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CO oxidation over titanate nanotube supported Au: Deactivation due to bicarbonate

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ABSTRACT

New experimental findings, which offer further information concerning the deactivation mechanism of CO oxidation over titania nanotube (TN) supported gold, are reported. Contrary to earlier reports by others, we have observed that the formation of bicarbonate species during CO oxidation on the Au/TN catalyst is a competing reaction that leads to catalyst deactivation. We regard the formation of bicarbonate species not as an intermediate step but rather a product of the CO_2 produced during CO oxidation. The bicarbonate species detected at 1290 cm^{-1} was very stable and only desorbed at relatively high temperatures. In the presence of water the bicarbonate species (1290 cm^{-1}) did not form under reaction conditions. CO_2-TPD results implied that water possibly reacted with and removed the already formed bicarbonate species and prevented its further formation and in the process promoted the reaction and prevented deactivation. The possible reactions of how water (OH) might remove the gold associated bicarbonate and hence reactivate and promote the oxidation of CO are discussed. The mechanisms for the formation of the observed bicarbonate may account for the deactivation of the Au/TN catalyst during CO oxidation; this reaction would consume the OH groups on Au which have been reported as essential in the mechanism of CO oxidation. The above hypothesis of CO_2 being able to chemisorb on gold nanoparticles is not unique. Based on IR studies [N.M. Schubert, A. Venugopal, M.J. Kalich, V. Plazk, R.J. Behm, J. Catal. 222 (2004) 32; B. Schumacher, Y. Denkwitz, V. Plzak, M. Kinne, R.J. Behm, J. Catal. 224 (2004) 449], evidence was provided which pointed to the fact that CO and CO_2 competed for adsorption on the same site on Au surfaces. To the best of our knowledge, this is the first time that DRIFTS and CO_2-TPD have been combined to show that CO_2 is adsorbed on the gold-nanoparticles in the form of bicarbonate to the detriment of the oxidation of CO.

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1. Introduction

Much of the interest in gold catalysis in the last decade stems from the pioneering work by Haruta et al. [1]. In particular, extensive work has been done on low temperature CO oxidation over metal oxide supported gold catalysts [2–7]. Despite the high initial activity for CO oxidation, gold catalysts suffer rapid deactivation within the first few hours of time-on-line. Although catalyst deactivation is an important phenomenon in industrial applications, the deactivation of gold catalysts has not always received the attention it deserves as evidenced by the lack of deactivation kinetic data.

There are conflicting arguments in the literature regarding the mechanism of CO oxidation catalyzed by supported gold. The most popular mechanistic models reported involve: (i) the importance of the interface, which is governed by the metal–support interaction [8–12], (ii) the importance of particle geometry which dictates the presence of low coordinated atoms on the nanoparticles [13,14] and (iii) quantum size effects due to the low dimensionality of the gold particles [15,16].

Generally, there is discord in the results that are reported in the literature regarding the rate of (de)activation and means of reactivation [17]. Some of the possible reasons cited in the literature for deactivation include growth of metal particles, blockage of (TiO_2) interfacial sites by water, build up of 'carbon species,' and the depletion of surface hydroxyl groups ([17] and refs. therein). Deactivation due to the reduction of Au^{x+} ions by carbon monoxide has also been reported [18].

Adsorbed carbonate species are formed at most metal oxide surfaces because of chemisorption of carbon dioxide [19]. The exact speciation and coordination of these species is crucial to understand fully, due to the important role they supposedly play in CO oxidation. Originally, Haruta et al. [2] proposed a mechanism involving the formation and decomposition of carbonates as the

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rate-limiting step in CO oxidation catalyzed by gold. Daniells et al. [20] later proposed that the active site was an ensemble of Au^{3+} and Au^0, with hydroxyls from the cationic gold and the support promoting bicarbonate formation and their subsequent decomposition to produce CO_2. However, Gupta and Tripathi [21] argued that both carbonates and bicarbonates were not possible intermediates in the mechanism. Formates [8] and bicarbonates [10] have also been reported as possible reaction intermediates during CO oxidation.

In this paper, new experimental findings, which offer further information concerning the deactivation mechanism of CO oxidation over titania nanotube (TN) supported gold, are reported. Contrary to earlier reports [22], we have observed that the formation of bicarbonate species during CO oxidation on the Au/TN catalyst is a competing reaction that leads to catalyst deactivation.

2. Experimental

2.1. Synthesis of titanate nanotube support

The synthesis procedure followed to generate the titanate and the structure of such materials have been described elsewhere [23,24]. Commercial TiO_2 (P25) powder (25 g) was added to a 200 ml solution of 2.8×10^{-1} M KOH in a 1 L stainless steel autoclave. The mixture was heated for 24 h at 120 °C (stirring at 500 rpm). The resulting material was cooled down to room temperature, then allowed to age for 2 days in the base solution. It was then repeatedly centrifuged with deionized water until the conductivity was below 100 $\mu S\,cm^{-1}$. The material was finally dried in air at 120 °C for at least 12 h. The potassium content may be expected to lie in the approximate rage 18–32 mass% K. From here onwards the resultant material shall be referred to simply as the titanate nanotube (TN).

2.2. Preparation of gold-supported catalysts

Deposition–precipitation was the method used to load gold onto the titanate nanotube support [17]. The support was slurried in distilled water (600 ml) under vigorous stirring. Required amount of diluted $HAuCl_4$ solution (10^{-2} M) was added slowly to the support slurry with continuous stirring. Due to the basicity of the titanate support, the pH was already at ∼9; so the addition of base was not necessary. The precipitated solution was aged for 15 h. A solution of $NaBH_4$ was prepared in ice water and added in the required amount for reduction of Au (III) to Au (0). The solid was washed with hot water (total volume approximately 3000 cm^3) and dried at room temperature. No further pretreatments were applied unless otherwise stated. In our experience with using borohydride reduction, the residual quantities of sodium and boron (and chlorine) on the surface are negligible provided that washing of the solid is carried out as described. The resulting catalyst powder of Au/TN contained 0.48 wt% Au, as determined by fire assay with atomic absorption finish (Performance Laboratories, South Africa).

2.3. Sample characterization

Nitrogen adsorption–desorption isotherms were measured on a Micromeritics TRISTAR 3000 analyzer. The samples were degassed under vacuum for several hours before the nitrogen adsorption measurements. The specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method.

2.4. DRIFT spectroscopic measurements

Samples (50 mg) were loaded into a DRIFTS cell with CaF_2 windows; the cell was equipped with a heating system that allowed operation under different atmospheres up to 600 °C. Spectra were collected at a resolution of 4 cm^{-1} on a Perkin–Elmer 1720 FTIR spectrometer. Gases were led into the cell via a computer-controlled gas blender and exit gases were analyzed by a Baltzers Prisma QMS. All samples were heat treated at 300 °C in air (20 ml/min) for 30 min prior to DRIFTS studies. A typical gas blend was 2% CO + 10% air, balanced in N_2. Water (100 μL) was injected with a syringe where it was used.

2.5. Temperature-programmed desorption (TPD)

All TPD experiments were carried out in a flow apparatus with helium as carrier gas (50 $ml\,min^{-1}$) using a quartz U-tube reactor (6 mm i.d.). For detection of desorbed CO_2 a Baltzers Prisma QMS was used. Prior to adsorption, samples (220 mg) were heat treated at 300 °C in a flow of 5% O_2 balanced in He. In a typical TPD experiment, adsorbents (e.g. 2% CO + 5% O_2 balanced in He) were passed over the catalyst bed at 343 K at a flow rate of 100 $ml\,min^{-1}$ for 30 min. Then the reactor was cooled down to room temperature for the start of CO_2-TPD. All samples were heated up to 873 K at the rate of 8 $°C\,min^{-1}$. A water bubbler-saturator was used where water was a co-adsorbent.

2.6. Catalytic activity measurement

The catalyst sample (Au/TN) was calcined at 300 °C in 10% O_2 (balance He) for 30 min prior to testing. The catalytic performance of the catalyst for CO oxidation was tested in a continuous flow quartz fixed-bed reactor (6 mm i.d.). 100 mg of solid catalyst (powder particle size about 150 μm) was loaded into the reactor. The gas mixtures consisted of 5% CO and 10% O_2 balanced in He and the total flow was generally 40 $ml\,min^{-1}$. The course of the reaction was monitored quantitatively by use of a gas chromatograph facility equipped with a thermal conductivity detector. All measurements were carried out at 70 °C and atmospheric pressure.

3. Results

3.1. Characterization of the support and catalyst

The BET surface areas of the both the support (TN) and catalyst (Au/TN) were approximately 148 m^2/g with a pore volume of 0.26 cm^3/g. The gold loading on the support was 0.48 wt% (intended loading was 1 wt%). Titanate nanotubes in aqueous suspension have a relatively high negative zeta-potential over a wide range of pH [23]. The fact that we used a negatively charged gold precursor ($HAuCl_4$) explained why our resultant gold loading was relatively low. The morphologies of the titanate nanotube (TN) and the catalyst Au/TN were studied by the use of HRTEM and the corresponding images are shown in Fig. 1. The average particle size of gold on the catalyst Au/TN was found to be 4.5 nm. Careful analysis of the TN material suggested that it was in the form of very thin sheets, which could roll up into two or more layered sheets of titanium dioxide [25]. The chemical composition of the TN sample was examined by EDS (Fig. 2), which revealed the presence of potassium.

3.2. CO oxidation

The primary aim of this paper is to interrogate the reasons why the Au/TN catalyst system deactivates during time-on-line of CO oxidation. In order to study deactivation properly, diffusion/mass transfer limitations must be avoided. This is best done by keeping catalytic conversions low where the rate of the reaction proceeds under kinetic control. Fig. 3 illustrates the deactivation observed during a typical CO oxidation run over the Au/TN catalyst. It is

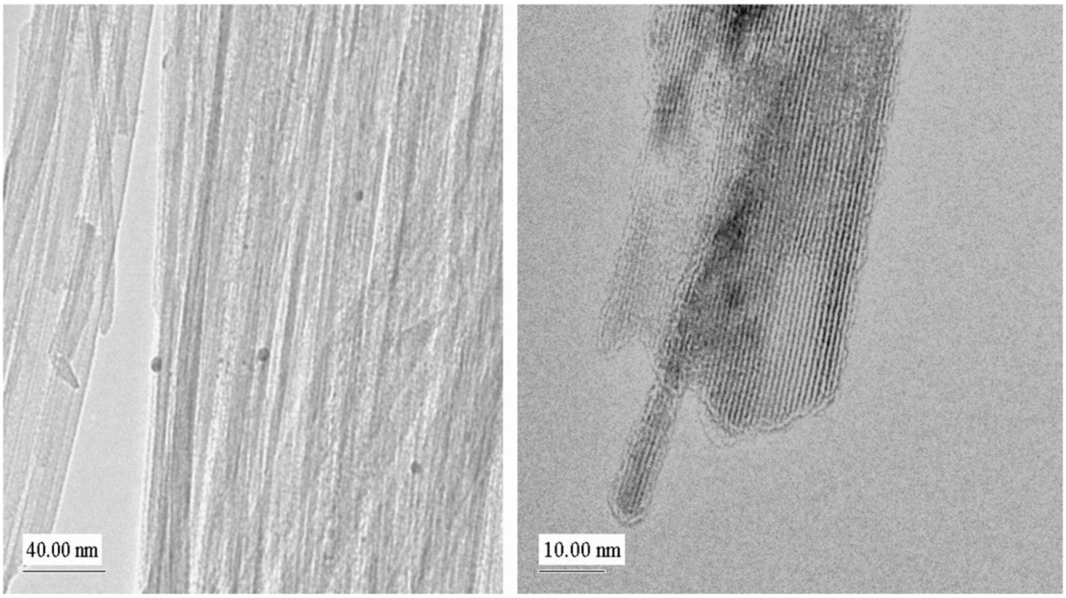


Fig. 1. The TEM images of the titanate nanotube support (right) and the catalyst Au/TN (left).

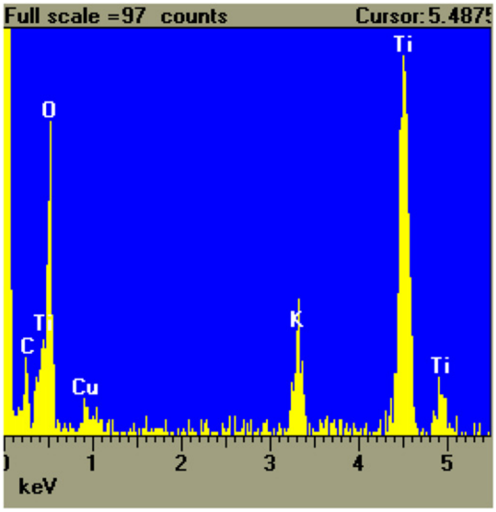


Fig. 2. EDS spectrum of the titanate nanotube support confirming the presence of potassium in the material.

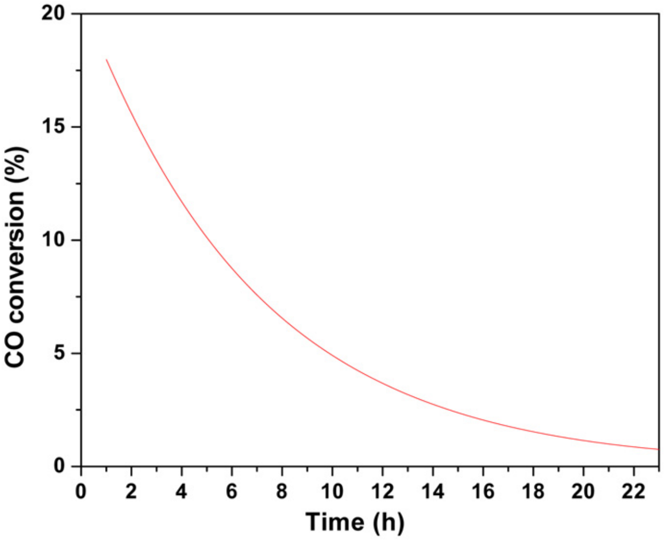


Fig. 3. Deactivation of the Au/TN catalyst during time-on-line during the oxidation of CO at 70 °C.

interesting to note that there was a short induction period, after which the catalyst gained maximum activity. However, after that, it could not sustain that activity as it rapidly deactivated. Data recorded during the first 1 h on stream are not regarded as significant for our present purposes, since the catalyst is essentially developing catalytic activity during this period.

Fig. 4 illustrates the effect of introducing water into the feed stream during CO oxidation. In this experiment, a DRIFTS cell was used as a reactor and the exit gases were analyzed using a quadrupole mass spectrometer. Water promoted the reaction and the corresponding DRIFTS spectra for these particular experiments are shown in Fig. 8. For operational reasons data were not recorded in a completely continuous fashion during the period when water was being removed from the reaction system.

3.3. CO_2-TPD

3.3.1. Titanate nanotube (TN)

The CO_2-TPD profiles illustrated in Fig. 5 show the desorption of carbon dioxide from the pure support material (TN); after a mixture of $CO + O_2$ (Fig. 5a) and CO_2 (Fig. 5b) were flowed for 30 min at 70 °C. Under both adsorption conditions ($CO + O_2$ and CO_2) the support material (TN) showed the presence of basic surface sites from which desorption took place at temperatures above 300 °C. However, below 300 °C there was no CO_2 desorbed for the case where $CO + O_2$ mixture was passed over the TN support. In the case where CO_2 was adsorbed, two low temperature desorption peaks were observed at 99 °C and 199 °C.

3.3.2. Au/TN catalyst

Fig. 6 shows the desorption profiles of CO_2 from the catalyst Au/TN. The desorption profiles were obtained after a mixture of $CO + O_2$ had been passed over the catalyst for 30 min at 70 °C under dry and wet conditions. Under dry conditions, there were CO_2 desorption peak species at 94, 153, and 229 °C. The latter two peaks were absent when the adsorption was done under wet conditions. Similarly, there were CO_2 desorption peaks at 89 and 102 °C under the wet adsorption/desorption experiment.

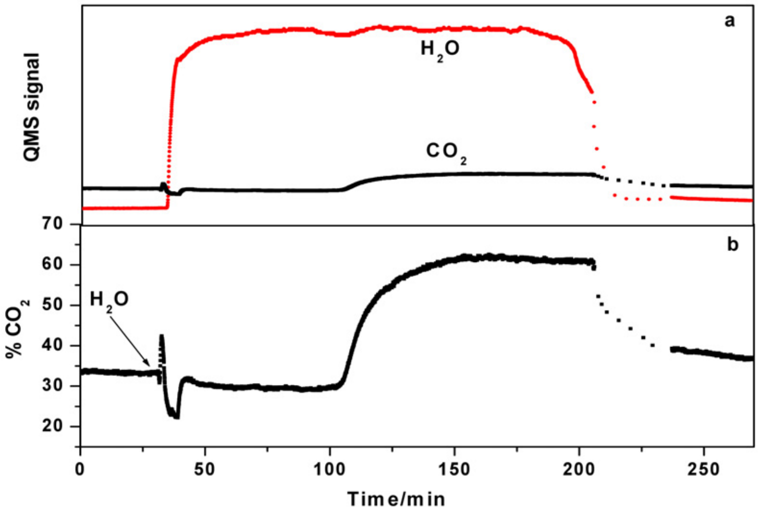


Fig. 4. Effect of water (100 µL) on the catalytic activity of the Au/TN catalyst measured in a DRIFTS cell: (a) promotion of the oxidation of CO reaction by added water, (b) graph showing the quantification of the CO_2 produced.

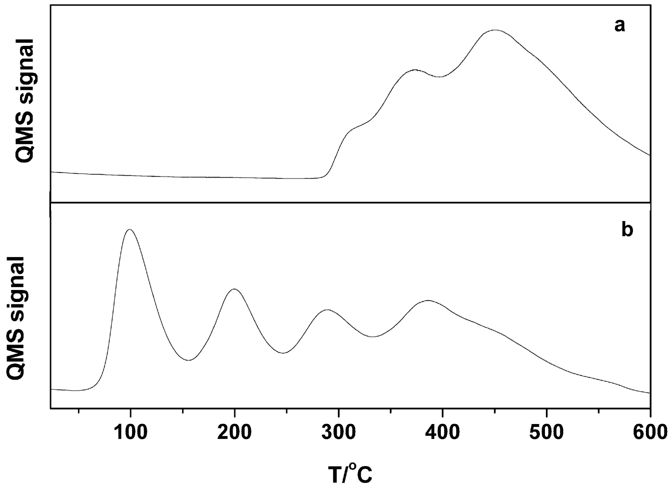


Fig. 5. CO_2-TPD spectra for the titanate nanotube (TN) support: (a) CO + O_2 co-adsorbed, (b) CO_2 adsorbed.

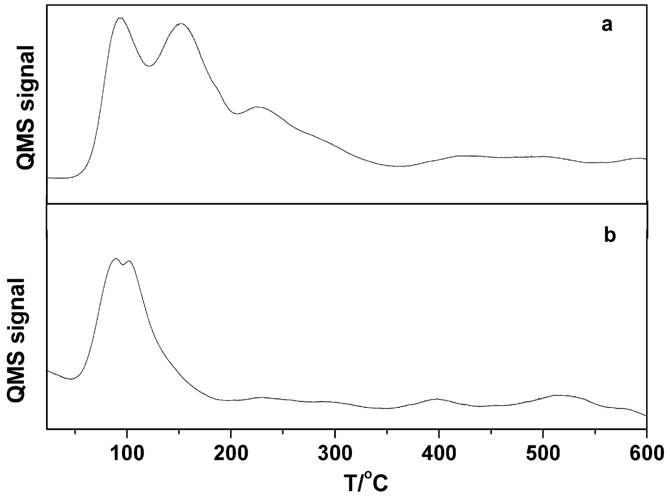


Fig. 6. CO_2-TPD spectra for the catalyst (Au/TN): (a) CO + O_2 co-adsorbed under dry conditions, (b) CO + O_2 co-adsorbed under wet conditions (~2% vol/vol H_2O).

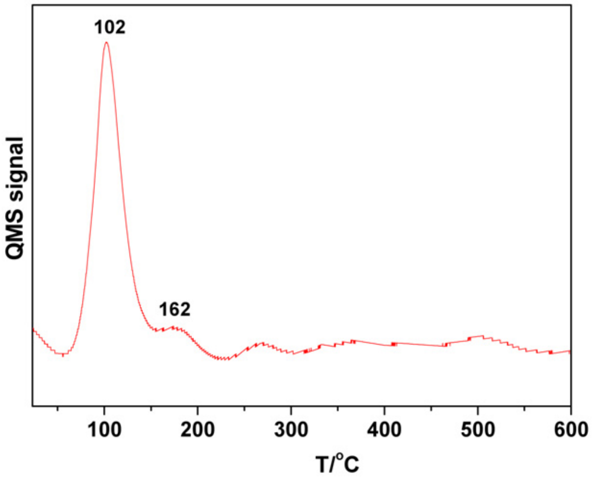


Fig. 7. CO_2-TPD for the Au/TN catalyst after adsorption of CO_2 at 70 °C.

Fig. 7 shows the typical CO_2-TPD spectrum of CO_2 after a 1% CO_2 (balance N_2) gas was passed over the catalyst for 30 min at 70 °C. The distinct feature from this figure was the CO_2 desorption peak at 162 °C, which for all intents and purposes, was due to the same CO_2 species that desorbed at 153 °C when CO + O_2 mixture was passed over the dry catalyst. These species of CO_2 seemed to be associated with the presence of Au on the support as it was not observed on the pure support when either CO + O_2 or CO_2 were adsorbed on the pure support.

3.4. DRIFT spectroscopic measurements

In order to characterize the adsorption state of carbon dioxide on both the pure support (TN) and the catalyst (Au/TN), DRIFT spectroscopic studies were carried out.

In principle, IR-active vibration frequencies are highly sensitive to the structure, protonation states, and speciation of carbonate (adsorbed CO_2) [26]. However, in practice, there are many inherent difficulties in assigning the molecular structure of carbonate from its vibrational frequencies. Accurate definition of the important carbonate asymmetric C–O stretching region (~1450–1600 cm^{-1}) is difficult when DRIFTS measurements are done on samples where H_2O is one of the co-reactants/adsorbents. Adsorbed water might

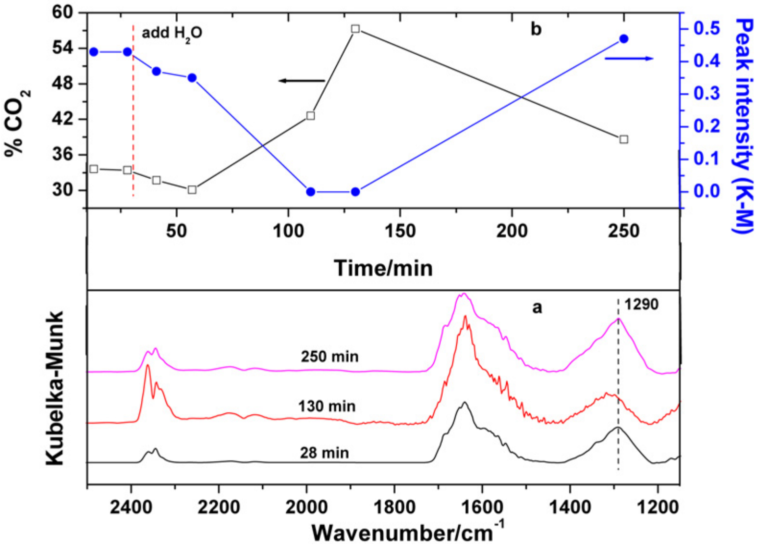


Fig. 8. FTIR spectra scanned before and after the addition of water (100 μL) into the feed stream: (a) spectra showing the build up of the peak at 1290 cm^{-1} in the absence of water in the feed, (b) plot of CO_2 yield vs the intensity of the peak at 1290 cm^{-1}.

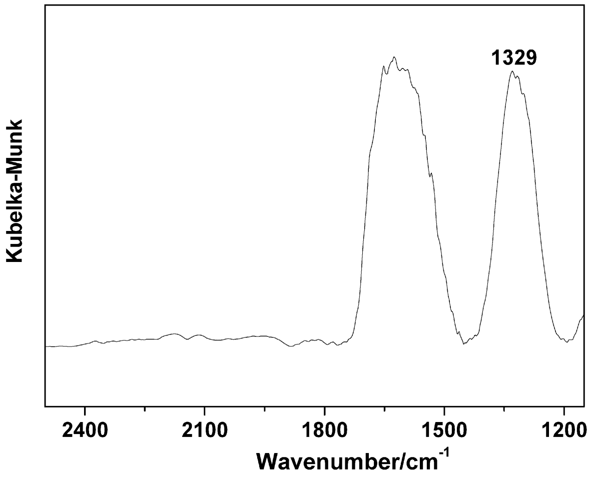


Fig. 9. FTIR spectrum scanned on the titanate nanotube (TN) support under 2% CO + 5% O_2 (bal. He) flow at 70 °C.

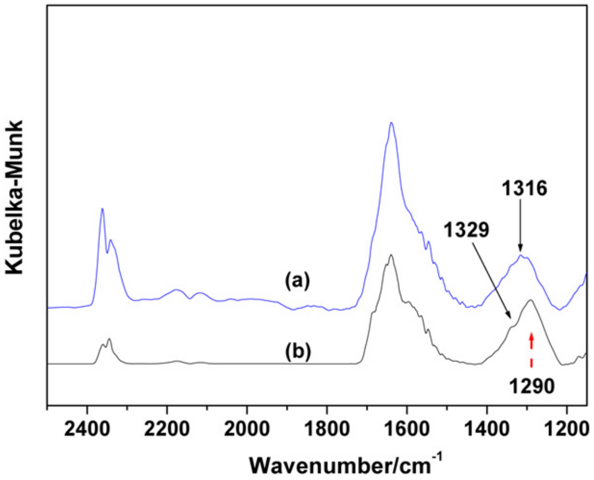


Fig. 10. FTIR spectrum scanned on the Au/TN catalyst under 2% CO + 5% O_2 (balance He) flow at 70 °C: (a) 100 min after addition of water (100 μL), (b) 28 min of reaction under dry conditions.

contribute H–O–H bending intensity at locations different from that of bulk water [26].

Fig. 8 shows the DRIFT spectra collected over the catalyst Au/TN during a typical $CO + O_2 + H_2O$ co-adsorption experiment. The experiment was done under the flow of the adsorbates ($CO + O_2$) at 70 °C. All the spectra were recorded at 70 °C. Spectra were recorded at 13 and 28 min during time-on-line; after which 100 μL of water was introduced into the feed and subsequently spectra were recorded as a function of time. The quantification of the CO_2 produced in this particular experiment is shown in Fig. 4.

What was concluded from Figs. 4 and 8 is that as previously reviewed [17], water had a promoting effect on the Au/TN catalyst system. Fig. 4 showed a doubling increase in amount of CO_2 produced when H_2O was introduced and the same promoting effect was shown in Fig. 8, characterized by the increased intensity of the V_3 vibration of linear, non-adsorbed (i.e. gas-phase) CO_2 at 2361 cm^{-1}.

In addition, in Figs. 4 and 8, it is shown that as soon as the amount of water decreases in the feed/surface the catalysts suffered rapid deactivation. Fig. 8 illustrates that the deactivation coincided with a rapid build up of carbonaceous species with a vibration band at 1290 cm^{-1}. This carbonate species has previously been assigned as an OH deformation of bicarbonate species [27]. To confirm whether these bicarbonate species needed the presence of gold to form or they could form on the support under reaction conditions without gold, a control experiment was performed and the result is illustrated in Fig. 9.

Indeed the absence of the peak at 1290 cm^{-1} (Fig. 9) confirmed that gold was a necessary ingredient to form the bicarbonate species (see Fig. 10). The vibration band at 1329 cm^{-1} in Figs. 9 and 10, due to unidentate carbonate species [27], was not affected by the presence of water; while that of the bicarbonate (1290 cm^{-1}) was almost completely removed by water (Fig. 10a).

4. Discussion

The high activity of gold catalysts for the oxidation of CO is well documented [17]. However, activity alone is not the only criterion that must be fulfilled for a suitable catalyst for CO oxidation [28]. Long term stability is also a crucial feature.

Fig. 3 illustrated the deactivation of the Au/TN catalyst while Fig. 4 showed the beneficial effect of water in the oxidation of CO. Also in Fig. 4 it was shown that as long as there was moisture in the feed, deactivation was inhibited. The observed deactivation in Fig. 3 was correlated to the growth of the bicarbonate band [1290 cm^{-1}]. As shown in Fig. 4, it took about one hour for water to effect the promotion of CO oxidation and that could be related to how long water takes to decompose the bicarbonate species (Scheme 1). Comparison of Figs. 5a and 6a shows that the TPD data for the catalyst do not show any signs of the desorption of co-adsorbed ($CO + O_2$) or carbonate decomposition products from the support alone. Rather the TPD data are dominated by the desorption of CO_2, formed from, for example $CO + O_2$ reaction on gold sites.

Also the CO_2-TPD data (Figs. 6 and 7a) showed desorption peaks (153 °C and 162 °C, respectively) due to some CO_2 species whose formation was directly linked to the presence of Au, as they were not formed on the pure support (Fig. 5) under reaction conditions. We deduce that the CO_2 species seen from the DRIFTS data (1290 cm^{-1}) and CO_2-TPD data (153 °C) are the same species which lead to the deactivation of the catalysts. This conclusion was reached because the formation of these CO_2 species coincided with the presence of Au on the support. The gradual accumulation of the CO_2 species (bicarbonate) leads to the blockage/occupation of active sites on the catalysts.

To understand the mechanism of deactivation one needs to first look at the proposed reaction mechanisms. There has been much debate concerning the nature of the active site for catalysts [17]. More than a decade ago, a reaction mechanism was proposed for Au–TiO_2 involving the effect of water in the CO oxidation reaction [29]. The mechanism involved the dissociative adsorption of water on the TiO_2 surface, followed by the formation of formate species (Au–COOH); which subsequently decomposes to CO_2 and H_2. However, this mechanism has recently been disputed [30]. Schubert et al. [22] proposed that water transforms the carbonate species formed during the oxidation of CO into less thermally stable bicarbonate species. They suggested that in the presence of water these bicarbonate species are possibly reaction intermediates.

From our work, what we found out is that the formation of bicarbonate species is not an intermediate step but rather a product of the CO_2 produced during CO oxidation. The bicarbonate species detected at 1290 cm^{-1} (Figs. 8 and 10a) was very stable and only desorbed at 153 °C (Fig. 6). The thermal stability of the bands due to bicarbonate has been also reported elsewhere [31]. In the presence of water the bicarbonate species (1290 cm^{-1}) did not form (Fig. 10) under reaction conditions. Our CO_2-TPD results implied that water possibly reacted with and removed the already formed bicarbonate species and prevented its further formation and in the process promoted the reaction and prevented deactivation. The possible reactions of how water (OH) might remove the gold associated bicarbonate and hence reactivate and promote the oxidation of CO are outlined in Scheme 1. Schumacher et al. [32] have also proposed that water reacts with the poisoning carbonate-like species (possibly via $CO_3 + H_2O \rightarrow CO_2 + 2OH$) preventing catalysts deactivation.

$$\text{Au–}CO_3\text{H–Ti} + 2HO \rightarrow \text{Au–OH} + \text{Ti–}CO_3 + H_2O \quad \text{(Reactivation)}, \tag{1.1}$$

$$\text{Au–O–Au} + H_2O \rightarrow 2\text{Au–OH}, \tag{1.2}$$

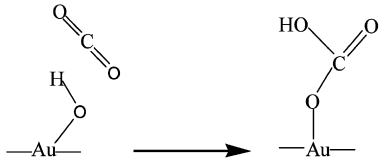
$$\text{Au–OH} + CO \rightarrow \text{Au–H} + CO_{2(g)} \quad \text{(Reaction)}, \tag{1.3}$$

$$\text{Au–O} + \text{Au–H} \rightarrow \text{Au–OH} + \text{Au}. \tag{1.4}$$

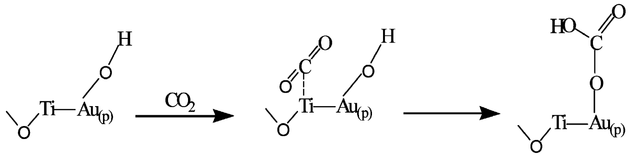
Scheme 1. Possible reactions of how water might reactivate and promote the oxidation of CO on Au/TN catalyst system.

Fig. 7 shows a very interesting result in that it shows the formation of the gold-associated CO_2 species (bicarbonate) by simply passing 1% CO_2 (balance N_2) over the catalyst. These species did not form on the pure support (Fig. 5). This result suggested that the formation of CO_2 did not go through the bicarbonate as an intermediate during the oxidation of CO but rather, CO_2 was a reactant in the formation of the bicarbonate. There are two obvious pathways by which CO_2 can react with gold (Au–OH) to form the gold-associated bicarbonate species (responsible for deactivation):

(i) The first possibility is the reaction of CO_2 (g) with Au–OH in a Rideal-Eley type mechanism,



(ii) The second possibility could be the reaction of CO_2 adsorbed on Lewis acid sites (Ti^{4+}) surrounding the gold particles [$Au_{(p)}$],



The above mechanisms for the formation of the observed bicarbonate may account for the deactivation of the Au/TN catalyst during CO oxidation; this reaction would consume the OH groups on Au which have been reported as essential in the mechanism of CO oxidation [17]. The above hypothesis of CO_2 being able to chemisorb on gold nanoparticles is not unique. Based on IR studies [22,33], evidence was provided which pointed to the fact that CO and CO_2 competed for adsorption on the same site on Au surfaces. However, we are not proposing that the adsorption of carbon dioxide on gold is so strong that each product CO_2 molecule undergoes adsorption. A simple calculation based on our experimental conditions shows that this is unlikely to occur. For the feed gas, 40 ml/min gas, containing 5% CO with an average conversion of 10 over the first 10 h will result in 3.2×10^{20} molecules CO converted per hour. 0.48% Au on 100 mg catalyst with an average clusters size of 4.5 nm with on 5% active gold atoms on the gold titania interface will result in 7.6×10^{16} active gold sites. In other words more than 4000 molecules of CO will be converted per active gold site per hour and thus more than 4000 molecules of CO_2 will be formed per hour per active gold site (assuming the entire interface active gold has the same performance). Nevertheless CO_2-mediated deactivation appears to be occurring. To the best of our knowledge, this is the first time that DRIFTS and CO_2-TPD have been combined to show that CO_2 is adsorbed on the gold-nanoparticles or support in the form of bicarbonate to the detriment of the oxidation of CO.

Acknowledgments

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References

[1] M. Haruta, T. Kobayashi, H. Sano, N. Yamanda, Chem. Lett. 2 (1987) 405.
[2] M. Haruta, S. Tsubota, T. Kobayashi, H. Kayeyama, M.J. Genet, B. Delmon, J. Catal. 144 (1993) 175.
[3] F. Boccuzzi, A. Chiorino, S. Tsubota, M. Haruta, J. Phys. Chem. 100 (1996) 3625.
[4] M. Daté, M. Okumora, S. Tsubota, M. Haruta, Chem. Int. Ed. 43 (2004) 2129.

[5] M.S. Chen, D.W. Goodman, Science 306 (2004) 252.

[6] P. Konova, A. Naydenov, C. Venkov, D. Mehandjiev, D. Andreeva, T. Tabakova, J. Mol. Catal. A 213 (2004) 235;
M. Manzoli, A. Chiorino, F. Boccuzzi, Appl. Catal. B 52 (2004) 259.

[7] M.A. Sachez-Castillo, C. Couto, W.B. Kim, J.A. Dumesic, Angew. Chem. Int. Ed. 43 (2004) 1140.

[8] G.C. Bond, D.T. Thompson, Gold Bull. 33 (2000) 41.

[9] M. Haruta, Gold Bull. 37 (2004) 27.

[10] K. Costello, M.C. Kung, H.S. Oh, Y. Wang, H.H. Kung, Appl. Catal. A 232 (2002) 159.

[11] L.M. Molina, B. Hammer, Appl. Catal. A 291 (2005) 21.

[12] Z.P. Lin, X.Q. Gong, J. Kohanoff, C. Sanchez, P. Hu, Phys. Rev. Lett. 91 (2003) 266102.

[13] N. Lopez, T.V.W. Janssens, B.S. Clausen, Y. Xu, M. Mavrikakis, T. Bligaard, J.K. Narskow, J. Catal. 223 (2004) 232.

[14] C. Lemise, R. Meyer, S. Shaikhutdinov, H.J. Freund, Angew. Chem. Int. Ed. 43 (2004) 118.

[15] M.S. Chem, D.W. Goodman, Science 306 (2004) 252.

[16] B. Yoon, H. Hakkinen, U. Landman, A.S. Worz, J.M. Antonetti, S. Abbet, K. Judai, Science 307 (2005) 403.

[17] G.C. Bond, C. Louis, D.T. Thompson, Catalysis by Gold, Imperial College Press, London, 2006.

[18] A.M. Visco, F. Neri, G. Neri, A. Donato, C. Milone, S. Galvagno, Chem. Phys. 1 (1999) 2869.

[19] J.C. Lavalley, Catal. Today 27 (1996) 377.

[20] S.T. Daniells, M. Makkee, J.A. Moulijn, Catal. Lett. 100 (2005) 39.

[21] N.M. Gupta, A.K. Tripathi, Gold Bull. 34 (4) (2001) 120.

[22] N.M. Schubert, A. Venugopal, M.J. Kalich, V. Plazk, R.J. Behm, J. Catal. 222 (2004) 32.

[23] D.V. Bavykin, A.A. Lapkin, P.K. Plucinki, L. Torrente-Murciano, J.M. Friedrich, F.C. Walsh, Top. Catal. 39 (2006) 151.

[24] L.C. Sikhwivhulu, N.J. Coville, T. Ntho, M.S. Scurrell, Catal. Lett. 123 (2008) 193.

[25] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, Langmuir 14 (12) (1998) 3160.

[26] J.R. Bargar, J.D. Kubicki, R. Reitmeyer, J.A. Davis, Geochim. Cosmochim. Acta 69 (2005) 1527.

[27] H. Knozinger, Adv. Catal. 25 (1976) 235.

[28] F. Moreau, G.C. Bond, Catal. Today 114 (2006) 362.

[29] D. Andreeva, V. Idakiev, T. Tabakova, A. Andreev, R. Giovanoli, Appl. Catal. 134 (1996) 275.

[30] M.A. Debeila, R.P.K. Wells, J.A. Anderson, J. Catal. 239 (2006) 162.

[31] M. Maciejewski, P. Fabrizioli, J. Grunwaldt, O.S. Becker, A. Baiker, Phys. Chem. Chem. Phys. 3 (2001) 3846.

[32] B. Schumacher, Y. Denkwitz, V. Plzak, M. Kinne, R.J. Behm, J. Catal. 224 (2004) 449.

[33] M.A. Bollinger, M.A. Vannice, Appl. Catal. B 8 (1996) 417.