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CO oxidation over Au/TiO_2 catalyst: Pretreatment effects, catalyst deactivation, and carbonates production

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ABSTRACT

A commercially available Au/TiO_2 catalyst was subjected to a variety of thermal treatments in order to understand how variations in catalyst pretreatment procedures might affect CO oxidation catalysis. Catalytic activity was found to be inversely correlated to the temperature of the pretreatment. Infrared spectroscopy of adsorbed CO experiments, followed by a Temkin analysis of the data, indicated that the thermal treatments caused essentially no changes to the electronics of the Au particles; this, and a series of catalysis control experiments, and previous transmission electron microscopy (TEM) studies ruled out particle growth as a contributing factor to the activity loss. Fourier transform infrared (FTIR) spectroscopy showed that pretreating the catalyst results in water desorption from the surface, but the observable water loss was similar for all the treatments and could not be correlated with catalytic activity. A Michaelis–Menten kinetic treatment indicated that the main reason for deactivation is a loss in the number of active sites with little changes in their intrinsic activity. In situ FTIR experiments during CO oxidation showed extensive buildup of carbonate-like surface species when the pretreated catalysts were contacted with the feed gas. A semi-quantitative infrared spectroscopy method was developed for comparing the amount of carbonates present on each catalyst; results from these experiments showed a strong correlation between the steady-state catalytic activity and amount of surface carbonates generated during the initial moments of catalysis. Further, this experimental protocol was used to show that the carbonates reside on the titania support rather than on the Au, as there was no evidence that they poison Au–CO binding sites. The role of the carbonates in the reaction scheme, their potential role in catalyst deactivation, and the role of surface hydroxyls and water are discussed.

1. Introduction

CO oxidation over Au-based catalysts has been widely studied because these materials have potential applications in the selective removal of CO from H_2 rich streams (CO Prox) [1–3]. A number of factors appear to contribute to the high activity at low temperatures that these catalyst exhibit, including: the presence of low coordination surface Au atoms, the importance of Au atoms located at or near the metal–support interface, the presence of surface hydroxyls located near the Au, and electronic interactions between the Au nanoparticles and the support [4–9]. Although the reaction stoichiometry is simple, the reaction mechanism for CO oxidation over Au appears to be complex [9,10]. A variety of oxygenated species have also been suggested to play a role in the catalysis, including support hydroxyls [11–15], water [10,16–20], and carbonates [21,22]. Additionally, O_2 activation, which is generally considered to be the key catalytic step, is not well understood [23–26] nor are the roles of perimeter sites around Au particles [27,28] or the causes of deactivation [29–31].

The catalytic activity reported for CO oxidation over Au catalysts varies widely; as an example, Kung et al. reviewed the reaction rates for CO oxidation using Au/TiO_2 finding up to a 10-fold variation in reaction rates (0.039–0.35 molCO $molAu^{-1}$ s^{-1}) for catalysts with similar Au particles size (2.1 and 1.7 nm, respectively) [11]. This variance in activity coincides with a lack of agreement regarding activation methods for the catalysts. Specifically, the temperature of calcination used during catalyst preparation varies widely [32–35]. Depending on the synthetic route chosen, activation temperatures range from 200 to more than 400 °C with large differences in the time chosen for activation treatments [36–38].

Bond reviewed the effects of temperature and treatment gas on the preparation of Au catalysts [39]. The main conclusions regarding the activation conditions can be summarized in a few points: (1) Heating in reducing atmospheres (H_2, CO) or Argon at temperatures under 393 K is preferred to oxidizing atmospheres (O_2 or Air) and higher temperatures. This is supported by the fact that reduction to Au^0 starts at low temperatures and residual Cl^- is rapidly eliminated (via HCl). (2) Au particle size increases with

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increasing treatment temperature, and at temperatures above 573 K, O_2 promotes particle growth more so than H_2 does. (3) Fully reduced particles do not show substantial mobility unless chloride remains on the catalyst surface. Therefore, Bond recommends low temperatures and short treatment times for preparing supported Au catalysts. Bond's considerations regarding the thermal activation are primarily focused on preparing small supported Au nanoparticles in the size regime (2–4 nm) that are catalytically active; however, there is little discussion regarding the effect that these thermal treatments have on the resulting catalytic activity.

The literature provides a wide variety of activation protocols (both oxidative and reductive) for Au-based catalysts [11,46]. Table 1 summarizes several different activation protocols applied to Au/TiO_2 catalysts and includes the size of the Au particles produced and the reported catalytic activities (CO oxidation between 273 and 300 K). It is readily apparent that there is almost no correlation between the pretreatment temperatures used and the catalytic activity reported. Catalysts with very similar Au particle sizes may differ by an order of magnitude. This may be influenced by residual chloride in the less active catalysts, as chloride is well known to be a poison for CO oxidation over Au catalysts [47]. Additionally, several studies report catalytic activities of approximately 0.1–0.3, yet the pretreatments differ by 300 K and up to 12 h. Given this variance in the literature, one might posit that pretreatment protocols are relatively unimportant so long as relatively small particles are maintained and chloride is sufficiently removed.

Behm et al. more systematically varied activation protocols to produce more active Au–CO oxidation catalysts [30]. They found that annealing the catalyst with a mixture H_2/N_2 at 473 K was more effective than the conventional oxidation at 673 K. They also pointed out that more severe reductions (with H_2/N_2 mixtures at 673 K) produce catalysts with a higher tendency for deactivation [30].

In preliminary studies using a commercial Au/TiO_2 sample, we found that changes in pretreatment conditions immediately prior to catalytic testing produced similarly marked variations in catalytic activity. We therefore undertook a more detailed examination of how thermal treatments change the catalyst in order to better understand the factors that control CO oxidation activity. Seven thermal treatments were chosen to prepare catalysts with markedly different reaction rates. These induced differences in catalytic activity were the basis of an experimental design composed of three related studies. First, the CO adsorption thermodynamics were studied to evaluate electronic changes to the Au nanoparticles. Second, a Michaelis–Menten analysis of CO oxidation kinetics measurements was used to evaluate changes in O_2 reactivity and in the relative number of active sites. Finally, in situ IR spectroscopy was used to monitor changes in surface composition caused by thermal treatments and during CO oxidation catalysis. These experiments provide a more complete picture of how the catalyst changes (and does not change) as a function of thermal treatments.

2. Experimental

2.1. Materials

The catalyst used in this study was a commercial AUROlite™ sample purchased from STREM Chemicals (nominal 1% Au/TiO_2). This catalyst was pretreated by the manufacturer to ensure that particles were of appropriate size (2–4 nm) to yield active CO oxidation catalysts. Further, this catalyst has proven to be active and stable over long periods of time [48,49]. The catalyst was crushed and stored in a dark refrigerator. Gases (N_2, H_2, O_2, and 5%CO/He) were 5.0 grade supplied by Praxair and used with no additional purification. Powdered Silicon Carbide (400 mesh) was purchased from Aldrich.

2.2. Catalyst pretreatments

Catalyst pretreatment was performed in situ at atmospheric pressure using various gas mixtures at 100 mL/min; heating rates were 5 °C/min. Treatment conditions are detailed in Table 2. After each treatment, the catalyst was purged with N_2 for 60 min at the treatment temperature and subsequently cooled to ambient temperature.

2.3. CO oxidation catalysis

The CO oxidation reactor consisted of a home-built laboratory-scale single-pass plug-flow micro-reactor [48,49]. The reaction zone consisted of 5 mg of finely ground fresh catalyst diluted in 750 mg of silicon carbide. Gas flows were controlled with 4 electronic low pressure mass flow controllers (Porter Instruments). The composition of the feed and reactor effluent (CO and CO_2) was determined using a Siemens Ultramat 23 IR gas analyzer.

Each treatment-reaction sequence was performed with a fresh sample of catalyst. After loading into a glass U-tube, the diluted catalyst was treated with one of the procedures shown in Table 2. CO oxidation activity was measured in a 60-min experiment immediately following the pretreatment. The feed (1% CO, 20% O_2, balance N_2, flowing at 180 mL/min; $\mathrm{WHSV} = 2.16 \times 10^3\ \mathrm{L} \cdot \mathrm{h}^{-1} \cdot \mathrm{g}_{\mathrm{cat}}^{-1}$) was held constant and the reaction temperature was maintained at 20 °C using a water bath.

O_2 pressure dependence was determined in separate experiments. After treating 4 mg of catalyst and cooling under N_2, the reactor was fed with 140 mL/min of a gas mixture containing 1%

Table 1

Activation conditions, Au particle size, and catalytic activity of Au/TiO_2 catalysts used in low-temperature CO oxidation (273–300 K).

Activation conditions	Au particle size (nm)	Rate/Au_{tot} (s^{-1})	T (K)	Ref.
No thermal treatment	2.9 ± 1.7	0.03	298	[7]
298 K, 1 h, H_2	2	1.4 ± 0.2[a]	273	[40]
310 K, 24 h, air	3.3 ± 0.5	0.34[b]	273	[41]
373 K, 1 h, H_2 + 298 K, CO/O_2	1.7	0.35	273	[23]
373 K, 0.5 h, H_2 + 373 K, 0.5 h H_2O/H_2	3.3 ± 0.7	0.013[b]	288	[10]
523 K, 0.5 h, air	3	3.0[b]	298	[20]
573 K, air	2.1	0.025	298	[42]
623 K, 4 h, He	3.3 ± 0.5	0.18[b]	298	[43]
623 K, 4 h, air + vacuum dried	3.0 ± 1.3	0.16	273	[8]
673 K, 4 h, air + 723 K, 10 h H_2	2.9 ± 0.5	0.13	300	[44]
673 K, 1 h 1% CO, 21% CO in Ar	2.1	0.039	273	[45]

[a] Based on the reaction of adsorbed CO species.

[b] Based on surface Au.