Catalytic Oxidation of Carbon Monoxide at Cryogenic Temperatures

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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 O₂ 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.

Keywords: Carbon Monoxide Oxidation, Heterogeneous Catalysis, Gold, Titania, Infrared Absorption Spectroscopy, Cryogenic Temperatures

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/TiO₂(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 O₂ versus reaction time using diffuse reflectance infrared absorption spectroscopy (DRIFTS). Details on the procedures used for the calibration of the DRIFTS signals and the calculations of reaction rates are also provided in the Supporting Information (Figures S1 and S2).

3. Results

The DRIFTS traces recorded in these studies, exemplified in Figure 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 Figure 1) [9-11], and hydroxo surface moieties 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 versus the other reference samples (Figure 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 $\sim 2000\text{--}2250\text{ cm}^{-1}$ range (blue-shaded area in Figure 1), and with carbon dioxide, observed in the $2300\text{--}2400\text{ cm}^{-1}$ window (red-shaded area).

The kinetics of the CO-to-CO₂ conversion was followed by using the integrated signal intensities of the corresponding CO and CO₂ DRIFTS peaks. A typical plot of the time-dependent evolution of those intensities, after conversion into number of moles, is shown in Figure 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 Figures 4 and 5. Analysis of these kinetic data turned out to not be simple in the cryogenic temperature regime, because condensation of the CO₂ 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 (Figures 4 and 5). Regardless, the cryogenic oxidation of CO with the Au/TiO₂(A)+NaOH catalyst is evidenced by both the decrease in the amount of CO (blue and green traces in Figure 3a) and the increase in the amount of CO₂ (red) detected by the DRIFTS signals as a function of reaction time. The CO₂ 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 CO₂ (because those were less noisy than the ones for CO) after 1 h of reaction . This choice may be somewhat arbitrary, but in any case the qualitative differences in cryogenic catalytic behavior between the Au/TiO₂(A)+NaOH catalyst and the rest of the samples, the main observation reported here, is evident even in the raw data (Figures 4 and 5). It should 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 CO₂ produced means that it can not be detected in the gas phase.

TOF data for the oxidation of carbon monoxide with O₂ 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/TiO₂(A) sample treated with NaOH, are shown as red solid squares in Figure 3b. This catalyst shows the same type of activated catalytic performance toward the oxidation of CO around room temperature seen with other Au/TiO₂-based catalysts, as shown in Figures 3c, 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 Figures 4 and 5. For instance, the consumption of CO over time

in reactions carried at 120 K is seen only with the Au/TiO₂(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 compare to the all 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/TiO₂(A)+NaOH catalyst active under cryogenic temperatures. Eight different catalysts were prepared and tested, namely:

- a. 1 wt% Au/TiO₂(A) + NaOH,
- b. TiO₂(A) + NaOH,
- c. 1 wt% Pt/TiO₂(A) + NaOH.
- d. 1 wt% Au/TiO₂-P25,
- e. 1 wt% Au/TiO₂-P25 + NaOH,
- f. 1 wt% Au/TiO₂(A),
- g. 1 wt% Au/TiO₂(A) + NaOH + HCl, and
- h. 1 wt% Au/Na₂Ti₃O₇.

All these samples were fully characterized, and proved 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 Figures 3b and 3c, and the raw kinetic data provided in Figures 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; Figure 3b, brown open downward triangles), nor catalysts where Au is replaced by Pt (Sample c; Figure 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 oxygen, possibly at the Au-TiO₂ interface [6, 7, 14, 15], given that it has been shown in surface-science studies that CO can be oxidized by atomic oxygen adsorbed on gold nanoclusters at temperatures as low as 35 K [16, 17]. It should also be mentioned that, although there have been suggestions in the literature that the active gold phase may consist of partially-charged Au atoms [18, 19], no evidence of such species was seen in X-ray photoelectron spectroscopy (XPS) data from our samples (Figure 6a): only the 4f_{7/2} and 4f_{5/2} XPS peaks for metallic gold [20, 21], at 83.5 and 87.05 eV respectively, were observed in all cases (some gold loss seems to take place upon treatment with NaOH and HCl, possibly from the outside of the pores of the support). The lack of any shifts in the Au 4f peaks upon NaOH treatment of the sample also argues against the formation of Au-Na intermetallic mixtures. Finally, it is surprising that our catalysts show oxidation activity in spite of the large size (~ 15 nm) of the gold nanoparticles used, given that most past studies report optimal activity in a nanoparticle diameter range of a few nanometers [2, 4]. Preliminary

data from our laboratory suggest that, indeed, smaller Au nanoparticles can lead to faster cryogenic oxidation rates.

2. Titania in amorphous form. Similar gold catalysts made with crystalline TiO_2 -P25 (the standard ~80:20 anatase:rutile Degussa formulation used in most studies with titania-based catalysts) display virtually no cryogenic-temperature activity, within our experimental error, either before or after treatment with NaOH (Samples d and e; solid blue circles and open red squares in Figure 3c, respectively), and the same is true with Au@TiO_2 yolk-shell catalysts made with pure anatase (data not shown). This observation points to the participation of defect sites within the oxide in the mechanism of the reaction. The small activity seen below 250 K in Figure 3c for some of these samples may reflect the presence of a few surface defects in the corresponding solids, similar to those present in the $\text{Au/TiO}_2(\text{A})+\text{NaOH}$ catalyst.
3. A surface treated with sodium hydroxide. Indeed, significant cryogenic activity was seen with Sample a (Figure 3b, solid red squares) but not with Sample f (Figure 3b, open blue circles). This is the novel addition to the synthesis of our samples that makes them unique and leads to their unprecedented cryogenic-temperature activity. The NaOH treatment may make the surface more basic, a change that has been reported in the past as a way to induce higher low-temperature catalytic activity [22]. Alternatively (or concurrently), it appears to lead to the creation of new catalytically active titanate sites on the surface of the catalyst. The formation of titanate species upon treatment of titania with sodium hydroxide is well established [23], and it is evidenced in the XPS data in

Figures 6b and 6c by the new Ti 2p_{3/2} peak that develops at 459.1 eV (with either amorphous or crystalline –P25– forms). The possibility of the addition of impurities to the samples during their treatment with NaOH, an alternative way to explain their cryogenic catalytic activity, was ruled out by XPS, since no elements other than Ti, O, Au, and Na (and a small amount of adventitious carbon due to sample handling) were ever detected. Moreover, the sodium seen in the XPS data of the NaOH-treated samples was always in the form of ionic Na⁺, and displayed spectra similar to that from sodium titanate (Figure S3). We believe that this sodium is associated with terminal Ti–O[–]–Na⁺ surface sites, product of ion exchange at the Ti–OH moieties of our amorphous titania during the NaOH treatment. The Na⁺ can be easily removed by HCl (Figure S3).

A couple of additional observations can be derived from the data in Figures 3 and 6: (a) the formation of the active titanate species is reversible: subsequent treatment with HCl removes those species from the surface (XPS evidence in Figure 6), and suppresses the cryogenic-temperature activity of the catalyst toward CO oxidation (Sample g; solid green upward-pointing triangles in Figure 3b); and (b) the titanate sites must be amorphous for the cryogenic catalysis to occur, because titanate-containing catalysts made either by treating P25 titania with NaOH (Sample e; Figure 3c, open red squares) or by using crystalline Na₂Ti₃O₇ (Sample h; Figure 3c, open green upward-pointing triangles) do not display much cryogenic catalytic activity. It is difficult to establish the exact nature of the active site in these amorphous titanate-based samples, but we speculate that the unique cryogenic catalytic activity may be associated with the titanium atoms that display the modified electronic structure highlighted in the XPS data, since the

adsorbed CO species seen in DRIFTS are believed to bind to titanium centers within the titania [24, 25].

The mechanism of this new cryogenic-temperature CO oxidation reaction was explored further by DRIFTS. A couple of kinetic differences between the cryogenic and room-temperature catalytic regimes were identified:

1. The time evolution of the CO and CO₂ signals during the catalytic oxidation reaction is clearly different between the two temperature regimes, and the detection of cryogenic reactivity unique to the Au/TiO₂(A)+NaOH sample, as made clear by the raw kinetic data provided in Figures 4 and 5.
2. CO₂ can be produced at 120 K, but not at 300 K, by sequentially exposing the catalyst to CO and then to O₂ (pumping the system in between), an indication that a weakly adsorbed CO species can be retained on the surface under cryogenic conditions (Figure 7). The reverse O₂–Pump–CO sequence fails to produce significant amounts of CO₂; no equivalent weakly-adsorbed O₂ species appears to form in these systems.

Our in-situ DRIFTS studies of the adsorbed species during the 120 K CO oxidation also point to a complex sequence of steps involving at least two adsorbed CO species:

1. An initial CO-titania species manifested in the DRIFTS traces by a sharp peak that grows around 2180 cm⁻¹ when O₂ is added to the cell in CO–Pump–O₂ experiments (Figure 8a).

The fact that this species is eventually oxidized to CO₂ is suggested by the inverse correlation seen between the time evolution of the 2180 cm⁻¹ CO DRIFTS signal intensity (blue trace in Figure 8b) and that for the feature at 2350 cm⁻¹ corresponding to CO₂ (red trace): after the initial appearance of the 2180 cm⁻¹ CO-titania species in the spectra, its intensity decreases monotonically as more CO₂ is produced. More interestingly, the 2180 cm⁻¹ DRIFTS peak intensity (again, the blue trace in Figure 8b) follows closely the trace for the CO₂ TOF versus time (green trace), calculated by taking the derivative of the CO₂ DRIFTS signal (red trace) with respect to time. In kinetic terms, such correlation suggests relatively simple first-order CO₂ formation kinetics with respect to the surface coverage of the 2180 cm⁻¹ CO-TiO₂ species, although some deviations are clearly seen in the initial stages of the reaction, when other mechanistic steps may be rate limiting. Notice that, in contrast, no correlation at all could be identified between the catalytic activity (CO₂ TOF, red trace) and the intensity of the DRIFTS peak due to CO adsorbed on the gold surface (purple trace, labeled CO-Au, from the DRIFTS peak centered at approximately 2110 cm⁻¹). This peak is quite weak and difficult to see in Figure 8a; its intensity has been magnified by a factor of 20 in Figure 8b). The latter observation indicates that such Au-adsorbed CO species do not play a direct role in the cryogenic oxidation reaction (as already suggested by Yates et al. [7]). Also, our evidence points to the 2180 cm⁻¹ CO-TiO₂ species being formed on the surface of the titania support, not on the titania-gold interface as proposed previously [26-28]: the same species is also seen on Au catalysts made out of TiO₂-P25, with and without NaOH treatment, and, to a lesser extent, on pure titania, in the absence of gold nanoparticles (Figure 9). In fact, some CO₂ can be made at 120 K with all of the Au/TiO₂ catalysts studied here under the sequential

CO–Pump–O₂ experimental modality (Figure 8c), although, of course, not in a sustained catalytic fashion.

2. A second CO-titania intermediate, evident in the in-situ DRIFTS data obtained under steady catalytic conditions by a peak at approximately 2160 cm⁻¹ (Figure 10a, 2nd-from-bottom red trace). The lowering in frequency with respect to the previous species has been associated with Ti⁴⁺ centers having less Lewis acidity [24], and in our case could be related to the titanate centers. It is in the formation of this intermediate, most likely via diffusion of the first intermediate to a new site, that the Au/TiO₂(A)+NaOH catalyst, which shows activity at cryogenic temperatures, shows a different behavior than the others: the transition from the 2180 cm⁻¹ to the 2160 cm⁻¹ site appears to occur to completion under reaction conditions on the cryogenic-temperature-active catalyst, whereas it seems to not be possible with any other catalyst (Figure 10a). Moreover, the exchange of CO surface sites associated with this transition must be assisted (or blocked) by oxygen, since it does not occur in the experiments where CO and O₂ are dosed separately; witness the absence of any signal at 2160 cm⁻¹ in the DRIFTS data from the CO–Pump–O₂ experiments reported in Figure 8a upon the addition of oxygen. The fact that the 2160 cm⁻¹ intermediate is consumed during the CO oxidation catalysis is suggested by the inverse correlation seen over time between its DRIFTS peak intensity and the production of CO₂ (Figure 10b): the intensity of the feature at 2160 cm⁻¹ (but not that at 2180 cm⁻¹) decreases with reaction time, as the peak for CO₂ grows. Because the population of this state also depends on the size of the Au nanoparticles (Figure 10c, which shows a selective increase in signal intensity for the 2160 cm⁻¹ peak with

increasing Au nanoparticle diameter), it can be envisioned that the final CO oxidation step occurs at the Au-titania interface, where O₂ dissociation may be assisted by the second CO intermediate [7]: the footprint of the gold nanoparticles is expected to be larger as their diameter increases, hence the increase in 2160 cm⁻¹-CO surface concentration indicated by the DRIFTS data (Figure 10c).

4. Discussion and Conclusions

Here, we have reported a new gold-titania catalyst capable of catalytically oxidizing carbon monoxide at record cryogenic temperatures. That catalyst is prepared by dispersing Au nanoparticles on a sol-gel-made amorphous titania support and treating the resulting material with NaOH. New titanate sites in amorphous form appear to be key in the promotion of the low-temperature catalysis. Based on the spectroscopic evidence provided above, it was concluded that a key aspect of the unique performance of our Au/TiO₂(A)+NaOH catalyst is the existence of a synergistic effect between the adsorption of CO and oxygen, which affects the ease with which the required final CO intermediate state becomes accessible at cryogenic temperatures. We suggest that the role of the new titanate sites is to allow for the diffusion of the adsorbed CO from the titania adsorption sites to the gold-titania interface, where the final CO₂ production step takes place. This idea is represented schematically in Figure 11.

Many gold-based catalysts have been reported in the past that display oxidation activity at so-called low temperatures [1, 29], which most authors mean to indicate values around room

temperature. Our catalyst shows similar behavior in that temperature range, but also a second catalytic regime at much lower temperatures, as low as 120 K. It should be indicated that there have been a handful of reports, including some early publications by Haruta and coworkers [2, 8], of catalysts active at intermediate temperatures between 120 and 300 K, but in all those cases the reaction appears to follow similar reaction mechanisms. Moisture has also been suggested to play an important role in the promotion of oxidation reactions with gold-based catalysts [22, 30], but that does not appear to be a critical factor in the cryogenic catalysis reported here, because water was not detected by DRIFTS either in the gas phase or condensed on the surface at any stage of the reactions. Also, although significantly different behavior was observed in the hydroxo region of the spectra with the different samples studied, none suggest any correlation of the concentration of those groups on the surface with catalytic activity (Figure 2). Instead, with our Au/TiO₂(A)+NaOH catalyst, the two temperature regimes where catalysis is observed display significantly different behavior, and appear to follow different reaction mechanisms. We believe that it is a combination of new defective titanate sites and their effect on the kinetics of the synergistic CO + O₂ adsorption that leads to the opening of the new cryogenic-temperature oxidation channel.

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Figure Captions

Figure 1. Typical diffuse-reflectance infrared absorption spectroscopy (DRIFTS) data used to characterize the performance of our gold-titania catalysts for the conversion over time of a mixture of 200 Torr CO + 200 Torr O₂ 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/TiO₂(A)+NaOH). Shown are features associated with CO (stretching C–O mode, blue-shaded area) and CO₂ (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.

Figure 2. Full-range DRIFTS data similar to those in Figure 1 for representative Au/TiO₂ catalysts during reaction with CO + O₂ gas mixtures at 120 K (except for b, which reports a reaction at 300 K). The catalysts reported are: (a) Au/TiO₂(A)+NaOH (the catalyst active at cryogenic temperatures, same as Figure 1); (b) The same Au/TiO₂(A)+NaOH, but for a reaction carried out at 300 K; (c) Au/TiO₂(A); (d) Au/TiO₂(A)+NaOH+HCl; and (e) Au/TiO₂-P25+NaOH. These data highlight the different behavior of the catalysts in terms of the formation of surface carbonates and hydroxo groups.

Figure 3. (a) Kinetic measurements, in the form of the evolution of the integrated signals of the CO and CO₂ DRIFTS peaks versus time, for the conversion at 120 K with the Au/TiO₂(A)+NaOH catalyst (estimated from spectra such as those shown in Figure 1). (b, c) Turnover frequencies (TOFs), in terms of CO₂ molecules produced per Au surface atom per second, for the conversion of mixtures of 200 Torr CO + 200 Torr O₂, calculated after 1 h of reaction. Reported

are TOFs as a function of reaction temperature in the range from 120 to 400 K for our Au/TiO₂(A)+NaOH catalysts as well as for a number of reference samples. Only the Au/TiO₂(A)+NaOH catalyst displays measurable catalytic activity at cryogenic (< 250 K) temperatures.

Figure 4. Raw DRIFTS kinetic data for the conversion of 200 Torr CO + 200 Torr O₂ mixtures with different gold-titania catalysts. The integrated DRIFTS signal intensities for the peaks corresponding to CO₂ (a, c, e) and CO (b, d, f) are reported as a function of time for our Au/TiO₂(A) catalyst, as prepared (c, d) and after sequential treatments with NaOH (a, b) and HCl (e, f). Catalytic CO oxidation below 250 K is seen only with the Au/TiO₂(A)+NaOH sample.

Figure 5. DRIFTS kinetic data similar to those in Figure 4 but for the Au/TiO₂-P25 catalysts, as prepared (a, b), and after NaOH treatment (c, d). As opposed to the Au/TiO₂(A)+NaOH sample, treatment of Au/TiO₂-P25 with NaOH does not lead to catalytic activation at cryogenic (< 250 K) temperatures.

Figure 6. X-ray photoelectron spectroscopy (XPS) data for our gold-titania catalysts. (a) Au 4f XPS traces for the 1 wt% 15-nm Au/TiO₂(A) catalyst, as prepared (top, blue trace) and after sequential NaOH (middle, red) and HCl (bottom, green) treatments. (b, c) Raw (b) and differential (c) Ti 2p XPS traces for several gold-titania samples, including our Au/TiO₂(A)+NaOH catalyst (3rd trace from top in Fig 2b, light blue). The formation of titanate sites upon treatment with NaOH is evidenced by the shift in some of the Ti 2p_{3/2} signal intensity

toward a binding energy of 459.1 eV, as highlighted in the differential traces (Figure 3c). This change can be reversed upon subsequent treatment with HCl.

Figure 7. DRIFTS kinetic evidence for the formation of the first adsorbed CO intermediate on the titania surface during the cryogenic-temperature catalytic oxidation of CO. The two panels contrast CO₂ product accumulation curves versus time for reactions carried out with our Au/TiO₂(A)+NaOH catalysts at 120 (a) versus 300 (b) K. Results are reported from three types of experiments in each case, with 200 Torr CO + 200 Torr O₂ mixtures (red traces), and where the gases are supplied sequentially (and pumped out of the system in between) in both CO–Pump–O₂ (blue) and O₂–Pump–CO (green) sequences. Particularly relevant to the identification of a new cryogenic catalytic regime is the activity seen with the CO–Pump–O₂ sequence at 120 but not at 300 K.

Figure 8. (a) DRIFTS data in the CO and CO₂ regions for a CO–Pump–O₂ experiment with the 1 wt% 15-nm Au/TiO₂(A)+NaOH catalyst at 120 K. No DRIFTS features at all are seen after pumping the gas-phase CO (2nd trace from bottom, green), but a new peak appears at ~2180 cm⁻¹ once O₂ is added (3rd from bottom, dark red). The 2180 cm⁻¹ signal decreases with time as the CO is converted to CO₂ (~2350 cm⁻¹ peak). (b) Time evolution of the CO₂ DRIFTS signal intensity (accumulated CO₂, red) and of its derivative (TOF, green) as well as of the signal intensities of the DRIFTS peaks for CO adsorbed on gold (2110 cm⁻¹, purple) and on titania (2180 cm⁻¹, blue), obtained during a CO–Pump–O₂ experiment at 120 K with a 1 wt% 3.5-nm Au/TiO₂(a)+NaOH catalyst. To note here is the correlation seen between the reaction TOF and the DRIFTS signal intensity for the CO-titania (but not the CO-Au) surface species. (c)

Accumulation of CO₂ versus time, in the form of turnover number (TON, number of CO₂ molecules per Au surface site per second), obtained in CO–Pump–O₂ experiments with the series of gold-titania catalysts indicated in the figure. The activity seen with all catalysts points to the fact that the NaOH treatment is not required to produce CO₂ in the sequential-dosing experiments. The data in Figure 8b are for a catalyst with smaller Au nanoparticles than in the rest of the report, 3.5 vs. 15 nm, because the correlation between CO coverage and CO₂ production rate is seen more clearly with that sample, but similar behavior was observed for the other nanoparticle sizes as well.

Figure 9. DRIFTS data in the C–O stretching/CO₂ region obtained at different stages of CO–Pump–O₂ sequential experiments with different gold-titania catalysts, namely: (a) Au/TiO₂(A); (b) Au/TiO₂(A)+NaOH; (c) Au/TiO₂-P25; (d) Au/TiO₂-P25+NaOH; (e) TiO₂(A)+NaOH; and (f) Au/TiO₂(A)+NaOH+HCl. The appearance of the ~2180 cm⁻¹ adsorbed CO species after introduction of O₂ to the reaction chamber is seen in all cases (although to a lesser extent in the case of the pure titania support, Figure 9e), indicating that this intermediate forms on the titania, not on the gold, surface.

Figure 10. DRIFTS evidence for the formation of a second CO-titania intermediate during the cryogenic-temperature steady oxidation of CO with O₂ on our Au/TiO₂(A)+NaOH catalyst. (a) DRIFTS data in the C–O stretching region, after subtraction of the signal from gas-phase CO, for different gold-titania catalysts. In most cases the dominant feature is the peak at 2180 cm⁻¹, but in the case of our Au/TiO₂(A)+NaOH (2nd from bottom, red), the only catalyst that promotes CO oxidation at 120 K, the 2180 cm⁻¹ feature is replaced by a strong peak at 2160 cm⁻¹. (b, c)

CO and CO₂ DRIFTS data as a function of reaction time (b, for the 1 wt% 15-nm Au/TiO₂(A)+NaOH catalyst) and of gold nanoparticle size (c) during the steady conversion of CO + O₂ mixtures at 120 K. The CO peaks have been deconvoluted into their 2160 and 2180 cm⁻¹ components to aid in their analysis. In both cases, the changes associated with CO₂ production are seen only in the first (2160 cm⁻¹) feature.

Figure 11. Schematic representation of the proposed cryogenic-temperature CO oxidation mechanism, highlighting the sequential formation of the two adsorbed CO-titania species identified in these studies and the synergistic effect of O₂ in the uptake of CO on the surface.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

TOC Graphics