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Intermetallic $NaAu_2$ as a Heterogeneous Catalyst for Low-Temperature CO Oxidation

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Supporting Information

ABSTRACT: The enhanced stability and modified electronic structure of intermetallic compounds provide discovery of superior catalysts for chemical conversions with high activity, selectivity, and stability. We find that the intermetallic $NaAu_2$ is an active catalyst for CO oxidation at low temperatures. From density functional theory calculations, a reaction mechanism is suggested to explain the observed low reaction barrier of CO oxidation by $NaAu_2$, in which a CO molecule reacts directly with an adsorbed O_2 to form an OOCO* intermediate. The presence of surface Na increases the binding energy of O_2 and decreases the energy barrier of the transition states.

Intermetallic compounds, consisting of two or more metallic/metalloid elements,[1,2] adopt specific crystal structures as well as electronic structures that are different from the constituent elements. The specific structures often result in unique bulk properties, such as the shape-memory effect, hydrogen storage, and superconductivity.[3−6] The modified electronic structures of intermetallic compounds also make them enticing catalytic materials because they will alter the binding energies of surface adsorbates (reactants, intermediates, and products) and thus change catalytic properties.[7−9] Developing catalysts using intermetallic compounds could also benefit from their structural stability arising from highly favorable formation enthalpies. It has been shown that intermetallic compounds could maintain their surface structure under reaction conditions,[10] whereas the surface composition and structure of alloys usually change under different reaction environments.[11] Combined, these two features, unique electronic structure and high stability, potentially circumvent problems with traditional, supported multimetal/alloy catalysts, such as chemical heterogeneity of particles (which is detrimental to selectivity), broad distributions of active sites, surface segregation, and the formation of carbides or hydrides.

Intermetallic compounds have been used as heterogeneous catalysts for chemical conversions. Tsai et al. showed that an Al-rich quasicrystal containing Cu and Fe could catalyze the steam reforming of methanol to produce hydrogen under mild conditions.[12] Schlögl et al. reported that Al−Co, Al−Fe, and Pd−Ga intermetallics are good catalysts for selective partial hydrogenation reactions.[9,13−17] Considering the availability of intermetallic compounds with different structures (∼ 100 000 binaries, ternaries, and quaternaries discovered so far),[18] their catalytic properties are largely unexplored.

Herein, we report, for the first time, the intermetallic compound $NaAu_2$ (Figure 1) is an active catalyst for CO oxidation at room temperature. Using density functional theory (DFT) methods, we determined the role of Na in $NaAu_2$ for CO oxidation and a reaction mechanism for the low-temperature CO oxidation. Upon O_2 exposure, Na atoms in the second layer of $NaAu_2$(111) surface (top-Na) pop out and act as bonding sites for O_2 atoms. The presence of the fourth layer Na atoms (fcc-Na) decreases the energy barrier of two transition states during CO oxidation. Due to these low-energy barriers, $NaAu_2$ can catalyze CO oxidation at a low temperature.

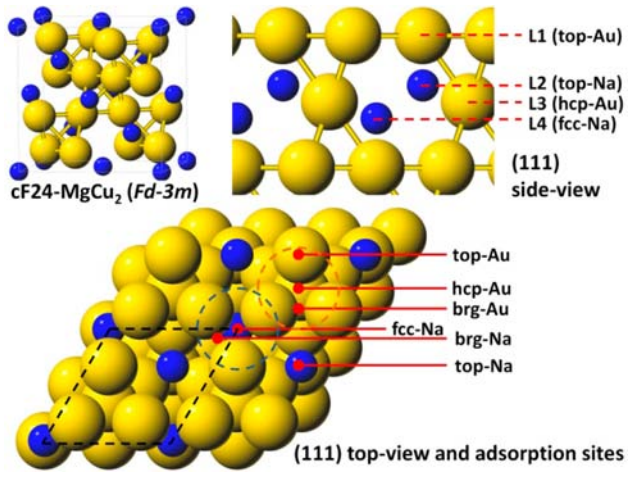

Figure 1. Bulk and (111) surface structures of C15 (cF24-$MgCu_2$) $NaAu_2$. Na (Au) are denoted by blue (yellow) spheres. Adsorption sites and (1 × 1) surface unit cell are highlighted in the top view. Notation "brg-Na" ("brg-Au") refers to the bridge Au site with a Na (Au) atom underneath, shown in dashed circles. The side view is in the $\langle 1\bar{1}0 \rangle$ direction. The layer numbers and the atoms underneath the associated adsorption sites are labeled.

Figure 1 shows the (111) surface of $NaAu_2$. This surface has a 2D Kagomé network of Au atoms. The $NaAu_2$(111)

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resembles Au(111) with a high density of vacancies, i.e., one out of every four Au atoms is missing. Underneath each vacancy in the second layer is a Na atom (the 'top-Na' site). Also, half of the Au surface triangles have a Na atom (the 'fcc-Na' site), in the fourth layer, whereas the other Au triangles have an Au atom underneath (the 'hcp-Au' site). Other sites include 'brg-Na' and 'brg-Au' sites at the edges of the Au triangles.

The intermetallic $NaAu_2$ catalyst was synthesized by annealing a stoichiometric mixture of elemental Na and Au at 1050 °C. The as-synthesized $NaAu_2$ crystals were ground into fine particles under N_2 and were used as catalysts after water treatment processes were completed (Supporting Information, SI). Figure 2 shows typical activities of $NaAu_2$ catalysts at

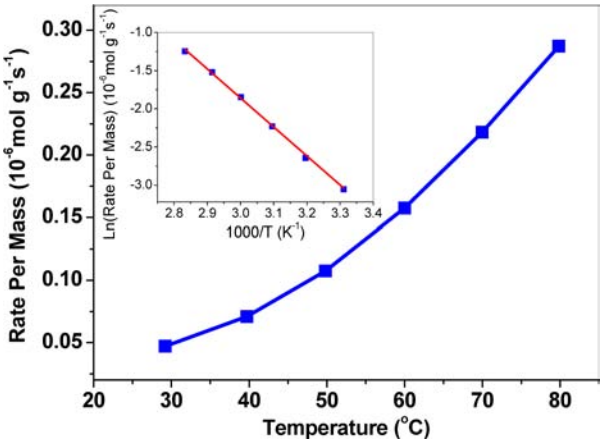

Figure 2. Activity of $NaAu_2$ in the CO oxidation reaction. Reaction rates were measured in a plug-flow reactor with 150 mg of $NaAu_2$ powder. The reaction gases are composed of 14 mL/min CO, 35 mL/min O_2, and 31 mL/min He at 1 atm. Insert: the Arrhenius plot shows that the activation energy of $NaAu_2$ for CO oxidation is 31.6 ± 0.7 kJ/mol.

different reaction temperatures. The apparent activation energy for CO oxidation on $NaAu_2$ is 31.6 ± 0.7 kJ/mol, calculated from the slope of the Arrhenius plot (insert in Figure 2). It clearly shows that $NaAu_2$ is active for CO oxidation at low temperatures. We also tested Au- and NaOH-coated Au powder under the same reaction conditions and found no activity. This indicates that Na in $NaAu_2$ is a critical component for the observed low-temperature CO oxidation activity. To understand the role Na plays in the intermetallic $NaAu_2$ on CO oxidation and the catalytic reaction mechanism, we performed DFT calculations to study reaction pathways.

For CO adsorption on $NaAu_2(111)$, DFT calculations suggest that the most preferred adsorption site (top-Au) has an adsorption energy (E_{ad}) of −0.32 eV, which is followed closely by the brg-Na site (E_{ad} = −0.28 eV). In contrast, O strongly prefers the fcc-Na site (E_{ad} = −0.60 eV) over the hcp-Au site (E_{ad} = −0.18 eV). Therefore, on $NaAu_2(111)$ the adsorption energy landscape for CO is relatively flat, but not for O.

Interestingly, the top-Na atom underneath the vacancy on $NaAu_2(111)$ only loses 0.03 eV if it pops out, overcoming a small barrier of 0.23 eV. Furthermore, we find such Na reconstruction is energetically favored with oxidative species near the site. For example, O_2 can pull out the Na atom through only ionic relaxation with a negligible barrier, giving E_{ad} of −0.38 eV for O_2. Otherwise, on pristine $NaAu_2(111)$ surfaces, O_2 has a rather weak binding energy even at the electron-rich fcc-Na site. With this top-Na 'pop-out' reconstruction, the change in E_{ad} of CO is very small. The pop-out Na binds O with an E_{ad} of −0.61 eV at the brg-Na site. This binding is as strong as the fcc-Na site on the pristine surface.

For a triatomic $NaAu_2$ cluster, previous DFT calculations showed that Na exhibits a positive natural bond orbital charge, indicating a partial electron transfer from Na to Au.[19] The electron-rich Au atom can further transferred part of its electron to adsorbed O_2 molecules to weaken the O═O bond, which could enhance the catalytic activity of the bimetallic cluster if the dissociation of adsorbed O_2 molecules is the rate-limiting step.[20] (See SI for electronic structure analysis on the influence of Na atoms.) Using DFT calculations, we found that the direct dissociation of O_2 to 2O* needs around 1.0 eV even after Na provides sizable charge transfer. This high-energy barrier indicates that the direct O_2 dissociation is not a viable pathway for the CO oxidation on $NaAu_2$ at room temperature.

We propose an alternative reaction pathway previously used to explain the CO oxidation mechanism on small Au clusters.[21] Figure 3 shows the reaction pathway on the $NaAu_2(111)$

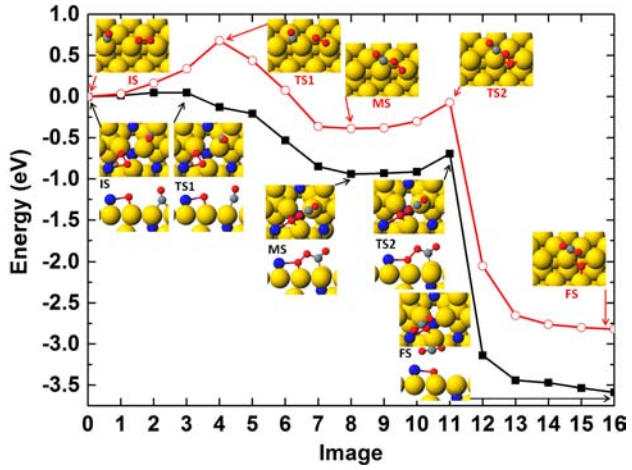

Figure 3. Reaction pathways of coadsorbed CO and O_2 on $NaAu_2(111)$ vs Au(221) from initial state (IS) via the intermediate complex OOCO* (MS) to final state (FS) of CO_2. Transition states are TS1 and TS2. The C, O, Au, and Na are denoted by gray, red, yellow, and blue spheres, respectively. Barriers on $NaAu_2(111)$ are 0.05 eV (TS1) and 0.25 eV (TS2), compared to 0.68 and 0.32 eV on Au(221).

surface for adsorbed CO and O_2 to form CO_2 via the intermediate state OOCO* versus the similar pathway on Au(221) with low-coordinated Au atoms only.[22] On $NaAu_2(111)$, the first step to form OOCO* (TS1) has a barrier of only 0.05 eV, which is lower than the second step of 0.25 eV (TS2) needed to break the O−O bond in OOCO* to form CO_2. In contrast, on Au(221) the 0.68 eV barrier for TS1 to form OOCO* is significantly higher than that of 0.32 eV for TS2.

The reason for such a dramatic difference in the reaction barriers can be explained as follows. Table 1 lists E_{ad} or E_{br} for the two-step reaction as well as the O−O bond length on both Au(211) and $NaAu_2(111)$. The O−O bond length is a good indicator of activation toward dissociation in O_2 or in OOCO*. For the IS, Na reconstruction provides strong binding for O_2 on $NaAu_2(111)$. Although E_{ad} of −0.56 eV for IS on $NaAu_2(111)$ is weaker than that of −0.71 eV on Au(221),

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Table 1. E_{ad} (negative) for IS, MS, and FS and E_{br} (positive) for TS1 and TS2 for the Two-Step Reaction[a]

	surface	IS	TS1	MS	TS2	FS
$E_{ad/br}$ (eV)	Au(221)	−0.71	0.68	−1.10	0.32	−3.53
	$NaAu_2$	−0.56	0.05	−1.50	0.25	−4.15
O−O (Å)	Au(221)	1.345	1.297	1.436	1.702	
	$NaAu_2$	1.421	1.418	1.453	1.717	

[a]Also listed are the O−O bond lengths except for FS.

the O_2 molecule on $NaAu_2(111)$ is more activated as seen by a longer O−O bond of 1.421 Å compared to 1.345 Å on Au(221). Alternatively, the E_{ad} for the IS on Au(221) mostly arises from strong CO binding, whereas that on $NaAu_2(111)$ mostly originates from O_2 binding. To form OOCO* on Au(221), CO and O_2 must share a single Au atom on the (111) step edge. Due to its weaker binding to Au than CO, O_2 is somewhat displaced from the Au atom as shown by a shrinking of O−O bond length to 1.297 Å, resulting in a large barrier of 0.68 eV. In contrast, this scenario is avoided on $NaAu_2(111)$. To form OOCO* on $NaAu_2(111)$, the O_2 molecule must rotate 90° toward the fcc-Na site, which binds strongly to O* due to the electron-rich Na atom underneath the Au trimer. For TS1 on $NaAu_2(111)$, the O−O bond length decreases only by 0.003 Å from the IS, resulting in a very small energy cost or barrier.

The MS is 0.40 eV more stable on $NaAu_2(111)$ than on Au(221). For TS2 to break the single O−O bond in OOCO*, the O−O bond in MS on $NaAu_2(111)$ is also more activated than that on Au(221) as indicated by the larger bond length. Therefore, the TS2 barrier on $NaAu_2(111)$ is slightly smaller than that on Au(221). The remaining O* on $NaAu_2(111)$ will react with the second CO with a barrier of 0.20 eV (see Figure S6) to complete the reaction cycle.

The above analysis shows the advantageous features of the intermetallic compound $NaAu_2$ as a catalyst, in which Na atoms help to anchor O_2, stabilize the intermediate OOCO* state, and also provide a favorable configuration for TS1, thus giving a much smaller barrier than TS2 and resulting in the overall barrier of 0.25 eV.

To evaluate the stability of the $NaAu_2$ catalyst under the CO oxidation conditions, we used X-ray diffraction (XRD) to characterize its crystal structure before and after reaction. We found no change in the XRD pattern (Figure S3). This indicates that the bulk structure of $NaAu_2$ is preserved under the CO oxidation conditions.

We used X-ray photoelectron spectroscopy (XPS) to measure the surface composition of the $NaAu_2$ catalyst (Figure S4). The freshly ground $NaAu_2$ powder shows a Na-rich surface with Na/Au ratio of 1.16, which is higher than the theoretical value, 0.50. The relatively high Na content at the surface of the $NaAu_2$ powder is possibly due to exposure of the powder to O_2 in air during preparation. The DFT calculations suggest that the Na atoms underneath the vacancies on $NaAu_2(111)$ easily pop out, which can be induced by adsorption of O_2. After washing with H_2O and drying in vacuum, the surface becomes Au rich (Na/Au = 0.12) because the surface Na species can be easily dissolved in H_2O. The pH of the wash water increases (Figure S1), which could be due to the presence of NaOH, Na_2O, or Na_2CO_3 on the surface of $NaAu_2$. After CO oxidation, the Na/Au ratio on the surface becomes 0.58. This value is very close to the theoretical Na/Au ratio in the $NaAu_2$ intermetallic compound (0.50), which suggests that the CO oxidation is catalyzed by a $NaAu_2$ surface.

Identifying the oxidation state of Na in the $NaAu_2$ catalyst would provide more insights on its active sites. However, we could not resolve the oxidation state of Na in $NaAu_2$ due to small binding energy shifts of different oxidation states in different compounds (SI). An *in situ* XPS characterization of a $NaAu_2$ single crystal in an ultrahigh-vacuum chamber is currently underway.

In conclusion, we have discovered that the intermetallic compound $NaAu_2$ is active for CO oxidation at a low temperature. DFT calculations suggest a reaction mechanism, in which a CO molecule reacts directly with an adsorbed O_2 to form an OOCO* reaction intermediate at the site with Na pop-out reconstruction. The dissociation of CO_2 from the OOCO* intermediate is the rate-limiting step. The barrier of this dissociation decreased in the presence of Na on the surface of $NaAu_2$. Recently, for Au_{12-19} clusters, a CO self-promoting oxidation mechanism via O−O scission was suggested as the low-energy reaction pathway when a sharp triangular Au_3 site is available.[23] Whether such a pathway remains competitive for $NaAu_2(111)$ having a 2D triangular Kagomé lattice of Au is under investigation. Nonetheless, theory has predicted the $NaAu_2$ surface (and line compound surfaces more generally) as more stable, controllable, and reactive media, as we experimentally confirmed.

Heterogeneous catalysis using intermetallic compounds is a largely unexplored research area. As demonstrated by the role of $NaAu_2$ in CO oxidation, the well-defined surfaces of intermetallic compounds provide exceptional platforms to facilitate understanding of structure-catalytic property relationships and to improve the rational design of high-performance catalysts.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures; Temperature dependent CO oxidation activities; XRD patterns and XPS of $NaAu_2$ before and after reaction; DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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