

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/237817838>

Intermetallic NaAu₂ as a Heterogeneous Catalyst for Low-Temperature CO Oxidation

ARTICLE in JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · JUNE 2013

Impact Factor: 12.11 · DOI: 10.1021/ja403175c · Source: PubMed

CITATIONS

7

READS

26

9 AUTHORS, INCLUDING:



Chaoxian Xiao

Iowa State University

41 PUBLICATIONS 959 CITATIONS

SEE PROFILE



Volodymyr Smetana

Iowa State University

54 PUBLICATIONS 252 CITATIONS

SEE PROFILE



Patricia A Thiel

Iowa State University

350 PUBLICATIONS 9,462 CITATIONS

SEE PROFILE



Duane D. Johnson

Iowa State University

294 PUBLICATIONS 3,900 CITATIONS

SEE PROFILE

Intermetallic NaAu₂ as a Heterogeneous Catalyst for Low-Temperature CO OxidationChaoxian Xiao,[†] Lin-Lin Wang,^{*,§} Raghu V. Maligal-Ganesh,[†] Volodymyr Smetana,^{†,§} Holly Walen,^{†,§} Patricia A. Thiel,^{†,‡,§} Gordon J. Miller,^{†,§} Duane D. Johnson,^{‡,§} and Wenyu Huang^{*,†,§}[†]Department of Chemistry and [‡]Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, United States[§]Ames Laboratory, U.S. Department of Energy, Ames, Iowa 50011, United States

S 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 NaAu₂ 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 NaAu₂, in which a CO molecule reacts directly with an adsorbed O₂ to form an OOCO* intermediate. The presence of surface Na increases the binding energy of O₂ 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 NaAu₂ (Figure 1) is an active catalyst for CO

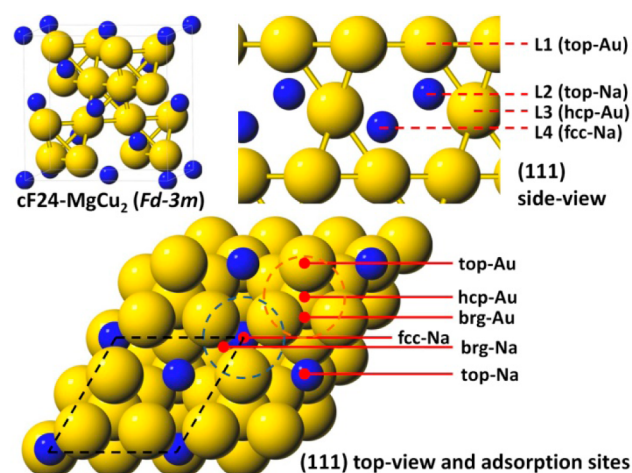


Figure 1. Bulk and (111) surface structures of C15 (cF24-MgCu₂) NaAu₂. Na (Au) are denoted by blue (yellow) spheres. Adsorption sites and (1 × 1) surface unit cell are highlighted in the top view. Notation “brg-Na” (“brg-Au”) refers to the bridge Au site with a Na (Au) atom underneath, shown in dashed 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.

oxidation at room temperature. Using density functional theory (DFT) methods, we determined the role of Na in NaAu₂ for CO oxidation and a reaction mechanism for the low-temperature CO oxidation. Upon O₂ exposure, Na atoms in the second layer of NaAu₂(111) surface (top-Na) pop out and act as bonding sites for O₂ 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, NaAu₂ can catalyze CO oxidation at a low temperature.

Figure 1 shows the (111) surface of NaAu₂. This surface has a 2D Kagomé network of Au atoms. The NaAu₂(111)

Received: March 29, 2013

Published: June 11, 2013

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 NaAu₂ catalyst was synthesized by annealing a stoichiometric mixture of elemental Na and Au at 1050 °C. The as-synthesized NaAu₂ crystals were ground into fine particles under N₂ and were used as catalysts after water treatment processes were completed (Supporting Information, SI). Figure 2 shows typical activities of NaAu₂ catalysts at

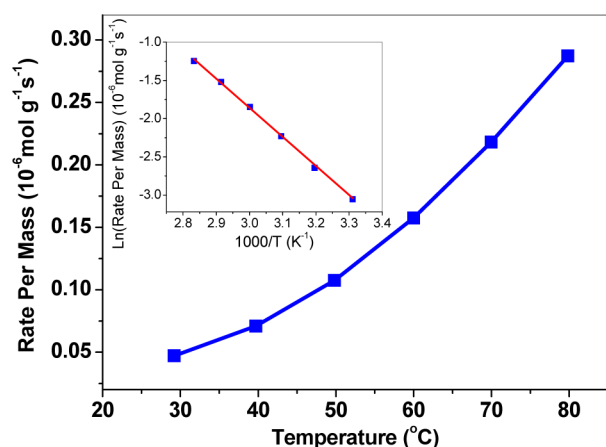


Figure 2. Activity of NaAu₂ in the CO oxidation reaction. Reaction rates were measured in a plug-flow reactor with 150 mg of NaAu₂ powder. The reaction gases are composed of 14 mL/min CO, 35 mL/min O₂, and 31 mL/min He at 1 atm. Insert: the Arrhenius plot shows that the activation energy of NaAu₂ for CO oxidation is 31.6 ± 0.7 kJ/mol.

different reaction temperatures. The apparent activation energy for CO oxidation on NaAu₂ is 31.6 ± 0.7 kJ/mol, calculated from the slope of the Arrhenius plot (insert in Figure 2). It clearly shows that NaAu₂ 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 NaAu₂ is a critical component for the observed low-temperature CO oxidation activity. To understand the role Na plays in the intermetallic NaAu₂ on CO oxidation and the catalytic reaction mechanism, we performed DFT calculations to study reaction pathways.

For CO adsorption on NaAu₂(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 NaAu₂(111) the adsorption energy landscape for CO is relatively flat, but not for O.

Interestingly, the top-Na atom underneath the vacancy on NaAu₂(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, O₂ can pull out the Na atom through only ionic relaxation with a negligible barrier, giving E_{ad} of -0.38 eV for O₂. Otherwise, on pristine NaAu₂(111)

surfaces, O₂ 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 NaAu₂ 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 O₂ molecules to weaken the O=O bond, which could enhance the catalytic activity of the bimetallic cluster if the dissociation of adsorbed O₂ 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 O₂ to 2O* needs around 1.0 eV even after Na provides sizable charge transfer. This high-energy barrier indicates that the direct O₂ dissociation is not a viable pathway for the CO oxidation on NaAu₂ 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 NaAu₂(111)

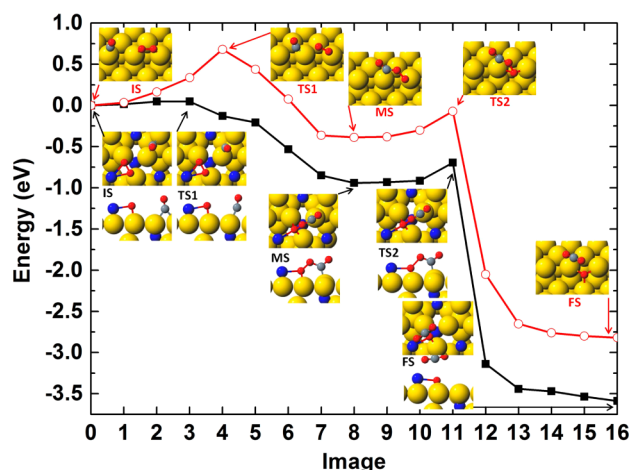


Figure 3. Reaction pathways of coadsorbed CO and O₂ on NaAu₂(111) vs Au(221) from initial state (IS) via the intermediate complex OOCO* (MS) to final state (FS) of CO₂. Transition states are TS1 and TS2. The C, O, Au, and Na are denoted by gray, red, yellow, and blue spheres, respectively. Barriers on NaAu₂(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 O₂ to form CO₂ via the intermediate state OOCO* versus the similar pathway on Au(221) with low-coordinated Au atoms only.²² On NaAu₂(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 CO₂. 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 NaAu₂(111). The O–O bond length is a good indicator of activation toward dissociation in O₂ or in OOCO*. For the IS, Na reconstruction provides strong binding for O₂ on NaAu₂(111). Although E_{ad} of -0.56 eV for IS on NaAu₂(111) is weaker than that of -0.71 eV on Au(221),

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
$E_{\text{ad/br}}$ (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	

^aAlso listed are the O–O bond lengths except for FS.

the O₂ molecule on NaAu₂(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 NaAu₂(111) mostly originates from O₂ binding. To form OOCO* on Au(221), CO and O₂ must share a single Au atom on the (111) step edge. Due to its weaker binding to Au than CO, O₂ 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 NaAu₂(111). To form OOCO* on NaAu₂(111), the O₂ 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 NaAu₂(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 NaAu₂(111) than on Au(221). For TS2 to break the single O–O bond in OOCO*, the O–O bond in MS on NaAu₂(111) is also more activated than that on Au(221) as indicated by the larger bond length. Therefore, the TS2 barrier on NaAu₂(111) is slightly smaller than that on Au(221). The remaining O* on NaAu₂(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 NaAu₂ as a catalyst, in which Na atoms help to anchor O₂, 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 NaAu₂ 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 NaAu₂ is preserved under the CO oxidation conditions.

We used X-ray photoelectron spectroscopy (XPS) to measure the surface composition of the NaAu₂ catalyst (Figure S4). The freshly ground NaAu₂ 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 NaAu₂ powder is possibly due to exposure of the powder to O₂ in air during preparation. The DFT calculations suggest that the Na atoms underneath the vacancies on NaAu₂(111) easily pop out, which can be induced by adsorption of O₂. After washing with H₂O and drying in vacuum, the surface becomes Au rich (Na/Au = 0.12) because the surface Na species can be easily dissolved in H₂O. The pH of the wash water increases (Figure S1), which could be due to the presence of NaOH, Na₂O, or Na₂CO₃ on the surface of NaAu₂. 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 NaAu₂ intermetallic

compound (0.50), which suggests that the CO oxidation is catalyzed by a NaAu₂ surface.

Identifying the oxidation state of Na in the NaAu₂ catalyst would provide more insights on its active sites. However, we could not resolve the oxidation state of Na in NaAu₂ due to small binding energy shifts of different oxidation states in different compounds (SI). An *in situ* XPS characterization of a NaAu₂ single crystal in an ultrahigh-vacuum chamber is currently underway.

In conclusion, we have discovered that the intermetallic compound NaAu₂ 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 O₂ to form an OOCO* reaction intermediate at the site with Na pop-out reconstruction. The dissociation of CO₂ from the OOCO* intermediate is the rate-limiting step. The barrier of this dissociation decreased in the presence of Na on the surface of NaAu₂. 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 Au₃ site is available.²³ Whether such a pathway remains competitive for NaAu₂(111) having a 2D triangular Kagomé lattice of Au is under investigation. Nonetheless, theory has predicted the NaAu₂ 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 NaAu₂ 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 NaAu₂ before and after reaction; DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

whuang@iastate.edu; llw@ameslab.gov

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

W.H. thanks Ames Laboratory for support through the Royalty Account and Iowa State University for startup funds. The U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering supported DFT structural stability calculations (D.D.J.) and synthesis of NaAu₂ (G.J.M.) at Ames Laboratory, and the Division of Chemical Science, Geosciences and Bioscience supported transition-state calculations (L.L.W., D.D.J.) through Iowa State under contract DEFG02-03ER15476. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under contract no. DE-AC02-07CH11358.

■ REFERENCES

- (1) Armbruster, M. *Intermetallic Compounds in Catalysis*; John Wiley & Sons, Inc.: Hoboken, NJ, 2002.
- (2) Nesper, R. *Angew. Chem.-Int. Edit.* **1991**, 30, 789.
- (3) Cava, R. J.; Takagi, H.; Zandbergen, H. W.; Krajewski, J. J.; Peck, W. F.; Siegrist, T.; Batlogg, B.; Vandover, R. B.; Felder, R. J.; Mizuhashi, K.; Lee, J. O.; Eisaki, H.; Uchida, S. *Nature* **1994**, 367, 252.
- (4) Dikshtein, I.; Koledov, V.; Shavrov, V.; Tulaikova, A.; Cherechukin, A.; Buchelnikov, V.; Khovailo, V.; Matsumoto, M.; Takagi, T.; Tani, J. *IEEE Trans. Magn.* **1999**, 35, 3811.
- (5) Evans, M. J.; Wu, Y.; Kranak, V. F.; Newman, N.; Reller, A.; Garcia-Garcia, F. J.; Haeussermann, U. *Phys. Rev. B* **2009**, 80, 064514.
- (6) Fernandez, J. F.; Cuevas, F.; Leardini, F.; Bodega, J.; Ares, J. R.; Garcés, G.; Perez, P.; Sanchez, C. *J. Alloys Compd.* **2010**, 495, 663.
- (7) Besenbacher, F.; Chorkendorff, I.; Clausen, B. S.; Hammer, B.; Molenbroek, A. M.; Norskov, J. K.; Stensgaard, I. *Science* **1998**, 279, 1913.
- (8) Studt, F.; Abild-Pedersen, F.; Bligaard, T.; Sorensen, R. Z.; Christensen, C. H.; Norskov, J. K. *Science* **2008**, 320, 1320.
- (9) Armbruster, M.; Kovnir, K.; Friedrich, M.; Teschner, D.; Wowsnick, G.; Hahne, M.; Gille, P.; Szentmiklósi, L.; Feuerbacher, M.; Heggen, M.; Girgsdies, F.; Rosenthal, D.; Schlogl, R.; Grin, Y. *Nat. Mater.* **2012**, 11, 690.
- (10) Shao, L.; Zhang, W.; Armbruster, M.; Teschner, D.; Girgsdies, F.; Zhang, B.; Timpe, O.; Friedrich, M.; Schlogl, R.; Su, D. S. *Angew. Chem., Int. Ed.* **2011**, 50, 10231.
- (11) Tao, F.; Grass, M. E.; Zhang, Y. W.; Butcher, D. R.; Renzas, J. R.; Liu, Z.; Chung, J. Y.; Mun, B. S.; Salmeron, M.; Somorjai, G. A. *Science* **2008**, 322, 932.
- (12) Tanabe, T.; Kameoka, S.; Tsai, A. P. *Catal. Today* **2006**, 111, 153.
- (13) Osswald, J.; Kovnir, K.; Armbruster, M.; Giedigleit, R.; Jentoft, R. E.; Wild, U.; Grin, Y.; Schloegl, R. *J. Catal.* **2008**, 258, 219.
- (14) Armbruster, M.; Kovnir, K.; Grin, Y.; Schlogl, R.; Gille, P.; Heggen, M.; Feuerbacher, M. Ordered Cobalt-Aluminum and Iron-Aluminum Intermetallic Compounds as Hydrogenation Catalysts, European Patent EP09157875.7, 2009.
- (15) Krajci, M.; Hafner, J. *J. Catal.* **2011**, 278, 200.
- (16) Armbruster, M.; Kovnir, K.; Behrens, M.; Teschner, D.; Grin, Y.; Schloegl, R. *J. Am. Chem. Soc.* **2010**, 132, 14745.
- (17) Armbruster, M.; Wowsnick, G.; Friedrich, M.; Heggen, M.; Cardoso-Gil, R. *J. Am. Chem. Soc.* **2011**, 133, 9112.
- (18) Villars, P. *Pearson's handbook: crystallographic data for intermetallic phases*; ASM International: Materials Park, OH, 1997.
- (19) Joshi, A. M.; Delgass, W. N.; Thomson, K. T. *J. Phys. Chem. B* **2006**, 110, 23373.
- (20) Woodham, A. P.; Meijer, G.; Fielicke, A. *Angew. Chem., Int. Ed.* **2012**, 51, 4444.
- (21) Yoon, B.; Häkkinen, H.; Landman, U.; Wörz, A. S.; Antonietti, J.-M.; Abbet, S.; Judai, K.; Heiz, U. *Science* **2005**, 307, 403.
- (22) Liu, Z.-P.; Hu, P.; Alavi, A. *J. Am. Chem. Soc.* **2002**, 124, 14770.
- (23) Liu, C.; Tan, Y.; Lin, S.; Li, H.; Wu, X.; Li, L.; Pei, Y.; Zeng, X. *J. Am. Chem. Soc.* **2013**, 135, 2583.