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Oxidation of formic acid on stepped Au(997) surface

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ABSTRACT

The adsorption and reaction of formic acid (HCOOH) on clean and atomic oxygen-covered Au(997) surfaces were studied by temperature-programmed desorption/reaction spectroscopy (TPRS) and X-ray photoelectron spectroscopy (XPS). At 105 K, HCOOH molecularly adsorbs on clean Au(997) and interacts more strongly with low-coordinated Au atoms at (111) step sites than with those at (111) terrace sites. On an atomic oxygen-covered Au(997) surface, HCOOH reacts with oxygen atoms to form HCOO and OH at 105 K. Upon subsequent heating, surface reactions occur among adsorbed HCOO, OH, and atomic oxygen and produce CO₂, H₂O, and HCOOH between 250 and 400 K. The Au(111) steps bind surface adsorbates more strongly than the Au(111) terraces and exhibit larger barriers for HCOO(a) oxidation reactions. The surface reactions also depend on the relative coverages of co-existing surface species. Our results elucidate the elementary surface reactions between formic acid and oxygen adatoms on Au surfaces and highlight the effects of the coordination number of the Au atoms on the Au catalysis.

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1. Introduction

HCOOH is an important intermediate of many industrial catalytic reactions and also has great potential for use in H₂ storage materials and fuel cells [1–7]. Thus, the adsorption and reaction of HCOOH on metal catalysts have been extensively studied [8–26]. HCOOH is very reactive on W(100) surfaces and completely dissociates to form C, O, and H [8], but undergoes partial dissociation on most transition metal surfaces to form either CO and H₂O or CO₂ and H₂ [9–18]. The latter reaction pathway makes HCOOH a potential H₂ storage material [3,6,7]. HCOOH molecularly adsorbs on coinage metal surfaces, such as Au and Ag [20–23,26]. However, it has also been reported that HCOOH dissociates on Au and Ag surfaces with rich defects [19,24].

Au catalysis has been one of the most fascinating topics in heterogeneous catalysis over the last three decades [27–29]. Supported Au catalysts have been reported to catalyze the decomposition of HCOOH to produce H₂ [2–5]. Meanwhile, formate (HCOO) or carboxylate (COOH) species were proposed as the key intermediates in the low temperature oxidation of CO catalyzed by supported Au catalysts in the presence of moisture [26,30]. Thus, the surface chemistry of HCOOH on Au surfaces is of interest and importance. Model catalyst studies of well-defined Au surfaces have greatly advanced the fundamental understanding of Au catalysis [31,32]. For example, Chtai and coworkers [19–21] compared the adsorption and reaction of HCOOH on Au foil, Au(111), and Au(110) surfaces. On Au foil, molecularly-adsorbed HCOOH dissociates upon heating, forming HCOO species on the surface and eventually producing CO₂

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and H₂. On Au(110), HCOOH adsorbs as a HCOOH monomer through H-bond interaction. On Au(111), HCOOH adsorbs as (HCOOH)₂ dimers that dissociate into HCOOCH surface species upon heating. A later study of the adsorption and reaction of HCOOH on clean and H₂O-covered Au(111) surfaces did not observe any dissociation [25]. HCOOH molecules were driven by H bonds to form HCOOH chains on Au(111). Upon heating, the H-bond network within the HCOOH chains was broken, and the adsorbed HCOOH formed H-bonds with co-adsorbed H₂O. Study of the adsorption and reaction of HCOOH on atomic oxygen-covered Au(110) (O(a)/Au(110)) surface revealed a typical acid-basis reaction between HCOOH and O(a) to form HCOO and hydroxyl species [22]. The formate species underwent both the oxidation reaction to produce CO₂ and H₂O and the disproportionation reaction to produce HCOOH. Another study of the adsorption and reaction of HCOOH on O(a)/Au(111) reported the formation of the HCOO species and its further decomposition [26].

Low coordinated Au atoms on supported Au particles have been demonstrated to play important roles in Au catalysis [29,33,34] and can be modeled using stepped Au single crystal surfaces. In previous work, we used a stepped Au(997) surface with both (111) terraces with ninefold-coordinated Au atoms and (111) steps with sevenfold-coordinated Au atoms to compare the reactivity of Au atoms with the same coordination environment but different coordination number. The results revealed that Au atoms on (111) terraces and (111) steps exhibited different reactivity toward NO_x and CO_x, and oxygen adatoms at different Au sites also exhibited different reactivity toward NO_x, CO_x, and H₂O [35–39]. In the present paper, we report on the adsorption and reaction of HCOOH on clean and O(a)-covered stepped Au(997) surfaces. The reaction pathways between HCOOH and O(a) were found to be sensitive to their relative coverages, and the (111) step sites were found to exhibit larger reaction barriers in catalyzing HCOOH oxidation than the (111) terrace sites.

2. Experimental

All experiments were performed in a Leybold stainless-steel ultra-high-vacuum (UHV) chamber with a base pressure of $1\text{--}2 \times 10^{-10}$ mbar that has been described in detail elsewhere [39]. The UHV chamber was equipped with facilities for X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and differentially pumped thermal desorption spectroscopy (TDS) measurements. A Au(997) single crystal purchased from MaTeck was mounted on the sample holder using two Ta wires spot-welded to the back of the sample. The sample temperature, which was measured with a chromel–alumel thermocouple spot-welded to the back of the sample, could be controlled between 100 and 1273 K. Prior to the experiments, the Au(997) surface was cleaned with repeated cycles of Ar ion sputtering and annealing at 800 K until a sharp LEED pattern was obtained and no contaminants could be detected by XPS. NO₂ (>99.9%, Nanjing Shang Yuan Industry Factory, China) was used as received. Formic acid (99.9%, Sinopharm Chemical Reagent Co., China) and ultrapure water (>18 M Ω) were puri-

fied by repeated freeze–pump–thaw cycles. The purities of all reactants were checked by quadrupole mass spectrometry (QMS) prior to the experiments. All exposures are reported in Langmuir ($1\text{ L} = 1.0 \times 10^{-6}$ Torr·s) without correction for the gauge sensitivity. Line-of-sight stainless steel dosers (diameter: 8 mm) positioned ~ 2 mm in front of the Au(997) surface were used for the relatively large NO₂ and HCOOH exposures to control the chamber pressure to below 5×10^{-10} Torr. The reported exposures obtained with the line-of-sight stainless dosers were corrected according to the enhancement effect of the doser (~ 1000) [40]. Oxygen adatoms were prepared on the Au(997) surface by thermal decomposition of amorphous N₂O₄ multilayers [39]. During the TDS experiments, the Au(997) surface was positioned ~ 1 mm from the collecting tube of a differentially pumped QMS instrument and heated at a rate of 3.0 K/s. XPS spectra were taken with a pass energy of 20 eV using Al K α radiation ($h\nu = 1486.6$ eV).

3. Results and discussion

Fig. 1(A) displays HCOOH TDS spectra obtained following various HCOOH exposures on clean Au(997) at 105 K. At a HCOOH exposure of 0.01 L, a tiny HCOOH desorption peak appeared at 190 K. Increasing the HCOOH exposure to 0.05 L led to the saturation of this peak as well as the development of an additional HCOOH desorption peak at 170 K. The desorption peak at 170 K grew in intensity without any shift in the peak temperature as the HCOOH exposure was increased to 10 L, a characteristic of first order desorption kinetics. When the HCOOH exposure exceeded 10 L, the desorption continued to grow with HCOOH exposure and the peak temperature shifted toward higher temperature, a characteristic of zero order desorption kinetics. A shoulder HCOOH desorption peak at 140 K was also observed at a HCOOH exposure of 20 L but did not change with further HCOOH exposure. No other desorption signals were observed except for the desorption traces of CO, CO₂, and water originating from the background adsorption from the residual gas. Fig. 1(B) and (C) show the C 1s and O 1s XPS spectra obtained after various exposures of HCOOH on clean Au(997) at 105 K, respectively. For HCOOH exposures below 10 L, a single C 1s component at 289.1 eV and a single O 1s component at 532.8 eV were observed and could be assigned to the C 1s and O 1s signals of molecularly adsorbed HCOOH on the Au surface [19,26]. The different chemical environments of the two O atoms within molecular HCOOH led to the broad FWHM of the O 1s XPS spectrum [17,19]. Both peaks increased in intensity with HCOOH exposure without any binding energy shifts. When the HCOOH exposure reached 20 L, both the C 1s and O 1s XPS features broadened and shifted to higher binding energy. At a HCOOH exposure of 50 L, the C 1s and O 1s peaks were located at 290.1 and 533.6 eV, respectively, corresponding to those of HCOOH multilayers on metal surfaces [19,26].

Fig. 2 shows the C 1s and O 1s XPS spectra obtained after exposure of the Au(997) to 10 L HCOOH at 105 K followed by annealing at different elevated temperatures. An exposure of 10 L HCOOH at 105 K gave rise to a C 1s XPS feature at 289 eV

Fig. 1. HCOOH ($m/z = 29$) TDS spectra (A), and C 1s (B) and O 1s (C) XPS spectra following various HCOOH exposures on clean Au(997) at 105 K.

Fig. 2. C 1s (A) and O 1s (B) XPS spectra after exposure of Au(997) to 10 L HCOOH at 105 K (a) followed by annealing at 145 K (b), 180 K (c), 220 K (d) and 700 K (e).

and an O 1s XPS feature at 532.8 eV. Neither feature changed much upon annealing at 145 K, but both were greatly attenuated upon annealing at 180 K and completely vanished upon annealing at 220 K, corresponding to the HCOOH desorption peaks at 170 and 190 K shown in the TDS results, respectively. No residual C 1s and O 1s features were observed in the XPS spectra after annealing at 220 K or above, indicating the molecular desorption of the adsorbed HCOOH from the Au(997) surface.

The above TDS and XPS results demonstrate the reversible molecular adsorption of HCOOH on Au(997) at 105 K. The HCOOH monolayer desorbed from the (111) steps and (111) terraces of the Au(997) surface at 190 and 170 K, respectively. This agrees with previous observations of enhanced adsorption energies on low-coordinated Au atoms [29,31,38,39]. A HCOOH multilayer formed at HCOOH exposures exceeding 10 L. Its desorption peak overlapped with that of HCOOH monolayer on the (111) terraces at 170 K, resulting in a change from first

order desorption kinetics to zero order desorption kinetics with increasing HCOOH exposure. This also indicates a weak interaction of HCOOH with the (111) terrace sites of Au(997) surface. The shoulder HCOOH desorption peak at 140 K appearing at large HCOOH exposures could be attributable to the desorption of HCOOH interacting via H bonding with co-adsorbed water from background water adsorption. A similar result has been reported in a previous study [25].

The adsorption and reaction of HCOOH on an O(a)-covered Au(997) surface were then studied. Fig. 3 shows the temperature-programmed reaction spectroscopy (TPRS) spectra of various m/z signals after exposure of O(a)/Au(997) surfaces with various coverages of O(a) to 0.5 L HCOOH at 105 K. 0.02 ML-O(a)/Au(997) with atomic oxygen at the (111) steps (peak denoted α in Fig. 3(E)), 0.12 ML-O(a)/Au(997) with atomic oxygen at both (111) steps and (111) terraces (peak denoted β in Fig. 3(E)), and 0.26 ML-O(a)/Au(997) with atomic oxygen at both (111) steps and (111) terraces and O(a) islands on the

Fig. 3. CO_2 ($m/z = 44$) (A), H_2O ($m/z = 18$) (B), HCOOH ($m/z = 29$) (C), HCOOH ($m/z = 45$) (D), O_2 ($m/z = 32$) (E), and CO ($m/z = 28$) (F) TDS spectra after an exposure of 0.5 L HCOOH at 105 K on 0.02 ML- $\text{O(a)}/\text{Au(997)}$ (a), 0.12 ML- $\text{O(a)}/\text{Au(997)}$ (b), and 0.26 ML $\text{O(a)}/\text{Au(997)}$ (c) surfaces.

(111) terraces (peak denoted γ in Fig. 3(E)) were reproducibly prepared by the thermal dissociation of different coverages of multilayer N_2O_4 [35–37,39]. As shown in Fig. 3(A), a sharp and strong CO_2 desorption peak at 340 K appeared for the 0.02 ML- $\text{O(a)}/\text{Au(997)}$ surface. This feature attenuated with increasing initial O(a) coverage, with the maximum shifting to higher temperature. Meanwhile, a shoulder CO_2 desorption peak emerged at 309 K for the 0.12 ML- $\text{O(a)}/\text{Au(997)}$ surface and was obviously larger for the 0.26 ML- $\text{O(a)}/\text{Au(997)}$ surface. The CO_2 desorption traces below 300 K originated from the oxidation of adsorbed CO from the residual gas with the pre-covered O(a) [35]. Fig. 3(B) displays the H_2O TPRS spectra. A single H_2O desorption peak appeared at 181 K for the 0.02 ML- $\text{O(a)}/\text{Au(997)}$ surface. In comparison with that observed in the H_2O TDS spectra for clean Au(997) [37], this H_2O desorption peak seemed to be reaction-controlled rather than desorption-controlled. However, H_2O desorption traces appear simultaneously with those of CO_2 for the 0.12 and 0.26 ML- $\text{O(a)}/\text{Au(997)}$ surfaces, suggesting that CO_2 and H_2O were produced from the same surface reaction.

Fig. 3(C) and (D) display HCOOH TPRS spectra with $m/z = 29$ and 45, respectively. For the 0.02 ML- $\text{O(a)}/\text{Au(997)}$ surface,

the $m/z = 29$ signal exhibited a main peak at 171 K and a shoulder peak at 200 K, which arose from the molecular desorption of HCOOH on the (111) terraces and (111) steps of Au(997) , respectively. However, no such signals were observed for the 0.12 and 0.26 ML- $\text{O(a)}/\text{Au(997)}$ surfaces. These observations suggest that the adsorbed HCOOH completely reacted on the 0.12 and 0.26 ML- $\text{O(a)}/\text{Au(997)}$ surfaces but not on the 0.02 ML- $\text{O(a)}/\text{Au(997)}$ surface. However, the $m/z = 45$ signal gave desorption traces that accompanied the corresponding CO_2 desorption peaks for all $\text{O(a)}/\text{Au(997)}$ surfaces, indicating that HCOOH was also formed in the surface reaction that produced CO_2 . It is noteworthy that the desorption traces of the signals with $m/z = 29$ and 45 did not accompany each other. It was previously reported that molecularly-adsorbed HCOOH likely desorbed in the form of HCOOH dimers, while HCOOH produced by surface reaction desorbs in the form of HCOOH monomers [15], resulting in the different fragmentation patterns observed in the present TPRS results.

Fig. 3(E) shows the obtained O_2 TPRS spectra. Corresponding O_2 -TDS spectra without HCOOH exposure are also included for comparison. In agreement with the HCOOH TPRS results, the pre-covered O(a) on the 0.02 ML- $\text{O(a)}/\text{Au(997)}$ surface

were completely consumed, while those on 0.12 and 0.26 ML-O(a)/Au(997) surfaces were not. We also monitored the H₂ and CO TPRS spectra during the experiments. No H₂ production was observed. CO desorption traces were observed (Fig. 3(F)), but the CO desorption peaks below 200 K originated from adsorbed CO on Au(997) owing to the background adsorption of CO while the CO desorption features above 300 K resulted from the fragmentation of CO₂ in the QMS. Thus, no CO was produced following adsorption of 0.5 L HCOOH on the O(a)/Au(997) surface.

The above results demonstrate the oxidation of HCOOH following the adsorption of 0.5 L HCOOH on O(a)/Au(997) surfaces, but the extent of oxidation varied with the initial O(a) coverage. Molecularly-adsorbed H₂O formed on the 0.02 ML-O(a)/Au(997) surface but not on the 0.12 and 0.26 ML-O(a)/Au(997) surfaces. The CO₂ production peak at ~350 K observed for all O(a)/Au(997) surfaces can be assigned to the oxidation of HCOOH by atomic O(a) at the (111) steps, while the CO₂ production peak at 309 K observed for 0.12 and 0.26 ML-O(a)/Au(997) surfaces can be assigned to the oxidation of

HCOOH by O(a) species at the (111) terraces. This suggests that the reaction barrier of the oxidation of HCOOH into CO₂ at the (111) step is slightly larger than that at the (111) terraces.

Fig. 4(A)–(E) display CO₂, H₂O, HCOOH, and O₂ TPRS spectra measured following various HCOOH exposures on a 0.26 ML-O(a)/Au(997) surface at 105 K. At 0.5 L HCOOH exposure, the oxidation of HCOOH on the (111) terrace sites and (111) step sites of the Au(997) surface produced CO₂, H₂O, and HCOOH at 309 and 356 K, respectively. The oxidation of HCOOH on the (111) terrace sites increased greatly with HCOOH exposure, resulting in rapid growth of the corresponding CO₂, H₂O, and HCOOH desorption peaks and the shift of the maximum from 309 to 300 K (Fig. 4(A)–(D)), a typical characteristic of second-order desorption kinetics. This demonstrates that the HCOOH oxidation involved a bimolecular surface reaction. CO₂ and HCOOH generation reached saturation at 5 L HCOOH exposure. Accordingly, the molecular desorption peaks of HCOOH from the (111) step and terrace sites appeared at 202 and 166 K, respectively (Fig. 4(C) and (D)). Again, the desorption of molecularly-adsorbed HCOOH and the desorption

Fig. 4. CO₂ ($m/z = 44$) (A), H₂O ($m/z = 18$) (B), HCOOH ($m/z = 29$) (C), HCOOH ($m/z = 45$) (D), and O₂ ($m/z = 32$) (E) TPRS spectra following exposure of 0.26 ML-O(a)/Au(997) surface to 0 (a), 0.5 L (b), 1 L (c), 5 L (d) and 10 L (e) HCOOH at 105 K; (F) TPRS spectra of various m/z signals following exposure of the 0.26 ML-O(a)/Au(997) surface to 10 L HCOOH at 105 K. The trace of water desorption trace from 0.26 ML-O(a)/Au(997) at 105 K is also included for comparison.

of reaction-formed HCOOH exhibited different fragmentation patterns for the signals of $m/z = 29$ and 45. The former exhibited a stronger $m/z = 29$ signal, while the latter exhibited a stronger $m/z = 45$ signal. In the water TPRS spectra (Fig. 4(B)), additional desorption peaks appeared and grew at 216 and 171 K, and were respectively attributed to the recombination of surface hydroxyl groups and the desorption of O(a)-stabilized water on the Au(997) surface by comparing the water TDS spectra measured after water adsorption on a 0.26 ML-O(a)/Au(997) surface [37]. This demonstrates the increased formation of surface hydroxyl groups and water upon HCOOH oxidation after larger HCOOH exposures. The corresponding O₂ TPRS spectra (Fig. 4(E)) show that the desorption peaks of all O(a) species attenuated with increasing HCOOH exposure, corresponding to the consumption of O(a) species owing to HCOOH oxidation. The consumption of various O(a) species followed the order of O(a) islands on the (111) terraces > atomic oxygen at the (111) terraces > atomic oxygen at the (111) steps. Furthermore, only atomic O(a) on the (111) steps remained on the surface after exposures of 5 and 10 L HCOOH. Fig. 4(F) compares the TPRS spectra of various signals measured after exposure of the 0.26 ML-O(a)/Au(997) surface to 10 L HCOOH at 105 K. It is clear that the HCOOH oxidation involved four surface reactions producing water at 175 K, water at 219 K, water, CO₂, and HCOOH at 300 K, and water, CO₂, and HCOOH at 356 K.

XPS was used to monitor the surface species of HCOOH oxidation on O(a)/Au(997) surfaces. Fig. 5 shows C 1s and O 1s XPS spectra obtained after exposing 0.26 ML-O(a)/Au(997) to 10 L HCOOH following by annealing at elevated temperature. On a clean Au(997) surface, 0.26 ML O(a) produced an O 1s peak at 529.3 eV, while the adsorption of 10 L HCOOH produced C 1s and O 1s peaks at 289 and 532.8 eV, respectively. In the C 1s XPS spectra (Fig. 5(A)), the 10 L HCOOH exposure at 105 K led to a broad C 1s spectrum in which a main component

at 288.6 eV and a shoulder feature at 287 eV were identified. In the corresponding O 1s spectrum (Fig. 5(B)), the O(a) peak almost vanished and a broad O 1s feature appeared at 531.2 eV. Upon annealing at 145 K, the C 1s component at 287 eV grew at the expense of that at 288.6 eV; accordingly, the low-binding energy part of the broad O 1s peak grew at the expense of the high-binding energy part, and three O 1s components at 530.7, 531.2, and 532.8 eV were distinguished. The C 1s component at 288.6 eV almost vanished upon annealing at 180 K, while the C 1s component at 287 eV did not change much upon annealing up to 220 K, weakened upon annealing at 270 K, and disappeared upon annealing at 300 K. The O 1s component at 532.8 eV almost disappeared upon annealing at 180 K, the O 1s component at 531.2 eV attenuated upon annealing at 180 K and vanished upon annealing at 220 K, and the O 1s component at 530.7 eV shifted to 530.2 eV upon annealing at 220 K owing to the disappearance of adsorbates, weakened upon annealing at 270 K, and disappeared upon annealing at 300 K.

Previous XPS results showed that the difference between the C 1s binding energy of adsorbed HCOOH and HCOO varied between 1.0–1.3 eV [19,26], thus we assign the C 1s peaks at 288.6 and 287 eV to adsorbed HCOOH and HCOO, respectively. Correspondingly, the O 1s components at 532.8, 531.2, and 530.7/530.2 eV should respectively arise from molecularly adsorbed HCOOH, hydroxyl groups, and HCOO. Thus the binding energies of adsorbed HCOOH and HCOO on Au(997) were easily affected by the co-adsorbates. The XPS results demonstrate that the reaction of HCOOH+O(a) already occurs upon HCOOH exposure on 0.26 ML-O(a)/Au(997) at 105 K to produce HCOO and OH and further occurs upon annealing at 145 K. The disappearance of the HCOOH component at 288.6 and 532.8 eV upon annealing at 180 K corresponded to the desorption peak of molecularly-adsorbed HCOOH from the surface at 166 K in the corresponding TPRS spectrum. The attenuation upon annealing at 180 K and disappearance upon annealing at

Fig. 5. C 1s (A) and O 1s (B) XPS spectra after exposure of 0.26 ML-O(a)/Au(997) surface to 10 L HCOOH at 105 K followed by annealing at elevated temperature. The C 1s XPS spectrum of 10 L HCOOH on Au(997) and the O 1s XPS spectrum of 0.26 ML-O(a)/Au(997) are also included for comparison.

220 K of the OH peak at 531.2 eV corresponded to the water desorption peaks at 171 and 216 K in the TPRS spectrum. The disappearance of the HCOO feature at 287 and 530.7/530.2 eV upon annealing at 300 K corresponded to the further oxidation of HCOO on the surface to produce water, CO₂, and HCOOH initiated above 250 K in the TPRS spectrum.

Thus, our TPRS and XPS results demonstrate that O(a) on Au(997) readily abstracts the acidic H of HCOOH to form HCOO and OH at 105 K, but the subsequent surface reactions depend both on the coordination number of Au sites and on the relative coverages of O(a) and HCOO.

For 0.5 L HCOOH oxidation on 0.02 ML-O(a)/Au(997) with atomic oxygen on the (111) steps with sevenfold-coordinated Au atoms (Fig. 3), O(a) is completely consumed, and the coadsorbed surface species are HCOO(a), OH(a) and HCOOH(a). The reaction products are H₂O at 181 K and CO₂ and HCOOH at 340 K. The surface reaction pathways are proposed to be as follows:

For 0.5 L HCOOH oxidation on 0.12 ML and 0.26 ML-O(a)/Au(997) surfaces with oxygen species on both the (111) steps with sevenfold-coordinated Au atoms and the (111) terraces with ninefold-coordinated Au atoms (Fig. 3), HCOOH is completely consumed and co-adsorbed surface species are HCOO(a), OH(a) and O(a). The reaction products are simultaneous H₂O, CO₂ and HCOOH at 309 K from the (111) terraces and at 356 K from the (111) steps. The surface reaction pathways are proposed as follows:

For 10 L HCOOH oxidation on 0.26 ML-O(a)/Au(997) surfaces with oxygen species on both the (111) steps with sevenfold-coordinated Au atoms and the (111) terraces with ninefold-coordinated Au atoms (Fig. 4), none of the HCOOH or O(a) is completely consumed and the coadsorbed surface species are HCOOH(a), HCOO(a), OH(a), and O(a). Besides the surface reactions producing H₂O, CO₂, and HCOOH at 309 K from the (111) terraces and at 356 K from the (111) steps, surface reactions also occur to produce water at 171 and 216 K following the proposed pathways:

Demonstrated by the reaction-controlled desorption temperatures of the reaction products (Figs. 3 and 4), the reaction barriers of all surface oxidation reactions of HCOO(a) into CO₂, including HCOO(a) + O(a) and HCOO(a) + HCOO(a), at the (111) steps are slightly larger than at the (111) terraces. Meanwhile, the occurrence of HCOO(a) + O(a) and HCOO(a) + HCOO(a) at either step sites or terrace sites at the same temperature indicates that both surface reactions should have a common rate-limiting elementary surface reaction. This should be the C–H bond rupture of HCOO(a) on the Au surface. Thus, the Au(111) steps bind HCOO(a) more strongly than the Au(111) terraces and exhibit a larger barrier for the C–H bond rupture of HCOO(a). These observations demonstrate that surface species that bind with the Au surface more weakly are more reactive. Similar results were previously observed for CO + O(a) and

NO + O(a) reactions on Au(997) surfaces, in which both surface reactions proceed with a larger barriers at the (111) steps than at the (111) terraces, in agreement with our previous results [35,36]. This also rationalizes the different relative consumptions of various oxygen species during HCOOH oxidation shown in Fig. 4. The H species resulting from the decomposition of HCOO(a) at the (111) steps should be lower in amount than at the (111) terraces owing to the higher decomposition barrier, and subsequently the amount of atomic oxygen at the (111) steps consumed by the water formation is lower than that at the (111) terraces.

4. Conclusions

Using a stepped Au(997) surface consisting of (111) terraces and (111) steps, we have successfully elucidated the surface reactions of HCOOH oxidation on an Au surface. O(a) on Au(997) readily abstracts the acidic H of HCOOH to form HCOO(a) and OH at 105 K. Upon subsequent heating, surface reactions among adsorbed HCOO(a), OH, and atomic oxygen produce CO₂, H₂O, and HCOOH between 250 and 400 K. The Au(111) steps bind surface adsorbates more strongly than the Au(111) terraces and exhibit larger barriers for the HCOO(a) oxidation reactions. Depending on the relative coverages of surface species, the generation of water by the reaction between HCOOH(a) and OH(a) and by the reaction between OH(a) at low temperature also occurs. These results deepen the fundamental understanding of HCOOH-involving reactions on Au-based catalysts and highlight the effects of the coordination number of Au atoms on the Au catalysis.

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Graphical Abstract

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Oxidation of formic acid on stepped Au(997) surface

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On the stepped Au(997) surface, (111) steps exhibit a larger activation energy than (111) terraces in catalyzing the oxidation of formic acid with atomic oxygen via formate and hydroxyl intermediates.

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甲酸在Au(997)台阶表面的氧化反应

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摘要: 金催化是纳米催化的代表性体系之一, 但对金催化作用的理解还存在争议, 特别是金颗粒尺寸对其催化作用的影响。金颗粒尺寸减小导致的表面结构主要变化之一是表面配位不饱和和金原子密度的增加, 因此研究金原子配位结构对其催化作用的影响对于理解金催化作用尺寸依赖性具有重要意义。具有不同配位结构的金颗粒表面可以利用金台阶单晶表面来模拟。我们研究组以同时具有Au(111)平台和Au(111)台阶的Au(997)台阶表面为模型表面, 发现Au(111)台阶原子在CO氧化、NO氧化和NO分解反应中表现出与Au(111)平台原子不同的催化性能。

负载型Au颗粒催化甲酸氧化反应是重要的Au催化反应之一。本文利用程序升温脱附/反应谱(TDS/TPRS)和X射线光电子能谱(XPS)研究了甲酸在清洁的和原子氧覆盖的Au(997)表面的吸附和氧化反应, 观察到Au(111)台阶原子和Au(111)平台原子不同的催化甲酸根氧化反应行为。与甲酸根强相互作用的Au(111)台阶原子表现出比与甲酸根弱相互作用的Au(111)平台原子更高的催化甲酸根与原子氧发生氧化反应的反应活化能。

在清洁Au(997)表面, 甲酸分子发生可逆的分子吸附和脱附。甲酸分子在Au(111)台阶原子的吸附强于在Au(111)平台原子的吸附。TDS结果表明, 吸附在Au(111)台阶原子的甲酸分子的脱附温度在190 K, 吸附在Au(111)平台原子的甲酸分子的

脱附温度在170 K. XPS结果表明, 分子吸附甲酸的C 1s和O 1s结合能分别位于289.1和532.8 eV.

利用多层NO₂的分解反应在Au(997)表面控制制备具有不同原子氧吸附位和覆盖度的原子氧覆盖Au(997)表面, 包括氧原子吸附在(111)台阶位的0.02 ML-O(a)/Au(997)、氧原子同时吸附在(111)台阶位和(111)平台位的0.12 ML-O(a)/Au(997)、氧原子和氧岛吸附在(111)平台位和氧原子吸附在(111)台阶位的0.26 ML-O(a)/Au(997). TPRS和XPS结果表明, 甲酸分子在105 K与Au(997)表面原子氧物种反应生成甲酸根和羟基物种, 但甲酸根物种的进一步氧化反应依赖于Au原子配位结构和各种表面物种的相对覆盖度.

在0.02 ML-O(a)/Au(997)表面暴露0.5 L甲酸时, Au(111)台阶位氧原子完全反应, 甲酸过量. 表面物种是Au(111)台阶位吸附的甲酸根、羟基和甲酸分子. 在加热过程中, 甲酸分子与羟基在181 K反应生成甲酸根和气相水分子($\text{HCOOH(a)} + \text{OH(a)} = \text{H}_2\text{O} + \text{HCOO(a)}$), 甲酸根在340 K发生歧化反应生成气相HCOOH和CO₂分子($2\text{HCOO(a)} = \text{CO}_2 + \text{HCOOH}$).

在0.12 ML-O(a)/Au(997)和0.26 ML-O(a)/Au(997)表面暴露0.5 L甲酸时, 甲酸分子完全反应, 原子氧过量. 表面物种是Au(111)平台位和Au(111)台阶位吸附的甲酸根、羟基和原子氧. 在加热过程中, Au(111)平台位和Au(111)台阶位的甲酸根分别在309和340 K同时发生氧化反应($\text{HCOO(a)} + \text{O(a)} = \text{H}_2\text{O} + \text{CO}_2$)和歧化反应($2\text{HCOO(a)} = \text{CO}_2 + \text{HCOOH}$)生成气相CO₂, H₂O和HCOOH分子.

在0.26 ML-O(a)/Au(997)表面暴露10 L甲酸时, 甲酸分子和原子氧均未完全消耗. 表面物种是Au(111)平台位和Au(111)台阶位吸附的甲酸根、羟基、甲酸分子和原子氧. 在加热过程中, 除了上述甲酸根的氧化反应和歧化反应, 还发生171 K的甲酸分子与羟基的反应($\text{HCOOH(a)} + \text{OH(a)} = \text{H}_2\text{O} + \text{HCOO(a)}$)和216 K的羟基并和反应($\text{OH(a)} + \text{OH(a)} = \text{H}_2\text{O} + \text{O(a)}$).

关键词: 金催化; 表面化学; 模型催化剂; 几何结构; 配位数

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