CO adsorption and oxidation on Au/TiO_2

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Received 16 October 1998; accepted 11 November 1998

Preoxidized Au/TiO_2 showed no initial activity during a first heating stage up to 70 °C, while prereduction yielded a high initial CO conversion at room temperature. With FTIRS, two different CO absorption bands were detected. One band is usually attributed to CO on an oxidic gold species (2151 cm^{-1}), the other one is characteristic of CO on metallic gold (2112 cm^{-1}). The presence of the first species appears to have a detrimental effect on the CO oxidation by O_2. The present results do not support a model in which the activity of supported gold catalysts in CO oxidation is ascribed to ionic Au particles.

Keywords: gold, carbon monoxide, titania

1. Introduction

Gold has long been regarded as catalytically inactive. Recent studies, however, revealed considerable activity of supported gold catalysts for various reactions [1–5]. For example, Au particles supported on transition-metal oxides (MO) are extremely active in CO oxidation at low temperatures. In particular, Au/Fe_2O_3, Au/TiO_2 and Au/Co_3O_4, are efficient combinations for CO oxidation by O_2.

The mechanism associated with the high activity of Au/MO catalysts is not yet known. Several reaction mechanisms have been suggested:

(1) both Au and MO participate in the catalytic actions, the reaction taking place at the Au/MO interface [6];

(2) very small gold particles are the active species, the role of MO is to stabilize the small particles [7,8];

(3) the active species is ionic gold, also stabilized by MO [9];

(4) low-coordination sites in the form of specific ensembles of gold atoms are the active sites.

A relevant contribution to the discussion concerning the nature of the active Au species is a recent paper by Minicò et al. [10]. The authors found a correlation between the presence of an IR band at 2159 cm^{-1} assigned to CO on Au^+ and the activity of Au/Fe_2O_3 catalysts in CO oxidation.

In the study described in this paper, we have examined CO adsorption by FTIR and oxidation on Au/TiO_2 catalysts under oxygen-rich conditions, thus trying to minimize reduction of possible oxidic gold species present.

2. Experimental

Au/TiO_2 catalyst was prepared via homogeneous deposition precipitation with urea [11]. $HAuCl_4\cdot 3H_2O$ (99.999%) was used as precursor. It was added to a solution with TiO_2 (Eurotitania-1, Tioxide) and urea (Acros). Under vigorously stirring the solution was kept at 80 °C until pH reached 8.5. After filtration the slurry was thoroughly washed and dried afterwards at 80 °C overnight.

The fresh sample was either oxidized by 4 vol% O_2 in He or reduced in 4 vol% H_2 in He at 400 °C for 2 h prior to catalytic testing. Characterization by XRD and HRTEM showed the presence of gold particles with an average diameter of 7.5 nm. Spectrometric analysis by AAS or UV-VIS indicated the gold loading to be 4.5 wt%. The activity measurements were performed in a microreactor at a GHSV of 2500 h^{-1}. The reactant flow consisted of 2 vol% CO, 2 vol% O_2 and balance He. The reaction was temperature-programmed and executed at 5 °C/min ramping speed. Two runs of one heating and one cooling stage were applied subsequently. Effluent gases from the reactor were analyzed by a gas chromatograph (Chrompack CP 2002) equipped with a Molsieve 5 Å column for CO and O_2 detection and a Haysep A column for CO_2 detection.

FTIR spectra were recorded at room temperature with an Mattson Galaxy 2020 spectrophotometer, operated with a resolution of 2 cm^{-1}. Catalyst powder was pressed into a self-sustaining disc that was placed in a vacuum cell. The sample was either oxidized with pure O_2 (99.998%) or reduced with pure H_2 (99.999%) for 1 h at 300 °C, in both cases up to 100 mbar. Prior to gas admittance, background spectra were recorded. The reactant mixture of CO (99.997%) and O_2 with a ratio of 1 was admitted in a range of 1–100 mbar. Afterwards, background spectra were subtracted and corrections for gas-phase CO were performed.

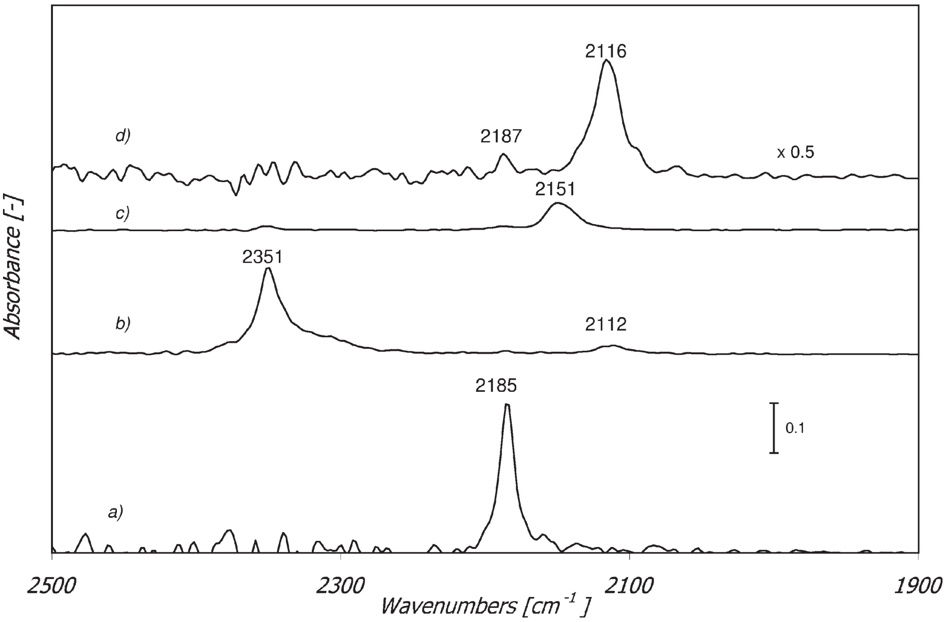

Figure 1. Infrared spectra at room temperature of (a) 100 mbar CO on TiO_2, (b) 30 mbar of $CO + O_2$ (1 : 1) on prereduced Au/TiO_2, (c) 30 mbar of $CO + O_2$ (1 : 1) on preoxidized Au/TiO_2, (d) 30 mbar of $CO + O_2$ (1 : 1) on reduced sample of (c).

3. Results and discussion

3.1. FTIR measurements

FTIR spectra of adsorbed CO on Au/TiO_2 or TiO_2 are presented in figure 1. In spectrum (a), CO was admitted to preoxidized TiO_2. The appearance of an absorption band at 2185 cm^{-1} clearly indicates the adsorption of CO on Ti^{4+} [12]. A CO–O_2 mixture admitted to prereduced Au/TiO_2 (spectrum (b)) gave rise to an absorption band of CO at 2112 cm^{-1} [12,13] as well as of CO_2 at 2351 cm^{-1}. For a preoxidized Au/TiO_2 catalyst, the absorption band of CO on Au appeared at 2151 cm^{-1} (see spectrum (c)). However, the 2151 cm^{-1} band was not stable. After several hours in the reaction mixture the band started to shift to lower wavenumbers and finally stabilized at around 2110 cm^{-1}. As pointed out by others [9,10], high-wavenumber bands of CO adsorbed on Au/TiO_2 could very well originate from the interaction of CO with oxidic gold. The apparent instability of the observed absorption band could be due to the slow reduction of oxidic gold species by CO, partly inhibited by the presence of excess O_2. Furthermore, the subsequent reduction by H_2 of an oxidized sample with characteristics similar to spectrum (c) yields an apparent reduced surface (spectrum (d)), as indicated by the CO–Au^0 band (2116 cm^{-1}). The band at 2187 cm^{-1} can be assigned, as in spectrum (a), to CO on Ti^{4+}.

3.2. Catalytic activity

Figure 2(a) shows the results of the four stages of activity experiments with preoxidized Au/TiO_2. At the first heating stage, the reaction did not proceed below 70 °C. Full conversion of CO into CO_2 was reached at temperatures above

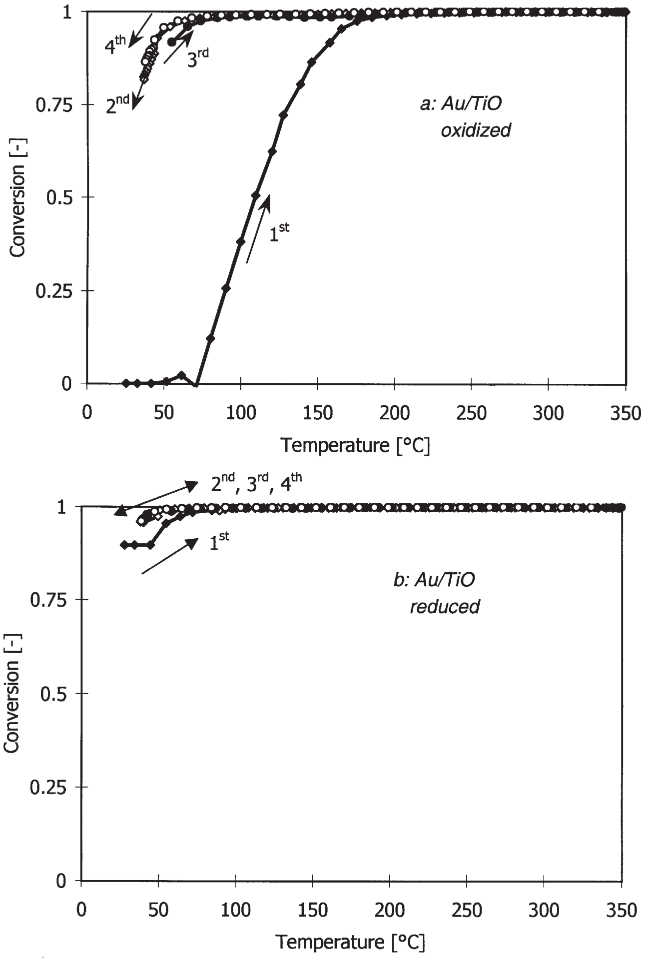

Figure 2. CO conversion vs. temperature for CO oxidation by O_2 over Au/TiO_2 after an oxidative (a) or a reductive (b) pretreatment. Note: 1 – first heating stage, 2 – first cooling stage, 3 – second heating stage, 4 – second cooling stage.

200 °C. Subsequent cooling in the reaction mixture resulted in a continuous 100% efficient CO oxidation down to room temperature. This high CO conversion and simultaneous CO_2 production could also be maintained in the following heating and cooling stages. Apparently, the active catalyst is formed in the reaction mixture.

Experiments with prereduced Au/TiO$_2$ exhibited a similar reproducibly high activity at all four ramping stages (see figure 2(b)). This indicates that a reduction step is essential for catalytic activity. This step could well be the reduction of oxidic gold species (Au$^{\delta+}$, $\delta > 0$) to metallic gold (Au^0) by CO. The conversion of CO caused by reduction would appear to be negligible. The amount of catalyst used was typically 0.2 g. The total amount of gold present would be 10^{-4} mol, given a $\sim$5 wt% loading. Hypothetically, if all gold would be present as Au$^+$, the amount of CO consumed by reduction would be far too small to be noticable in the CO conversion plot.

Regardless of pretreatment, carbon monoxide oxidation by oxygen proceeds easily on Au/TiO$_2$. However, when preoxidized the catalyst needs an initial activation step before full CO conversion at low temperatures is reached. The activation step consists of reduction in a hydrogen atmosphere or leaving the catalyst in the CO/O$_2$ mixture at 200 °C. FTIR spectra of adsorbed CO reveal a different nature of adsorbed CO depending on the pretreatment (reductive or oxidative). After an oxidative pretreatment, Au/TiO$_2$ exhibits a CO absorption band at 2151 cm^{-1}. Reduction in hydrogen or by exposure in the CO/O$_2$ mixture results in an absorbance band at 2112 cm^{-1}, characteristic of adsorbed CO on metallic Au. The present results do not favor a model in which the catalytic activity of gold is related to the presence of the 2151 cm^{-1} band, usually assigned to CO adsorbed on Au$^+$.

Acknowledgement

This work was supported by the Dutch Organisation for Scientific Research (NWO).

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