Oxygen-assisted reduction of Au species on Au/SiO$_2$ catalyst in room temperature CO oxidation†

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An unexpected oxygen-assisted reduction of cationic Au species by CO was found on a Au/SiO$_2$ catalyst at room temperature and the produced metallic Au species plays an essential role in CO oxidation on Au/SiO$_2$.

Tremendous research interest in Au catalysis has been sparked since the pioneering work by Haruta showed that supported Au nanoparticles are exceptionally active for low temperature CO oxidation.[1] Although there is a consensus that the Au particle size, support, preparation methods and pretreatment conditions are the leading factors affecting the performance of supported Au catalysts, no consensus has been reached regarding the oxidation state of a catalytically active Au species.[2] Catalytic activity in CO oxidation has been variously attributed to zerovalent, anionic, and cationic gold, present in mixtures[3,4] or as individual species.[5–8] These investigations were conducted on Au supported on almost all kinds of supports such as reducible oxides, non-reducible oxides and zeolite. However, no evidence has been reported for the role of Au species in different oxidation states in CO oxidation supported on non-reducible SiO$_2$. It has only recently been recognized that gold deposited on silica with a strong interaction is comparable to gold on TiO$_2$ for low temperature CO oxidation.[9–11] In this communication, a Au/SiO$_2$ catalyst (4 wt% Au as determined by ICP measurement) prepared using Au(en)$_2$Cl$_3$ (en = ethylenediamine) as the precursor, an active catalyst for low temperature CO oxidation as reported recently,[9] was tested for CO oxidation at room temperature (23 °C) using *in situ* diffuse reflectance infrared spectroscopy (DRIFTS) coupled with quadruple mass spectrometry (QMS). It was found that a metallic gold species which is derived from the *in situ* reduction of cationic Au during reaction plays a major role in CO oxidation while the cationic Au species alone is inactive. Surprisingly, the room temperature reduction of cationic Au by CO is assisted by oxygen.

Upon room temperature introduction of the reactants (CO + O$_2$) onto a Au/SiO$_2$ sample calcined at 500 °C in O$_2$, adsorbed CO appears initially at 2141 cm^{-1} in the infrared spectra. This CO band shifts as a function of time on stream (TOS) as plotted in Fig. 1: it red shifts slowly from 2141 to 2113 cm^{-1} within about 10 h and levels off afterwards (for detailed IR spectra see Fig. S1 in ESI†). This red shift of the CO band is not due to a change in particle size since TEM results (Fig. S2 in ESI†) show essentially the same average particle size ($\sim$ 5 nm) of calcined Au/SiO$_2$ sample before and after CO oxidation reaction. The red shift is also not due to coverage change since desorption of adsorbed CO after reaction shows that the 2113 cm^{-1} band shifts up only to 2119 cm^{-1}, not back to 2141 cm^{-1}. Therefore, this red shift has to do with the change of Au oxidation state during the reaction. According to the few IR studies of Au/SiO$_2$[12,13] and a vast amount of IR studies of CO adsorption on other supported Au catalysts,[14–20] the 2141 cm^{-1} band can be assigned to CO adsorbed on cationic Au (Au$^{\delta+}$, $0 < \delta < 1$) while the band at around 2113 cm^{-1} is due to adsorbed CO on metallic Au (Au^0). The 2141 cm^{-1} band is not due to CO adsorption on SiO$_2$ as an individual experiment on CO adsorption on pure SiO$_2$ at room temperature did not yield any adsorbed CO band. The assignment of the 2113 cm^{-1} band to adsorbed CO on metallic Au is also confirmed by CO adsorption on a Au/SiO$_2$ sample pre-reduced in H$_2$ at 500 °C which shows CO adsorption at 2110 cm^{-1}. Therefore, apparently a reduction of the cationic Au species occurs during CO oxidation at room temperature on the calcined Au/SiO$_2$ catalyst.

Also plotted in Fig. 1 are the integrated area of the CO$_2$ IR signal (at 2342 cm^{-1}) and CO conversion from QMS as a function of TOS. It is interesting to note that the activity of the catalyst correlates well with the red-shift of the CO band. As the CO band moves to lower frequency, the CO oxidation activity and CO$_2$ IR area simultaneously increase and then stabilize as the CO band levels off at around 2113 cm^{-1}. The excellent correlation among the three plots clearly indicates that metallic Au species play a major role in CO oxidation on Au/SiO$_2$ at room temperature, while cationic Au species alone are weakly or not active. We note that this is the first report about the role of different Au species in low temperature CO

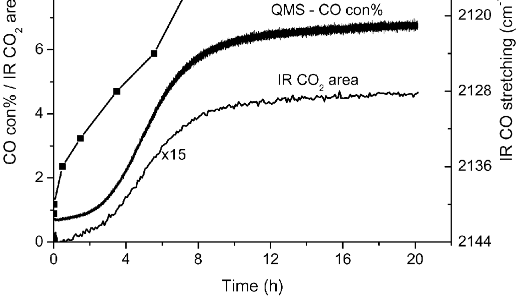

Fig. 1 Plots of CO band position, CO conversion and IR CO$_2$ area as a function of reaction time. CO : O$_2$ = 1 : 4.

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oxidation on a functioning Au/SiO_2. There are similar observations in the literature that the activity of other supported Au catalysts increases with TOS before reaching a pseudo-steady state[21–23] and some also attributed the activity change to the reduction of Au^{3+} in the precursor to Au^+ and/or Au^0.

The reduction of cationic Au species during CO oxidation is naturally thought to be due to the reduction by CO as is also indicated in the literature.[20,23] To test this, a calcined Au/SiO_2 sample was exposed to a CO flow for 20 h (the same length of time as the reaction time in Fig. 1) and the CO band position is plotted in the left part of Fig. 2 as a function of time. The reduction was expected to be more complete in CO without the presence of oxygen, however, the CO band shifts only to 2124 cm^{-1} within 20 h, about 10 cm^{-1} higher than the band from adsorbed CO during CO oxidation after 20 h (Fig. 1). This unexpected observation suggests that CO alone is not able to completely reduce cationic Au to the metallic state on Au/SiO_2 at room temperature. Therefore, the reduction of cationic Au to metallic Au during CO oxidation on Au/SiO_2 is altered by the presence of oxygen.

After CO flow for 20 h on calcined Au/SiO_2, O_2 was added into the stream and the reactant mixture was adjusted to the same condition as in CO oxidation. The right side of Fig. 2 presents the plots of CO conversion from QMS and CO band shift as a function of time. Interestingly, introduction of oxygen into the CO stream induces a shift in the CO band from 2124 cm^{-1} down to 2112 cm^{-1} within 2 h. Simultaneously CO oxidation activity (conversion) parallels the CO band shift, a similar observation as in Fig. 1. It is noted that upon O_2 introduction, the CO band abruptly shifts upward from 2125 to 2128 cm^{-1}, and then gradually shifts downwards to 2112 cm^{-1}. The small blue shift of the CO band is likely due to the coadsorption of oxygen with CO on Au sites because adsorbed oxygen abstracts an electron from Au sites, making them more cationic.[24]

The shift of the CO band from 2124 to 2112 cm^{-1} upon oxygen addition is surprising and intriguing. Before attempting an explanation, five related observations should be stated. (1) Co-feeding a smaller amount of O_2 ($O_2 : CO = 1 : 14$ instead of $4 : 1$ as in Fig. 2) is also effective in shifting the CO band down to 2112 cm^{-1} within 2 h, implying that excess oxygen is not needed to induce the change. (2) Oxygen alone does not induce the shift, since on stopping the CO flow after 20 h, then flowing O_2 alone, re-adsorption of CO still gives a band at around 2124 cm^{-1}. It seems co-existence of CO and O_2 is necessary for the shift. (3) Co-feeding CO_2 during CO reduction does not change the CO band position at 2124 cm^{-1}, an indication that product CO_2 formed during reduction (or reaction) is not relevant to the shift. (4) Co-feeding $^{18}O_2$ with CO can also shift the CO band down to 2112 cm^{-1} but at a slower rate than when using $^{16}O_2$, indicating that oxygen is directly related to this shift. (5) The shift from 2124 to 2112 cm^{-1} accompanied by a small intensity increase (*ca.* 20%) is more likely due to the extinction coefficient change (as the state of the Au species may have changed) of Au–CO species than to a coverage effect.

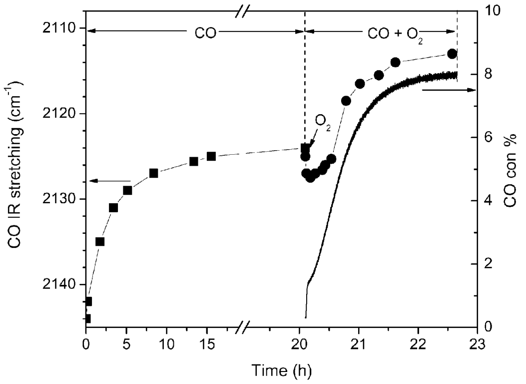

Fig. 2 CO flow on calcined Au/SiO_2 at room temperature and subsequent addition of O_2. Square – CO IR band position with CO alone; Solid circle – CO IR band position with CO + O_2; Solid line – CO conversion.

Based on the above results, we assume that the unusual CO band shift upon oxygen introduction is due to oxygen-assisted reduction of Au species by CO. This seems contradictory to the intuitive expectation that molecular oxygen should be excluded from the reaction media when reduction is to be performed. To the best of our knowledge, there exist very few examples in which oxygen induces or accelerates reduction in certain organic reactions.[25] A reduction involving a radical chain mechanism initiated by oxygen has been proposed. In our study, the exact nature of this oxygen-assisted reduction of cationic Au by CO is not clear. We propose that the reduction of cationic Au by CO involves a hydroxyl group on cationic Au sites and proceeds *via* a carboxyhydroxyl (COOH) intermediate as in the following: $CO + Au^{\delta+}\text{–}OH^{\delta-} \rightarrow CO\text{–}Au^{\delta+}\text{–}OH^{\delta-} \rightarrow Au^{\delta+}\text{–}COOH^{\delta-} \rightarrow H\text{–}Au^0\text{–}CO_2$. The carboxyhydroxyl intermediate has been proposed in several other studies[26–29] for either CO oxidation or water gas shift reactions on Au and Cu catalysts. The presence of surface OH groups associated with Au is critical for the formation of COOH species and they probably originate from water accumulated on the surface during CO flow (trace water, *ca.* 1 ppm, contained in the gases) as evidenced by an increase in intensity of OH stretching (broad feature from 2700–3700 cm^{-1} centered at *ca.* 3380 cm^{-1}) *vs.* TOS. The promotional effect of water is further confirmed by the fact that the reduction of cationic Au is greatly enhanced (shift from 2142 to 2112 cm^{-1} takes less than 2 h) as water (*ca.* 5000 ppm) is co-fed with CO/O_2. The broad OH stretching band may also contain OH stretching from COOH which is calculated to be at 3530 cm^{-1} for OH stretching on Au(110).[28] The CO and OCO stretchings in the COOH species are expected to be in the 1500–1800 cm^{-1} region[28,30] but were not observed in our spectra, probably due to the strong absorption of SiO_2 in this region. The COOH species is somehow stable on Au/SiO_2 and thus prevents cationic Au from reduction by CO. However, when O_2 is present, the removal of H atoms is accelerated by forming water/hydroxyl, thus facilitating the decomposition of carboxyhydroxyl and the eventual reduction of cationic Au ($O_2 + Au^{\delta+}\text{–}COOH^{\delta-} \rightarrow O_2 + H\text{–}Au^0\text{–}CO_2 \rightarrow CO_2 + H_2O/OH + Au^0$). Our IR result seems to support this proposal. The difference IR spectra (see Fig. S3 in ESI†) before and after the addition of oxygen into CO show a gradual increase of a broad negative band in the region 3200–3570 cm^{-1}, and simultaneous build up of a broad positive band centered at

3130 cm^{-1}. The negative band is possibly due to the consumption of OH groups associated with carboxyhydroxyl intermediate and/or cationic Au species. The appearance of the positive band at around 3130 cm^{-1} is likely due to adsorbed water and/or OH groups formed from the oxidation of surface H atoms. Further theoretical investigation is warranted to gain insight into this oxygen-assisted reduction. This unusual finding is of fundamental importance in understanding the channels leading to the reduction of metal oxide by CO.

It is interesting to note the nature of the supports for Au catalysts seems to affect the reduction behavior of cationic Au by CO in addition to its known effect on CO oxidation behavior. The reduction is easy and fast for Au supported on reducible oxides such as TiO_2[23] but difficult on non-reducible oxides such as Al_2O_3[6] and SiO_2 (this study). This seems to be related to the support reducibility. The reduction of cationic Au by CO was also found to be promoted by water on Au/Al_2O_3.[6] It is possible that a COOH intermediate is involved in the reduction of cationic Au on both Au/Al_2O_3 and Au/SiO_2. Therefore, our finding of the oxygen-assisted reduction of cationic Au by CO may have a general implication for Au supported on non-reducible metal oxide supports.

In summary, the activity of calcined Au/SiO_2 catalyst for CO oxidation at room temperature increases simultaneously with the oxygen-assisted reduction of cationic Au species by CO under reaction conditions. It points to the essential role of metallic Au species in CO oxidation on a Au/SiO_2 catalyst.

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