/Ar ambient at 300 °C (GC2) and 350 °C (GC3) for 2 h. Note that the GC2 and GC3 catalysts were prepared on purpose in a sodium-free environment by using urea, ultrapure water, glassware of quartz for the decomposition of $TiOC_2O_4$ and for catalytic tests, and scrupulously cleaned utensils of polypropylene. This effort guaranteed that catalysts were exempt of any spurious alkaline contamination. However, different from GC3, which was kept free of any alkali and alkali-earth elements, GC2 was prepared by adding $MgNO_3{\cdot}6H_2O$ (>98%, Riedel-de Haën) to the solution during precipitation of $TiOC_2$O4, in amounts necessary for doping TiO_2 with 0.04 wt% Mg.

In addition, a commercial Au/TiO_2 (Degussa P25) reference catalyst prepared by DP with NaOH as precipitating agent and provided by the World Gold Council (WGC) (Lot No. #02-4, sample 23A) was studied for comparison. According to the certificate, the Au loading in the Au/TiO_2 WGC was 1.51 wt% (ICP data) and the BET specific surface area ~50 m^2/g.

Brunauer–Emmett–Teller (BET) specific surface areas of the GC1, GC2 and GC3 catalysts were obtained to be ~65, 100 and 100 m^2/g, respectively. The actual Au content in the GC1, GC2 and GC3 catalysts was determined by inductively coupled plasma atomic emission spectroscopy analysis (ICP-AES; Perkin–Elmer Optima 3000XL).

The catalytic activity of the Au/TiO_2 samples was determined in a U-type fixed-bed flow reactor at room temperature with a reactive gas mixture containing 2% CO and 2% O_2 (Ar balance). Gases were purchased from Praxair, Inc. with the following purities: O_2 (4.5), CO (4.7) and Ar (5.0). In all the catalytic tests, we used the same amount of catalyst (100 mg) and a flow rate of 50 mL/min (WHSV = 30,000 $mL{\cdot}g_{cat}^{-1}\,h^{-1}$) at overall atmospheric pressure. After heat pre-treatment in air or 10% O_2/Ar, the catalyst was cooled down to room temperature under the same ambient and purged with a stream of Ar (50 mL/min) for 30 min. Then the stream was switched to the reactive gas mixture. After equilibrating the gas flow, the CO conversion was monitored for 1–2.5 h; the reaction temperature was maintained at 20 °C. The inlet and outlet gas compositions were analyzed on-line by a quadrupole mass spectrometer (Balzers Omnistar QMS 200). The CO conversion was calculated from the measured amount of CO_2 product formation. The catalytic activity in CO oxidation was determined under steady-state conditions (millimoles of CO converted per gram of Au in the sample per second).

2.2. Characterization techniques

Surface characterization of the catalysts was performed in a combined XPS/ToF-SIMS instrument at a base pressure of $5.2 \cdot 10^{-10}$ mbar. In addition to the Au/TiO_2 catalysts, TiO_2 anatase powder was investigated for comparison. For XPS-SIMS analyses, the powder of a sample was pressed uniformly over an indium film on a flat sample holder to form a layer typically about 0.1 mm thick. Two samples could be placed at once on the sample holder and sequentially analyzed under the same experimental conditions. Prior to analysis, the samples were outgassed for 120 h in a preparation chamber at a base pressure of $6 \cdot 10^{-10}$ mbar.

For XPS, a non-monochromatic Mg K_α radiation was used at an operating power of 15 kV × 10 mA. Photoelectron core-level spectra were acquired with a hemispherical analyzer in the constant-pass-energy mode at E_p = 50 eV using a 0.03 eV energy step. The overall resolution of the spectrometer in this operating mode was 0.96 eV measured as a full width at half maximum (FWHM) of the Ag $3d_{5/2}$ line. As a reference for bulk metallic gold, the Au 4f core-level spectrum was recorded from a pure Au foil sputter-cleaned with 500 eV Ar^+ ions for 15 min, and the spectrometer was calibrated against the Au $4f_{7/2}$ line set at 84.0 eV. Furthermore,