Journal of Catalysis 319 (2014) 155–162

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Catalytic oxidation of carbon monoxide at cryogenic temperatures

Ilkeun Lee, Francisco Zaera *

Department of Chemistry, University of California, Riverside, CA 92521, USA

ARTICLE INFO

Article history:
Received 14 July 2014
Revised 28 August 2014
Accepted 31 August 2014
Available online 20 September 2014

Keywords:
Carbon monoxide oxidation
Heterogeneous catalysis
Gold
Titania
Infrared absorption spectroscopy
Cryogenic temperatures

ABSTRACT

Although solid gold is often considered chemically inert, it has been shown that, in the form of nanometer-size particles, it is capable of promoting many catalytic reactions. This behavior is typified by the ease with which catalysts made out of gold nanoparticles dispersed on titania supports oxidize carbon monoxide to carbon dioxide around room temperature. Here, we report on a unique gold/titania-based catalyst that, in addition to such room temperature catalysis, displays a second active regime at much lower temperatures, as low as 120 K. We show that this new catalytic regime follows a mechanism different to that operative at room temperature, involving at least two titania-adsorbed CO species and a synergy between the uptake of CO and O_2 on the surface. New titanate sites, formed upon treatment of catalysts made out of dispersing Au nanoparticles on amorphous titania with NaOH, appear to be responsible for the opening of this new reaction channel.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Much excitement has been generated in recent years by the discovery that gold, when dispersed as nanoparticles on certain high-surface-area supports, can be quite active in promoting many reactions under mild conditions, usually around room temperature [1]. The oxidation of carbon monoxide in particular has been used as a prototypical example to show the potential of gold in catalysis [2,3]. Extensive discussion has been reported on the mechanistic details of that reaction [4–7], and samples have been identified capable of catalytically promoting such oxidation at temperatures as low as 200 K [2,5,8], However, in all reported cases, to the best of our knowledge, these oxidation reactions have been shown to be activated, with significant catalytic activity starting only at moderate (~room) temperatures. Here, we report on a unique case where the steady catalytic rate of oxidation for carbon monoxide increases again at lower temperatures, all the way down to 120 K (the lowest temperature we were able to achieve with our experimental setup), and displays an unusual apparent negative activation energy. Cryogenic catalysis such as this is rather uncommon, and typically seen only for more esoteric cases such as the interconversion between ortho and para hydrogen. We argue that the behavior observed here is the consequence of a change in the mechanism of the reaction: The way this cryogenic-temperature reaction proceeds is different than in the other reported cases. Below we discuss the requirements in terms of both the properties of the catalyst and the surface reaction intermediates involved for the cryogenic oxidation to occur.

2. Experimental details

Our catalyst exhibiting this unique cryogenic activity is based on gold nanoparticles dispersed on an amorphous titania support made by sol–gel chemistry and modified via treatment with sodium hydroxide ($Au/TiO_2(A) + NaOH$). Details of the synthesis of this and other reference catalysts are provided in the Supporting Information. The activity of all catalysts was evaluated by following in situ both the consumption of carbon monoxide and the accumulation of carbon dioxide during the conversion of mixtures of CO and O_2 versus reaction time using diffuse reflectance infrared absorption spectroscopy (DRIFTS). Details of the procedures used for the calibration of the DRIFTS signals and the calculations of reaction rates are also provided in the Supporting Information (Figs. S1 and S2).

3. Results

The DRIFTS traces recorded in these studies, exemplified in Fig. 1, are complex, and display a multitude of features covering several frequency ranges. Fortunately, these systems have been studied extensively in the past, and most of the DRIFTS peaks have been identified already. For one, carbonate and formate species are detected in the frequency range between 1300 and 1800 cm^{-1} (brown-shaded area in Fig. 1) [9–11], and hydroxo surface moieties

---

* Corresponding author.
E-mail address: zaera@ucr.edu (F. Zaera).

http://dx.doi.org/10.1016/j.jcat.2014.08.018
0021-9517/© 2014 Elsevier Inc. All rights reserved.

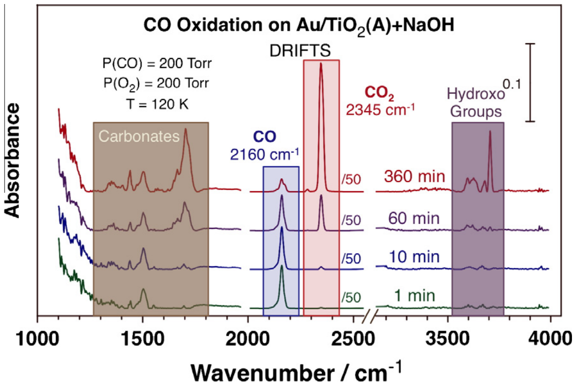

Fig. 1. Typical diffuse reflectance infrared absorption spectroscopy (DRIFTS) data used to characterize the performance of our gold–titania catalysts for the conversion versus time of a mixture of 200 Torr CO + 200 Torr O_2 at 120 K. The catalyst consists of 1 wt% 15-nm Au nanoparticles dispersed on an amorphous titania support treated with a NaOH solution (Au/TiO$_2$(A) + NaOH). Shown are features associated with CO (stretching C–O mode, blue-shaded area) and CO_2 (red), the species relevant to the reaction, as well as with carbonate (brown) and hydroxo (purple) surface groups, which do not participate in this catalysis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

are responsible for the signals in the 3500–3800 cm^{-1} window (purple-shaded area) [12,13]. These DRIFTS signatures were found to be different in the cryogenically-active catalyst compared to in the other reference samples (Fig. 2), indicating that the surface species observed in the spectroscopic experiments are intrinsically associated with each catalyst. On the other hand, the associated species were found not to change in nature either during or after reaction, an observation that suggests that they do not participate directly in the cryogenic-temperature CO oxidation reaction. The main information relevant to the cryogenic oxidation reaction was extracted from the DRIFTS peaks associated with carbon monoxide, seen in the ~2000–2250 cm^{-1} range (blue-shaded area in Fig. 1), and with carbon dioxide, observed in the 2300–2400 cm^{-1} window (red-shaded area).

The kinetics of the CO-to-CO_2 conversion was followed by using the integrated signal intensities of the corresponding CO and CO_2 DRIFTS peaks. A typical plot of the time-dependent evolution of those intensities, after conversion into number of moles, is shown in Fig. 3a (details of the DRIFTS signal calibration and rate calculation procedures are provided in the Supporting Information), and the raw data for all the runs with all the samples used in this study are provided in Figs. 4 and 5. Analysis of these kinetic data turned out to not be simple in the cryogenic temperature regime, because condensation of the CO_2 produced by the reaction inside the pores of the catalysts interferes with the DRIFTS measurements. As a consequence, many of the kinetic traces display two time regimes, a fast transient possibly reflecting the initial gas condensation process, and a subsequent slower steady evolution due to the CO conversion (Figs. 4 and 5). Regardless, the cryogenic oxidation of CO with the Au/TiO$_2$(A) + NaOH catalyst is evidenced by both the decrease in the amount of CO (blue and green traces in Fig. 3a) and the increase in the amount of CO_2 (red) detected by the DRIFTS signals as a function of reaction time. The CO_2 DRIFTS feature does saturate after about approximately 1 h of reaction, likely because of the preferential absorption of that gas inside the pores of the catalyst, and therefore diverges from the values measured for the CO DRIFTS peaks at longer times. In order to avoid errors due to this gas condensation while also minimizing any experimental artifacts due to the initial transient regime, turnover frequencies (TOFs, in CO molecules converted per gold surface atom per second) for the steady conversion regime were calculated by estimating the slope of the signal intensity-versus-time DRIFTS curves for CO_2 (because those were less noisy than the ones for CO) after 1 h of reaction. This choice may be somewhat arbitrary, but it should be emphasized that the qualitative differences in cryogenic catalytic behavior between the Au/TiO$_2$(A) + NaOH catalyst and the rest of the samples, the main observation reported here, are evident even in the raw data (Figs. 4 and 5). It should also be pointed out that, in spite of the limitations encountered with the quantitation of the DRIFTS signals in the experiments carried out at cryogenic temperatures, we believe that this technique is still better suited than others such as gas chromatography for these studies, because the condensation of the CO_2 produced means that product cannot be detected in the gas phase.

TOF data for the oxidation of carbon monoxide with O_2 were acquired between 120 and 350 K with all of our catalysts. The results obtained with the main catalyst, a 1 wt% 15-nm Au/TiO$_2$(A) sample treated with NaOH, are shown as red solid squares in Fig. 3b. This catalyst shows the same type of activated catalytic performance toward the oxidation of CO around room temperature seen with other Au/TiO$_2$-based catalysts, as shown in Figs. 3c and 4 and 5. In addition, though, it also displays a second regime of high catalytic activity at cryogenic temperatures, as mentioned already, with significant TOFs resurging below approximately 250 K. High TOFs were in fact measured all the way down to 120 K, the lowest temperature available with our instrumentation. This difference in behavior is clearly observable in the raw DRIFTS kinetic data shown in Figs. 4 and 5. For instance, the consumption of CO over time in reactions carried at 120 K is seen only with the Au/TiO$_2$(a) + NaOH catalyst. Regardless of any experimental limitations in the quantitative estimation of the TOFs of the low-temperature oxidation reaction discussed above, there is a clear qualitative difference in the behavior of this catalyst as compared to that seen with all the other reference samples used in our study. The activity seen with our catalyst in this second temperature regime has, to the best of knowledge, not been matched by any other reported catalyst; it is the key result of this report.

Additional spectroscopic and kinetic studies were performed with a number of reference catalysts in an attempt to systematically isolate the specific characteristics that make the Au/TiO$_2$(A) + NaOH catalyst active under cryogenic temperatures. Eight different catalysts were prepared and tested, namely:

a. 1 wt% Au/TiO$_2$(A) + NaOH,
b. TiO$_2$(A) + NaOH,
c. 1 wt% Pt/TiO$_2$(A) + NaOH.
d. 1 wt% Au/TiO$_2$-P25,
e. 1 wt% Au/TiO$_2$-P25 + NaOH,
f. 1 wt% Au/TiO$_2$(A),
g. 1 wt% Au/TiO$_2$(A) + NaOH + HCl, and
h. 1 wt% Au/Na$_2$Ti$_3$O$_7$.

All these samples were fully characterized, and shown to be similar in nature except for the specific parameter varied in each case with respect to the others, as discussed below. The CO oxidation TOF data obtained with these samples are summarized in Fig. 3b and 3c, and the raw kinetic data provided in Figs. 4 and 5. The following required surface elements were identified for cryogenic catalytic activity:

1. Gold in the form of nanoparticles dispersed on the titania support. No samples based on pure titania, not even after NaOH treatment (Sample b; Fig. 3b, brown open downward triangles), nor catalysts where Au is replaced by Pt (Sample c; Fig. 3c, brown solid downward triangles), display any measurable oxidation catalytic activity (within our experimental error) at temperatures below ~250 K. The role of this gold phase is likely to be to facilitate the low-temperature activation of molecular

Download English Version:

https://daneshyari.com/en/article/61004

Download Persian Version:

https://daneshyari.com/article/61004

Daneshyari.com