Studies on three-way catalysis with supported gold catalysts. Influence of support and water content in feed

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A B S T R A C T

The potential of gold for the reactions of three-way catalysis was examined by converting a model exhaust consisting of 1.1% CO, 0.1% propene, 0.1% NO, O_2 (0.95% - stoichiometric, 0.85% - rich, or 1.05% - lean), and water (10% or none) over catalysts containing 1–2 wt-% Au supported on Al_2O_3, La-Al_2O_3, TiO_2, and $CeZrO_x$ supports. For comparison, CO and propene were also reacted stoichiometrically with oxygen in absence of further reactants, likewise, reduction of NO with CO was examined. It was found that propene is a strong poison for CO oxidation, but the intensity of the poisoning effect depended on the support (Al_2O_3 > La-Al_2O_3 > TiO_2 > $CeZrO_x$). The poisoning was strongest in dry feed but was partly alleviated in moist feed. NO was poorly converted both in the TWC mixture and in binary feed. In the model exhaust, NO conversion resulted in significant N_2O formation at low temperatures, but selectivity to N_2 increased with temperature. Despite poisoning by propene, Au/$CeZrO_x$ outperformed a commercial reference catalyst in CO and propene oxidation. Calcination in moist dilute air at 923 K inflicted only moderate damage to the Au catalysts. Over Au/$CeZrO_x$, CO oxidation in stoichiometric feed was not significantly affected at all, but the poisoning effect of propene became more severe in the TWC model feed. Analogous treatment at 1223 K resulted in inacceptable damage to all reactions involved and on all supports.

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1. Introduction

Research on gold catalysts has attracted huge attention during the past three decades. Among gas-phase redox reactions catalyzed by supported Au nanoparticles are CO oxidation in the absence or presence of H_2 [1–3], the oxidation of volatile organic compounds [4], water gas shift [5], alkane oxidation [6,7], propene epoxidation [8], the synthesis of hydrogen peroxide [9], and hydrochlorination of acetylene [10] (see also reviews in [11]). While attention has meanwhile shifted to liquid-phase reactions, e.g. the selective oxidation of alcohols, glycerol [12,13] and of other oxygenated molecules [11], it turns out that three-way catalysis (TWC) has hardly ever been a topic in the open literature on gold catalysis. This is surprising because the high oxidation activity of gold might allow for solving cold-start problems while literature data on gold activity in the reduction of NO by CO and by H_2 [14] and even in

the selective reduction of NO by propene in presence of O_2 [14–17] suggest that Au might be able to catalyze NO reduction also in the exhaust of gasoline cars.

To our best knowledge, there is only one study of TWC with gold-containing catalysts in the open literature. Mellor et al. [18] converted simulated effluent (net oxidizing or reducing) in stationary regime over a catalyst containing 1% Au on a mixed support comprising CeZrOx, ZrO_2, anatase, and various promoters. The results confirmed expectations as far as related to CO oxidation while hydrocarbon oxidation was more sluggish though proceeding still in the temperature range of interest. NO could be converted in the reducing feed over the monometallic catalyst with a light-off temperature T_{50} of 650 K, which was decreased by 80 K by addition of 0.1 wt-% Rh. Although no significant NO conversion was observed in net oxidizing feed, this result suggests that the full functionality of a three-way catalyst might be achieved even with a monometallic Au catalyst under fluctuating feed composition (λ oscillations) if the catalyst is endowed with appropriate storage properties.

The problem expected in the use of gold in TWC is rather related to catalyst stability because three-way catalysts are at least temporarily exposed to temperatures around the melting point of bulk

gold. Although appropriate preparations may result in surprising stabilization effects exerted by the support on supported Au nanoparticles [19–23], binding the gold in alloys may be a more promising route for the utilization of its potential in three-way catalysis. Our group has embarked on an exploration of the opportunities of such approach. In an first step, the catalytic behavior of gold alone on some typical supports (but without the additives used in Ref. [18]) has been studied, and first results related to the influence of the support and of moisture on activity, selectivity, and stability will be reported in the present communication.

2. Experimental

2.1. Catalysts

Gold nanoparticles were deposited on various supports: on Al_2O_3, on a La-stabilized Al_2O_3, on a mixed CeZrOx and on TiO_2. The Al_2O_3 used was PURALOX SCFa-140, which was donated by Sasol Germany GmbH, the La-stabilized alumina was obtained from the same source and contained ca. 2 wt-% La. The ceria-zirconia mixed oxide was a commercial product donated by Umicore & Co. KG Hanau (Germany) and was used without further analysis. The 1 wt-% Au/TiO_2 catalyst employed was AUROlite™ (Strem 79-0165 [24]). The reference TWC is a commercial sample donated by Interkat Katalysatoren GmbH (Königswinter, Germany), with a total precious metal content of ca. 2 wt.% consisting predominantly of Pd (Pd: Pt: Rh 13:1:1). The catalysts were compacted, crushed and sieved to get a 255–350 μm sieve fraction for the catalytic experiments.

Deposition of Au nanoparticles on Al_2O_3, La-Al_2O_3, and CeZrO$_x$ was achieved by the deposition-precipitation technique [25] using a procedure similar to that described previously [26]: A weighed amount of support dried at 383 K for 8 h immediately before catalyst preparation was shaken with an aqueous solution containing 2.5 mg Au per L for 1 h at 343 K. The solution had been obtained by neutralization of HAuCl$_4$ with NaOH to pH 7. After the interaction of support and Au solution, the powder was washed several times with large portions of warm distilled water (200 mL H_2O/g sample), dried in vacuo at room temperature overnight and calcined in air at 573 K for 4 h. Preparations were done with pre-granulated supports obtained by tableting support powder under a pressure of 106 N (pellet diameter 20 mm) for 60 min, crushing and sieving to 200–500 μm particles.

For stability studies, the catalysts were subjected to calcinations in a flow of 5% O_2 and 10% H_2O in He for 6 h at 923 K and 1223 K.

2.2. Characterization

The gold content of the catalyst samples was determined by X – ray Fluorescence on an ARL instrument equipped with a Rh anode (X-ray tube voltage: 50 kV, tube current: 40 mA, exposure time: 10 s). Textural characteristics of the supports were obtained from nitrogen physisorption measurements at 77 K by using an ASAP 2400 (Micromeritics) instrument. Before adsorption, the samples were outgassed at 573 K to a residual pressure of ca. 10^{-3} Torr. Specific surface areas and total pore volumes in the 3.5–100 nm range were calculated from the isotherms in the range of $p/p_0 = 0.05–0.2$ using the standard BET equation, and at $p/p_0 = 0.98$, respectively, mean pore diameters were derived from standard BJH analysis.

Transmission electron microscopy (TEM) studies were performed by using a JEM-2010 (JEOL, Japan) electron microscope with a lattice resolution of 0.14 nm and a 200 kV accelerating voltage. The mean diameters of gold particles for each catalyst sample were determined by counting over 300 particles in TEM images taken with a medium magnification and calculated by assuming a simple model of metal nanospheres [27].

X-ray photoelectron spectroscopy (XPS) studies were carried out on a SPECS spectrometer equipped with a PHOIBOS-150-MCD-9 hemispherical analyzer and a FOCUS-500 X-ray monochromator (Al Kα emission = 1486.6 eV, 150 W). Spectra were recorded with a constant pass energy of 20 eV. A low voltage electron flood gun was used for charge compensation. Quantitative analysis was performed using areas of XPS peaks integrated over Shirley backgrounds and corrected for the relative sensitivity factors (RSFs) taken from Ref. [28].

2.3. Catalytic studies

Catalytic measurements were performed in a microflow reactor (V4A-stainless steel) at atmospheric pressure in the temperature range 323–673 K using a temperature ramp of 5 K/min. Model feeds simulating stoichiometric, rich, and lean conditions were employed and consisted of CO (1.1%), NO (0.1%), and propene (0.1%), combined with O_2 (stoichiometric: 0.95 %; rich: 0.85%; lean: 1.05 %), H_2O (10 % or none), and He (balance). Following recent studies in literature [29,30], propene was chosen to represent unburned exhaust hydrocarbons because of the mostly unsaturated character of the latter and the wide range of carbon numbers spanning from (predominant) C_2 to >C_8 [31]. The mixture was fed to the reactor through electronic mass-flow controllers at a gas-hourly space velocity (GHSV) of 60,000 h^{-1} (183 ml/min feed on 125 mg catalyst). Steam was dosed by help of a saturator kept at 319 K. Subsequent tube connections were heated to 393 K. Before product analysis, moisture was removed from the effluent stream by a cold trap cooled with an ice bath. Effluent products were analyzed by a combination of calibrated mass spectrometry (O_2, NO, propene) and non-dispersive IR photometry (CO, CO_2, N_2O). The influence of the N_2O fragmentation pattern and its contribution the m/e = 30 (NO) QMS signal was taken into account in the evaluation of NO concentrations. CO, propene, and NO conversions of were calculated according to Eq. (1) (example – CO, index 0–initial)

$$X_{CO} = (c_{CO,0} - c_{CO})/c_{CO,0} \tag{1}$$

N_2O formation will be reported as ppm content in the effluent. To describe catalyst activity, light-off temperatures T_{50} (T of 50% reactant conversion) were recorded and compared.

To examine interactions between reactants, oxidation of CO and of propene and reduction of NO by CO were also studied individually in the same setup. Feeds employed contained 1.1% CO, 0.55% O_2, and 10% (or no) H_2O in He for CO oxidation, 0.1% propene, 0. 45% O_2, and 10% (or no) H_2O in He for propene oxidation, and 0.4% of both NO and CO for NO reduction (only dry feed). The GHSV was 60,000 h^{-1} in all cases. These experiments were made with Au on La-Al_2O_3 and on CeZrO$_x$.

3. Results

3.1. Characterization

In Table 1, basic data of the catalysts employed in this study are summarized. The Au content was 1.5–1.8 wt-% except for the commercial Au/TiO_2 catalyst where an Au content of 1 wt-% is specified. Texture data of catalysts on the basis of Al_2O_3 and TiO_2 are as expected for these supports. The values are very close to those of the pure supports, which have not been included. Apparently, loading of gold by deposition-precipitation (at least in quantities <2 wt-%) has little effect on the texture of these supports.

In Fig. 1, representative TEM micrographs of our catalysts are presented. Average Au particle sizes and particle size distributions