Operando infrared spectroscopy of low temperature CO oxidation on Au/SiO_2 catalyst

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Introduction

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. Catalytic activity in CO oxidation has been variously attributed to zerovalent, anionic, and cationic gold, present in mixtures or as individual species. 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 for CO oxidation when supported on non-reducible SiO_2. It's been only recently recognized that gold deposited on silica with strong interaction is comparably as effective as gold on TiO_2 for low temperature CO oxidation[2,3]. In this study, a Au/SiO_2 catalyst (4 wt% Au) prepared using $Au(en)_2Cl_3$ (en = ethylenediamine) as the precursor, an active catalyst for low temperature CO oxidation as reported recently[2], was tested for CO oxidation at room temperature using *operando* diffuse reflectance infrared spectroscopy (DRIFTS) coupled with quadruple mass spectrometer (QMS). The objective is to investigate the nature of Au species on SiO_2 and their catalytic role in room temperature CO oxidation. The effect of water in CO oxidation on Au/SiO_2 will also be studied.

Materials and Methods

The Au/SiO_2 sample was prepared by deposition-precipitation method using $Au(en)_2Cl_3$ (en=ethylenediamine) as Au precursor. In the DRIFT study, the sample was pretreated at 500°C under different atmosphere (either oxidative (O_2) or reductive (H_2 and CO)) before room temperature CO adsorption or CO oxidation. In a typical IR study of room temperature CO oxidation on Au/SiO_2, a stream of 2% CO/2%Ar/He and 2%O_2/He were mixed to create CO/O_2 of 1/4 and space velocity of 110, 000 $cm^3/(h\ g_{cat})$.

Results and Discussion

Room temperature CO adsorption was used to probe the nature of Au species on Au/SiO_2 after different pretreatments. For O_2-pretreated sample, initial CO adsorption showed the presence of cationic Au species ($CO\text{-}Au^{\delta+}$ ($0<\delta<1$) at 2142 cm^{-1}). For prolonged adsorption time (>10 hours), cationic Au species were partially reduced by CO. Addition of O_2 into CO enhanced the reduction to metallic Au ($CO\text{-}Au^0$ at ~2113 cm^{-1}). This unusual oxygen-assisted reduction is proposed to proceed via a carboxyhydroxyl (COOH) intermediate[4]. For both H_2- and CO-pretreated sample, CO adsorption indicated the presence of metallic Au species on the surface.

To access the role of the different Au species on Au/SiO_2, room temperature CO oxidation was followed by real time DRIFT and QMS. For O_2-pretreated Au/SiO2, the catalyst is initially inactive for CO oxidation when the surface Au is cationic. Interestingly, CO oxidation activity parallels with the red-shift of the adsorbed CO band ($2142 \rightarrow 2113$ cm^{-1}), i.e., when the CO band moves to lower frequency (reduction of cationic Au to metallic Au), the CO oxidation activity simultaneously increase and then stabilize as the CO band levels off at around 2113 cm^{-1} ($CO\text{-}Au^0$). This excellent correlation 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 is weakly or not active. The essential role of metallic Au species is further demonstrated by the immediate activity of CO oxidation on reductively pretreated Au/SiO_2. The accompanying slight deactivation with the oxidation of metallic Au species on reductively treated Au/SiO_2 in CO oxidation suggests that cationic Au species may play a negative role in CO oxidation.

The effect of water in room temperature CO oxidation was also explored. The IR results provide evidence for the promotional role of water on the activation of oxygen on Au/SiO_2 catalyst, which enhances CO oxidation activity. Another effect of water on Au/SiO_2 is its promotional effect in reducing cationic Au to metallic Au by CO. This role of water has not been reported in the literature. Our results show that the presence of water accelerates the reduction channel via a COOH intermediate during the CO-reduction of cationic Au on O_2-treated Au/SiO_2. This promotional effect of water may also play an important role during CO oxidation reaction, i.e., the presence of water may keep metallic Au from being oxidized, contributing to an increased and stable CO oxidation activity.

Significance

This work presents the first spectroscopic evidence for the nature and role of Au species on a Au/SiO_2 catalyst during room temperature CO oxidation. The data points to the essential role of metallic Au species in CO oxidation while cationic Au plays no role or negative role. Two positive roles played by water in CO oxidation on Au/SiO_2 have been identified: activation of O_2 and assistance the reduction of cationic Au species.

References

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