Tandem catalysis for Enhanced CO Oxidation over the Bi-Au-SiO2 Interface

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Abstract

Bimetallic catalysts typically exploit unique synergetic effects between two metal species to achieve their catalytic . Understanding the mechanism of CO oxidation using hybrid heterogeneous catalysts is important for effective catalyst design and environmental protection. Herein, we report a Bi-Au/SiO2 tandem bimetallic catalyst for CO oxidation reaction over the Au/SiO2 surface, which was monitored using near-ambient-pressure X-ray photoelectron spectroscopy. The Au-decorated SiO2 catalyst exhibited scarce activity in the CO oxidation reaction; However, the introduction of Bi to the Au/SiO2 system promoted the catalytic activity. The mechanism is thought to involve the dissociation O2 molecules in the presence of Bi, which results in spillover of the O species to adjacent Au atoms, thereby forming Au$\delta+$. Further CO adsorption, followed by thermal treatment, facilitated the oxidation of CO at the Au-Bi interface, resulting in a reversible reversion to the neutral Au valence state. Our work provides insight into the mechanism of CO oxidation on tandem surfaces and will facilitate the rational design of other Au-based catalysts

Full Text

Preamble

Tandem Catalysis for Enhanced CO Oxidation over the Bi-Au-SiO2 Interface

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Abstract

Bimetallic catalysts typically exploit unique synergistic effects between two metal species to achieve enhanced catalytic performance. Understanding the mechanism of CO oxidation using hybrid heterogeneous catalysts is crucial for effective catalyst design and environmental protection. Herein, we report a Bi-Au/SiO_2 tandem bimetallic catalyst for CO oxidation over the Au/SiO_2 surface, monitored using near-ambient-pressure X-ray photoelectron spectroscopy. The Au-decorated SiO_2 catalyst exhibited minimal activity for CO oxidation; however, introduction of Bi to the Au/SiO_2 system significantly promoted catalytic activity. The mechanism involves dissociation of O_2 molecules in the presence of Bi, resulting in spillover of O species to adjacent Au atoms, thereby forming Auδ^+. Subsequent CO adsorption, followed by thermal treatment, facilitated oxidation of CO at the Au-Bi interface, leading to reversible reversion to the neutral Au valence state. Our work provides mechanistic insight into CO oxidation on tandem surfaces and will facilitate rational design of other Au-based catalysts.

Keywords: APXPS; CO oxidation; Au-Bi interface; tandem catalysis; in-situ

Introduction

The unique synergistic effects between two metal species in bimetallic catalysts have been studied for decades [1-6]. Active sites with specific geometries can be regulated by introducing a second metal via the ensemble effect, which has increased interest in bimetallic catalytic systems in recent years [7-10]. Goodman et al. first demonstrated that numerous factors significantly affect the catalytic performance of Au catalysts [11-12], including the addition of a second metal. Au-based bimetallic catalysts (Au-X, where X = Pd, Ag, Pt, etc.) have emerged as attractive catalytic systems for many reactions, particularly CO oxidation [13-18].

For example, addition of Pd to Au/SnO_2 and Au/TiO_2 systems enhances their catalytic activity in low-temperature CO oxidation reactions [19-20]. In such systems, Au atoms provide active sites for CO adsorption while contiguous Pd sites are responsible for O_2 dissociation [21-23]. Despite numerous investigations on bimetallic catalysts for CO oxidation published in the last decade, effective advanced bimetallic catalysts and their intrinsic mechanisms and synergistic effects remain to be discovered and explored.

Bi is commonly used in liquid-phase alcohol oxidation [23-26] and electrochemical applications [27-29] owing to its low toxicity, low cost, and environmental sustainability. In bimetallic systems, it is generally accepted that Bi exists in a higher oxidation state and prevents oxidation of noble metals [30-34]. We previously demonstrated that the Bi-Cu interface exhibited higher catalytic activity for CO_2 activation and dissociation than pure Cu(111). Introduction of Bi atoms causes dissociated O to migrate to Cu-Bi sites, thereby freeing Cu active sites for CO_2 dissociation and thus boosting catalytic activity [35]. Nan et al. recently reported enhanced catalytic activity of Pt-Bi catalysts for CO oxidation [36], where unique Pt-Bi interfaces provided superior activation of oxygen species at low temperatures and increased CO_2 production. An Au-Bi catalyst exhibited an interesting phenomenon during acetylene hydrochlorination, where electron transfer between Au and Bi led to dispersion of Au nanoparticles in a higher-valence state, which enhanced C_2H_2 absorption [37]. Based on these results, we investigated whether similar effects could be achieved by adding Bi to Au-based catalysts for other typical catalytic reactions.

Recent advances in in situ characterization have enabled exploration of surface segregation and reductive/oxidative evolution of model catalysts under near-ambient pressures. Near-ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS) is a powerful tool for elucidating reaction mechanisms because changes in the core-level orbitals of each reactant can be measured directly during the reaction. Herein, NAP-XPS was employed to investigate the role of Bi in improving the catalytic performance of the Au-Bi/SiO_2 surface for CO oxidation.

To achieve this goal, the catalytic activities of Au/SiO_2, Bi/SiO_2, and Au-Bi/SiO_2 catalysts with different coverages were evaluated using several separate in situ experiments. The Au 4f peaks in NAP-XPS spectra of Au/SiO_2 catalysts did not significantly change during reactions under both oxidative and reductive conditions, while Bi sites in Au-Bi/SiO_2 facilitated contiguous dissociation of O_2 with further spillover of O species to Au, thus forming Auδ^+. Furthermore, strong interactions between Bi and CO were identified. Meanwhile, a reversible shift of the Au 4f peaks was observed, indicating reversion of Auδ^+ to metallic Au and thus confirming the catalytic activity of Au-Bi surfaces in CO oxidation under the employed reaction conditions. This study illustrates the enhanced catalytic activity of a Au-Bi/SiO_2 tandem surface for CO oxidation, which may facilitate design of bimetallic catalysts containing Au species.

Materials and Methods

This study was conducted at Beamline 20U at the Shanghai Synchrotron Radiation Facility (SSRF). All NAP-XPS spectra were recorded with a Hipp-2 analyzer (Scienta Omicron) using a monochromated Al Kα radiation source (h = 1486.6 eV, SPECS) [38]. The ultrahigh vacuum (UHV) system was equipped with analysis and preparation chambers with base pressures of 7×10^{-10} mbar and 5×10^{-10} mbar, respectively. The SiO_2 substrate (MaTeck) was mounted on a Ta sample holder and heated via laser heating from the rear. The surface was cleaned by repeated annealing at 1000 K in UHV until C species were no longer detected by C 1s XPS. The gas pipelines were purified using a mixture of alcohol and liquid nitrogen at approximately 173 K and monitored in situ using mass spectrometry to ensure no additional gas cross-contamination. The dosing gases were introduced into the analysis chamber using a leak valve and equilibrated for at least 30 min prior to analysis. The XPS spectra were fitted with Gaussian-Lorentz peaks [39] using CasaXPS software after subtraction of the Shirley background.

Results

The catalytic activities of Au/SiO_2, Bi/SiO_2, and bimetallic Au-Bi/SiO_2 in CO oxidation were compared by exposing these samples to O_2 and CO atmospheres. The Au 4f and O 1s XPS spectra of a 0.4 monolayer (ML) Au/SiO_2 sample are shown in Fig. 1 [Figure 1: see original paper]. Photoelectron spectra were recorded in the presence of O_2 (0.1 mbar) from room temperature (RT) to 373 K, and subsequently in the presence of CO (0.1 mbar) from RT to 473 K. The Au 4f spectrum obtained prior to any catalytic reactions shows peaks corresponding to metallic Au at 84.0 eV (Au $4f_7/_2$) and 87.7 eV (Au $4f_5/_2$), demonstrating that only standard metallic Au species are present.

Under these conditions, a single O peak characteristic of the SiO_2 substrate was observed at 531.7 eV. The shape and position of the Au 4f spectra remained essentially unchanged during the O_2/CO switching exposure process (Fig. 1a), indicating preservation of metallic Au species. Upon exposure to O_2 (0.1 mbar) at RT, a peak at 531.7 eV (OI) was observed, which increased slightly at 373 K and thereafter remained essentially unchanged with increasing temperature (Fig. 1b). Greg et al. reported that the highest occupied molecular orbital (HOMO) in Au clusters and rough Au surfaces is localized, and its charge density distribution facilitates charge transfer into the π^* orbital of O_2, which induces binding of the molecule to gold. The HOMO of a flat face of a bulk surface tends to be delocalized, which diminishes the ability of the surface to bind O_2 [40]. Conversely, oxidation of the Au(111) surface increases with temperature [41], contrary to the results depicted in Fig. 1. The Au 4f peak (Fig. 1a) does not indicate oxidation of Au; thus, we attributed the OI component to chemisorption of O_2 molecules on Au species. At 373 K, the O_2 coverage of the surface, reflected by the peak intensity, approached a relative maximum. The intensity of the peak corresponding to O increased after dosing with CO (Fig. 1b, upper part), indicating CO adsorption on the surface at the same binding energy (BE). Metallic Au exhibits poor CO adsorption activity because adsorption requires negatively charged Au atoms, which are formed by back-donation from Au d-electrons to the antibonding π^* orbital of adsorbed CO molecules [42-44]. Thus, CO is most likely adsorbed on the SiO_2 surface in this case, as Au remains in an inert metallic state (Fig. S1). No BE shift of the Au 4f peaks was observed upon gas molecule adsorption, which was attributed to the following: the sample surface exhibits poor activity under the experimental conditions, causing the concentration of adsorbed gas-phase molecules to be below the detection limit.

Considering the role of bismuth in promoting catalytic activity of bimetallic catalysts [35], in situ NAP-XPS spectra of Bi/SiO_2 samples were also obtained to elucidate the effect of O_2/CO atmosphere and annealing temperature (Fig. 2 [Figure 2: see original paper]). To obtain a dense Bi surface, multiple layers of Bi were deposited on SiO_2 via vacuum sublimation of Bi powder, followed by thermal annealing at 473 K to ensure uniform distribution. The Bi 4f spectrum obtained under UHV at RT presents peaks characteristic of metallic Bi at 157.0 eV (Bi $4f_7/_2$) and 162.3 eV (Bi $4f_5/_2$). After introducing 0.1 mbar O_2 to the system at RT, immediate changes were observed in the Bi 4f spectrum, where the pristine metallic Bi component weakened along with new sharp peaks appearing at 159.0 eV and 162.3 eV, respectively, suggesting formation of bismuth oxidation state (Biδ^+) [46]. In addition to the OI component, another peak corresponding to O emerges at 529.7 eV (Fig. 2b), which was assigned to oxygen-metal (O-M) bonding (denoted as OII) [46]. Thus, in this case, Bi-O bonding was induced by O species originating from O_2 dissociation [47-48]. Additionally, the O 1s peak with a higher BE at 531.7 eV (the same BE as O_2 adsorption on SiO_2, Fig. 1) arises from bonding between Bi and absorbed O_2 [48].

After evacuating the chamber to UHV and subsequently introducing CO (0.1 mbar) at RT, the signal corresponding to metallic Bi (green shadow) was reduced in intensity, demonstrating further oxidation of Bi. This behavior is similar to that observed under an O_2 atmosphere and may result from CO adsorption and subsequent dissociation on the Bi/SiO_2 surface. To test this hypothesis, a control experiment was conducted in which Bi/SiO_2 was directly exposed to CO (Fig. S2a and S2b). Similarly, CO adsorption resulted in oxidation of Bi at RT, and the degree of oxidation increased with temperature, as reflected by both the OI (Bi-CO in red) and OII (Bi-O in blue) components in the Bi 4f and O 1s spectra. This oxidized state is rather stable, and the Bi 4f and O 1s spectra remained essentially unchanged upon further introduction of a 0.1 mbar H_2 reductive atmosphere followed by annealing (Fig. S2c and S2d). Thus, we conclude that the weakened metallic Bi component in the spectra after CO introduction at RT (Fig. 2a) originates from CO adsorption and dissociation. After further thermal treatment, the intensity of the peak corresponding to metallic Bi increased with temperature from 373 to 473 K (Fig. 2a) owing to reduction of the oxidative surface. This may be explained by oxidation of CO by O species adsorbed on the surface, resulting in formation of CO_2 product. Without O_2 pretreatment, the Bi/SiO_2 surface underwent continuous oxidation, and the reduction reaction that prevailed after annealing in a CO atmosphere did not occur.

To explore the CO oxidation reaction on the bimetallic surface, an Au-Bi/SiO_2 sample was prepared by depositing 0.4 ML Au particles on a Bi/SiO_2 surface. The XPS spectra of the bimetallic surface are shown in Fig. 3 [Figure 3: see original paper]. In contrast to spectra of the Au/SiO$_2$ sample during O$_2$ exposure, wherein Au maintained a metallic state (Fig. 1), the Au 4f peaks in the spectrum of the bimetallic sample shifted upward by 0.2 eV (4f$_5$/$_2$ at 87.9 eV and 4f$_7$/$_2$ at 84.2 eV) relative to the metallic Au peak in the presence of O$_2$ (0.1 mbar) at RT (Fig. 3a), indicating existence of Auδ^+, which did not appear in the absence of Bi under equivalent experimental conditions. Formation of an Au-Bi alloy, which can also result in an Au BE shift [6], can be excluded in this case as the Au BE in the spectrum of another Au-Bi/SiO$_2$ sample remained unchanged under CO atmosphere (Fig. S3). Therefore, the upward shift in the Au BE was reliably attributed to the Au oxidation state.

Similarly, Biδ^+ was also formed upon O$_2$ introduction, with Bi 4f peaks appearing at 159.0 eV and 162.3 eV (Fig. 3b), indicating oxidation of Bi. The O 1s peak located at a BE of 529.7 eV (Fig. 3c) increased compared with that observed under UHV, providing evidence of O$_2$ dissociation and formation of O-M bonds. The component at 531.7 eV (Fig. 3c) arising from O$_2$ adsorption on the surface also increased. Considering the strong role of adjacent Bi atoms in capture and decomposition of O$_2$ molecules (Fig. 2), we concluded that the upward shift of the Au BE was caused by migration of adsorbed O atoms (originating from O$_2$ dissociation) from contiguous Bi sites. This conclusion is also consistent with Goodman's mechanism [15-16], which suggests that O$_2$ dissociation occurs at contiguous metal sites with further spillover of adsorbed O species to Au atoms, enabling subsequent CO oxidation. After annealing at 373 K, the fraction of metallic Bi was reduced and the intensity of the two signals in the O 1s region increased, suggesting that the surface had a higher oxidation state owing to intensification of the oxidation reaction.

After addition of CO gas followed by annealing to 473 K, the fraction of metallic bismuth was strengthened (green component in Fig. 3b; the intensity ratio evolution of Biδ^+/Si 2p is given in Fig. S4), which agrees with the phenomenon exhibited by the Bi/SiO$_2$ sample where CO oxidation occurs at Bi sites. After annealing, the total amount of the O component decreased (Fig. 3c and Fig. S4), suggesting that CO molecules reduced the surface oxides (Fig. 3c). Additionally, the Au 4f peak shifted back to its original position under UHV (Fig. 3a) after annealing at 473 K in a CO atmosphere, indicating that Auδ^+ was reduced to metallic Au. Thus, we achieved reversible alternation of the Au state in oxidizing and reducing atmospheres by adding Bi to the Au/SiO$_2$ system. The XPS analysis demonstrates enhanced catalytic activity of the Bi-Au-SiO$_2$ interface for CO oxidation relative to the case shown in Fig. 1. The universality of this phenomenon was further verified in Fig. S5 with lower Au coverage.

Fig. 4 [Figure 4: see original paper] shows schematic models of the proposed mechanism for CO oxidation on (a) Au/SiO$_2$, (b) Bi/SiO$_2$, and (c) Au-Bi/SiO$_2$ catalyst surfaces: (I) fresh sample surface; (II) generation of Auδ^+ or Biδ^+ after O$_2$ adsorption; (III) dissociation of O$_2$ molecules on Bi and oxidation of Au owing to spillover of adsorbed O from neighboring Bi sites; (IV) Bi-CO bonding resulting from strong adsorption; and (V) generation of CO$_2$ from adsorbed CO and O, with neutralization of Au and recovery of the catalyst.

To clearly demonstrate the mechanism of CO oxidation on different samples, models illustrating the proposed mechanism are shown in Fig. 4. The original Au/SiO_2 surface was essentially inactive for both O_2 dissociation and CO adsorption, thereby blocking further reactions (Fig. 4a). The Bi/SiO_2 catalyst exhibited some activity for CO oxidation owing to the strong CO adsorption capacity and O_2 dissociation ability of Bi (process IV in Fig. 4b). The reversible shift of the Au 4f peaks in the spectrum of the Au-Bi/SiO_2 sample suggests that CO oxidation was indeed activated by the bimetallic surface. Based on these observations, a mechanism for CO oxidation on the Au-Bi/SiO_2 surface can be proposed (Fig. 4c). After exposure to O_2, rapidly dissociated oxygen species on Bi sites migrate to neighboring Au atoms and form Au-O bonds (process III). The relatively strong interaction between Bi and CO enables the surface to capture CO molecules (process IV). Thus, combination of adsorbed CO and O on both Bi and Au sites occurs simultaneously with desorption of CO_2 product from the surface (process V), resulting in recovery of the Au valence state. The Au and Bi species, indicated by orange and dark blue spheres in Fig. 4, may be atoms or clusters. Thus, adjacent Bi sites facilitate adsorption of O_2 and CO molecules on Au/SiO_2, and the tandem surface catalyzes the CO oxidation reaction. Because bismuth species are partly oxidized in O_2 at RT (Fig. 2a and Fig. 3b), the subsequent upshift in the Au BE observed under a CO atmosphere may be a consequence of Au-BiO formation and enhanced catalytic activity of the interface. We also considered changing the sequence of introduced gas to explore the Au-BiO interface and CO adsorption state on the sample surface, as Bi atom sites may be permanently occupied by CO adsorption, in which case no distinct difference in the chemical states of Bi would be distinguishable during subsequent processes. Therefore, NAP-XPS alone may not be sufficient to elucidate the role of the Au-BiO interface in enhancing catalyst activity, and additional characterization methods may be required to provide deeper insight.

Conclusion

AP-XPS was employed to investigate the surface evolution of Au-Bi/SiO_2 tandem catalysts for CO oxidation and to elucidate the origin of enhanced catalytic activity. O_2 dissociation and CO adsorption do not readily occur on Au particles supported on SiO_2 substrate, and consequently the CO oxidation reaction was highly suppressed. Conversely, introduction of Bi improves the O_2 dissociation ability of the surface, and adsorbed O atoms subsequently spill over to adjacent Au atoms, resulting in formation of Auδ^{+}. Further CO adsorption on Bi, followed by thermal treatment, facilitated the CO oxidation reaction at the Au-Bi interface, resulting in reversible shift of the Au valence state to neutral. This study illustrates that the performance of Au/SiO_2 catalysts can be manipulated by Bi doping, which will shed new light on the design of bimetallic catalysts containing inert Au species.

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