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Short communication

Origin of CO promoted methanol oxidation in alkaline media catalyzed by gold: A first-principle investigation

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ABSTRACT

We performed density functional theory calculations to investigate the kinetics of methanol oxidation into formic acid catalyzed by Au(111) with and without CO in alkaline media. The calculation results show that the surface with pre-adsorbed molecular CO reduces the adsorption energy of possible species. The pre-adsorbed CO species promotes almost every step of methanol oxidation both thermochemically and kinetically, which agrees well with the experimental observation. This finding may be associated with the relatively strong basicity of OH species in the presence of adsorbed CO species, thereby enhancing their ability to strip the H atoms.

Given that carbon monoxide exhibits a strong tendency to adsorb on the catalyst surface to hinder the sites needed by reactants in heterogeneous catalysis and electrocatalysis, the adsorbed CO always acts evidently as a poison or poisoning intermediate in alcohol oxidation. The adsorbed CO can also pass through the membrane. Thus, it can poison not only the anode but also the cathode [1]. To solve this problem, many new catalysts have oxidized the trace CO, such as alumina-supported Au nanoparticles [2] and Cu_2O nanoparticles [3] supported on silica gel. Among these catalysts, gold often exhibits unexpected properties. Gold has also been an active electrode material for carbon monoxide oxidation since 1965 [4], and this material has elicited considerable attention in recent decades. As a material with surprising activities for catalytic oxidation reactions, electrocatalytic gold remarkably requires neither nanoparticles nor an oxidic support. However, alkaline conditions are important prerequisites for efficient aqueous-phase gold electrocatalysis. Zhang et al. [5] observed an interesting stabilizing co-adsorption system of CO and electronegative NO_2 on Au(111) in ultra-high vacuum (UHV); they proposed that such stabilizing system may be responsible for catalytic promotion, particularly for the association reaction in IB metals. A theoretical study reported by Gan and Zhao [6] also indicated that other electronegative ions, such as S, can enhance the co-adsorption of CO. Rodriguez et al. [7] proposed a model for CO oxidation on gold electrodes in alkaline media, which stipulated that irreversibly adsorbed CO may enhance the nearby bonding of OH to the surface; moreover, the adsorbed OH may act as the oxidant for CO oxidation, leading to a significant rate enhancement. Recent electrochemical experiments for the oxidation of several alcohols, including methanol, on clean Au(111) and CO-modified Au(111) electrodes showed an intriguing consequence that CO can also promote alcohol oxidation in a solution [8]. However, although some theoretical studies have been performed on methanol oxidation on Au [9,10], the physical origin remains unclear. Therefore, in the present work, we performed density functional theory calculations to investigate the oxidation of methanol on Au(111) and CO-modified Au(111) surfaces using the continuum solvation model.

Detailed information about the calculation methods and models is provided in the Supporting information (see Fig. S1). Table 1 lists the calculated adsorption energies for CO, OH, and co-adsorption of CO + OH on Au(111). Fig. S2 shows the optimized co-adsorption configurations. When CO adsorbs on the atop site, the adsorption energy of OH will be enhanced by −0.20 eV (Table 1); by contrast, CO adsorbed on the other two sites, bridge and fcc, will reduce the adsorption energy of OH. These findings agree with previous DFT calculations [7]. Bader charge analysis (Table 1) indicated that in the case of OH(fcc) + CO(top), OH species exhibited a negative charge, whereas CO species showed a positive charge; thus, an attractive electrostatic interaction occurred between CO and OH, leading to a stronger co-adsorption between the two species. Two types of effects originate from pre-adsorbed species as follows: direct through adsorbate–adsorbate interaction and indirect through surface (or surface-mediated)

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Table 1
DFT results of binding energy of CO/OH and co-adsorption on Au(111).

	Adsorption site	Binding energy/eV	e/Bader charge
OH	top	−1.78 (−1.85)[a]	−0.44
	br	−2.06 (−2.09)[a]	−0.47
	fcc	−2.10 (−2.15)[a]	−0.49
CO	top	−0.24 (−0.29)[a]	−0.03
	br	−0.24 (−0.31)[a]	−0.14
	fcc	−0.22 (−0.29)[a]	−0.17
OH + CO	OH(top) + CO(top)	−1.89/−0.35	−0.46/−0.03
	OH(br) + CO(top)	−2.11/−0.29	−0.48/−0.06
	OH(fcc) + CO(top)	−2.30/−0.45	−0.45/+0.03
	OH(fcc) + CO(br)	−2.09/−0.24	−0.45/−0.10
	OH(fcc) + CO(fcc)	−2.04/−0.17	−0.50/−0.18
H_2O + OH	fcc	−2.18	–
H_2O + CO	top	−0.26	–
H_2O + OH + CO	OH(fcc) + CO(top)	−2.37/−0.45	−0.44/+0.05

[a] The data relate to the case of kpoints = 4 × 4 × 1.

interaction. Thus, through-surface interaction should be investigated by analyzing the electron density distribution of the topmost Au atom on both bare surfaces when an adsorbed CO exists on a neighboring Au atom (as shown in Fig. S3 in the Supporting information). The electron density distribution of the Au atom is almost unaffected by the presence of CO at the neighborhood (similar finding has been confirmed by Bader charge analysis: −0.01 and −0.03 e before and after CO adsorption). This result indicates that direct instead of indirect interaction occurred in the co-adsorption of the CO–OH system. In other co-adsorption cases, such as OH(fcc) + CO(br) and OH(fcc) + OH(fcc), a repel interaction existed between CO and OH species because of the same signs of charges for CO and OH. We then added a monolayer of water, and OH adsorption became more enhanced (−2.37 eV; Table 1). A similar attractive electrostatic interaction existed between OH and CO species based on Bader charge analysis. To further elucidate the mechanism by which the CO adsorbed on the top site can enhance the co-adsorption of OH and CO, the energy decomposition scheme proposed by Hammer [11] was applied (see Table S1 in the Supporting materials). The adsorption energy of OH is similar to all these three cases, and the interaction between OH and CO on OH(fcc) + CO(top) is larger than that of OH(fcc) + CO(fcc) (i.e., −0.48 eV vs. −0.40 eV) (Table S1). The CO adsorption energy is also more stable on the top site than on the fcc site (i.e., −0.08 eV vs. 0.10 eV; Table S1). Considering these two factors, the OH(fcc) + CO(top) system is the most stable among the configurations studied in this work. To systematically determine the effect of slab thickness on the adsorption energy, CO and OH on three-, four-, five-, and six-layer models were also selected (Table S2). In general, the adsorption energy on the even layers (four or six) is slightly larger than that on the odd layers (three or five). This finding is close to that of our previous study about formate (HCOO) on Cu [12].

Rodriguez et al. [8] showed that the final products of methanol oxidation on gold catalyst in the presence of CO are formaldehyde and formic acid. Therefore, the following possible reaction mechanism was considered in our present work.

$CH_3OH + OH \rightarrow CH_3O + H_2O$ M1 $CH_3O + OH \rightarrow CH_2O + H_2O$ M2
$CH_2O + OH \rightarrow CHO + H_2O$ M3 $CHO + OH \rightarrow HCOOH$ M4

Methanol oxidation may also occur via the C–H bond scission to form hydroxymethyl, that is, $CH_3OH + OH \rightarrow CH_2OH + H_2O$. Previous DFT calculation results indicated that the oxidation of methanol to methoxy is more favorable than that of hydroxymethyl [13–16]. The detailed discussion of the adsorption properties of CH_3OH, CH_3O, CH_2O, HCO, and HCOOH species on Au(111), OH/Au(111), and CO/OH/Au(111) is provided in the Supporting information (Table S3 and Fig. S4). The adsorption energy of species mainly follows the order Au(111) > OH/Au(111) > CO/OH/Au(111), in which the presence of CO would reduce the binding energy. Given that the oxidative dehydrogenation reaction is disproportionate, and the relatively weak adsorption of the reactant may decrease the activation energy barrier to some extent, the presence of adsorbed CO species may facilitate the oxidative dehydrogenation reaction process. Subsequently, the kinetics of methanol oxidation on pure Au(111) and Au(111)–CO were explored (see Table 2 as well as Figs. 1 and 2) to further confirm such issues.

$CH_3OH + OH \rightarrow CH_3O + H_2O$. For the initial oxidative dehydrogenation step of methanol, molecular methanol is adsorbed at the top site with its oxygen atom, and the relative adsorption energy is reduced in the presence of pre-adsorbed CO caused by block effect (−0.20 eV vs. −0.49 eV). The distance between the O atom of OH species and the H atom of the CH_3O-H is approximately smaller by 0.06 Å on the Au(111)–CO surface than that without pre-adsorbed CO Au(111); thus, methanol can easily strip the hydrogen atom. On the OH/Au(111) surface, the oxidative dehydrogenation for methanol is slightly endothermic with the reaction energy of 0.06 eV. By contrast, the reaction becomes exothermic on the CO/OH/Au(111) surface, releasing 0.31 eV of energy. The activation energy barrier for such elemental step is also 0.08 eV on Au(111) and becomes non-activated with further decline in the presence of adsorbed CO (i.e., a barrierless process). This result suggests that the initial oxidation step of methanol induced by the pre-adsorbed CO is favorable both thermochemically and kinetically.

$CH_3O + OH \rightarrow CH_2O + H_2O$. After CH_3O is formed, it can be further oxidized by OH to produce CH_2O. In pure Au(111), CH_3O adsorbs vertically at the fcc site, as well as at the bridge site in the presence of CO because of the site-blocking effect. Given that the most stable adsorption configuration on Au(111) is the fcc site for CH_3O, the binding strength of CH_3O on CO/OH/Au(111) would be smaller than that on OH/Au(111) (Table S3), thereby facilitating an easier oxidative dehydrogenation step. The pre-adsorbed CO can significantly enhance CH_3O oxidation both thermochemically and kinetically (Table 2): the reaction energy changes from −1.88 eV on OH/Au(111) to −2.02 eV on CO/OH/Au(111), and the activation energy barrier for CH_3O oxidation to CH_2O with only 0.29 eV on CO/OH/Au(111) compared with 0.56 eV on the OH/Au(111). As for the TS2, the bond length between OH and H of CH_3O is 1.45 Å on the Au(111)–CO surface, which becomes slightly shorter by 0.05 Å than on the OH/Au(111) surface. After the TS, CH_2O is formed, and water is desorbed from the surface.

$CH_2O + OH \rightarrow CHO + H_2O$. For the third step, the molecular CH_2O is adsorbed on the Au(111) (Au(111)–CO) and it is closer to the OH species. In this co-adsorption configuration, the adsorbed CH_2O is far away from the surface because of the existence of a water layer but reacts with OH via its C–H bond. The reaction energies for this process are −0.84 and −0.88 eV, and the associated energy barriers are 0.72 and 0.61 eV on Au(111) and Au(111)–CO, respectively. These findings suggest that the oxidative dehydrogenation of CH_2O into HCO by OH can be promoted by the pre-adsorbed CO both thermochemically and kinetically. At the TS, the C–H/H–O bond length is 1.358/1.241 Å on Au(111) and 1.372/1.238 Å on Au(111)–CO. After the TS, the formed HCO is adsorbed with height of 2.078 Å on both surfaces.

$CHO + OH \rightarrow HCOOH$. For the final step, HCO reacts with OH to produce HCOOH. The CO slightly influences such reaction with only 0.01 eV difference in the reaction energy. This result may be ascribed to the association type of this reaction, which is different from the abovementioned disproportional reaction type. Thus, slight effect of CO

Table 2
Energetic data for methanol oxidation reaction processes on OH/Au and CO/OH/Au(111) (eV).

	M1		M2		M3		M4	
	Ea	ΔH	Ea	ΔH	Ea	ΔH	Ea	ΔH
OH	0.08	0.06	0.56	−1.88	0.72	−0.84	0.00	−2.04
CO–OH	0.00	−0.31	0.29	−2.02	0.61	−0.88	0.00	−2.05

Note: Ea is the activation energy, and ΔH is the reaction energy.