

Cite as: S. Yao *et al.*, *Science*
10.1126/science.aah4321 (2017).

Atomic-layered Au clusters on α -MoC as catalysts for the low-temperature water-gas shift reaction

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The water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$) is an essential process for hydrogen generation and CO removal in various energy-related chemical operations. This equilibrium-limited reaction is favored at a low working temperature. Potential application in fuel cells also requires a WGS catalyst to be highly active, stable and energy-efficient and match the working temperature of on-site hydrogen generation and consumption units. We synthesized Au layered clusters on an α -MoC substrate to create an interfacial catalyst system for the ultra-low-temperature WGS reaction. Water was activated over α -MoC at 303 Kelvin (K), while CO adsorbed on adjacent Au sites is apt to react with surface hydroxyl groups formed from water splitting, leading to a high WGS activity at low-temperatures.

Low-temperature efficient catalysts for the WGS reaction, especially those operating under 423 K (1–7), are of interest for applications in fuel cells, especially those use H_2 generated by hydrocarbon reforming processes that are contaminated with CO, which deactivates the catalysts. For the heterogeneous catalysis, besides Cu based catalysts which display low activity at low temperature, (8, 9) Pt group noble metals and Au supported on reducible metal oxides, like ceria (1) or FeO_x (10) which contain oxygen-vacancies, are commonly used. Flytzani-Stephanopoulos and co-workers demonstrated that noble metal catalysts dispersed on alkali promoted inert supports can also be active for WGS, making a reducible oxide support no longer a requirement (4, 6). The alkali ion-associated surface -OH groups are reactive toward CO in the presence of atomically dispersed platinum or gold, giving the catalyst superior metal atom efficiency in the WGS reaction. Metal carbide, (e.g. hexagonal closest packing (hcp) β - Mo_2C) supported noble metal catalysts provide similar functionalities and are more active for the reaction at low temperature (7, 11, 12). However, none of these systems displays an activity higher than 0.1 mol_{CO}/(mol_{metal}·s) between 393 and 423 K (Table 1).

In order to achieve high WGS activity at low temperature, we searched for catalysts that could dissociate water

efficiently and reform the generated oxygen-containing species (reaction of surface oxygen or hydroxyl with CO^*) at low temperature. We report that Au confined over face centered cubic (fcc) structured α -MoC is at least one order of magnitude more active than previous reports for the WGS reaction below 423 K. The α -MoC substrate facilitates epitaxially-grown atomic Au layers with altered electronic structure for favorable bonding with CO. Its synergy with adjacent Mo sites in α -MoC can effectively activate water at low temperature.

Gold supported over pure phase α -MoC catalysts were synthesized by a precipitation method followed by sequential temperature programmed ammonization and carburization. For comparative purposes, α -MoC, 2wt%Au/ β - Mo_2C (13, 14), 2wt%Au/ SiO_2 (15) and 2wt%Au/ CeO_2 (1) catalysts were also prepared. The high dispersion of Au for the 2wt%Au/ α -MoC catalyst was evidenced by the lack of x-ray diffraction (XRD) peaks associated with Au crystallites. Operando XRD studies (1% CO -3% H_2O -He, 10 ml/min) revealed that the bulk structure of the 2%Au/ α -MoC catalyst remained intact up to 523 K, beyond which the α -MoC was gradually oxidized by water (Fig. 1A). Ex-situ XRD experiments (10.5% CO -21% H_2O -20% N_2 -Ar, GHSV=180,000/h) confirmed that at higher water partial pressure, the bulk structure of

catalysts is stable up to 473 K. Neither the oxidation of α -MoC nor the aggregation of Au was observed at temperatures up to 473 K (fig. S1).

The WGS activity was evaluated under product-free (10.5%CO-21% H_2O -20% N_2 -Ar) and full reformate gas feeds (11%CO-26% H_2O -26% H_2 -7% CO_2 - N_2). In the product-free gas (GSVH=180,000 hours $^{-1}$), α -MoC shows very low CO conversion (3.4%) at 393 K (Fig. 1B), and none of the reference catalysts achieved > 5% CO conversion < 423 K. However, for the 2%Au/ α -MoC catalyst, CO conversion was > 95% at 393 K and reaching 98% at only 423 K. For reaction temperatures to 523 K and beyond, CO conversion dropped, which may result from the thermodynamic limitation as well as the gradual transformation of α -MoC to molybdenum oxide, as confirmed by the operando XRD results (Fig. 1A and fig. S2). The Au normalized activity of the 2%Au/ α -MoC catalyst in product-free gas was 0.012, 0.13, 1.05, 1.66 and 3.19 mol $_{CO}$ /(mol $_{Au}$ *s) at 313, 353, 393, 423 and 473 K, respectively, this high activity at low temperatures compares favorably with other reported WGS catalysts (Table 1, fig. S3, CO conversion below 15%). Due to the limitation of the water saturation vapor pressure, at low temperature the composition of reactant gas was adjusted). We determined that 2% is the optimal Au loading for the Au/ α -MoC catalyst (fig. S4).

In full reformate gas feed under similar space velocity, the activity dropped slightly (62% activity at 393 K) because of product (H_2 and CO_2) inhibition (Fig. 1D). However, the activity of the 2%Au/ α -MoC catalyst remained as high as 0.62 s $^{-1}$ and 2.02 s $^{-1}$ at 393 and 473 K, respectively. The apparent barriers E_{app} of α -MoC itself is actually low E_{app} value of 58 ± 10 kJ/mol, and even lower for the 2%Au/ α -MoC catalyst, 22 ± 1 kJ/mol. Thus, the addition of Au greatly enhanced the low-temperature reactivity of a good WGS catalyst (Fig. 1E). Its exceptional activity and high equilibrium CO conversion at low temperature can be exploited simultaneously (fig. S5), and the catalyst shows an excellent total turnover number (TTN), reaching up to 385400 mol $_{CO}$ /mol $_{Au}$ in a single-run reaction (fig. S6 and table S1).

We designed a two-step temperature programmed surface reaction (TPSR) experiment to explore the reaction route. After pre-activation of the catalysts, 2% H_2O /Ar (100 ml/min, 10 min) was introduced into the reactor at 303 K. Production of H_2 was immediately observed on both 2%Au/ α -MoC and α -MoC catalysts, indicating the presence of a low-temperature water dissociation center on α -MoC that led to the formation of H_2 and surface OH species (Fig. 2, A and B; see also figs. S7 and S8). In contrast, no H_2 production was observed on 2%Au/ SiO_2 or 2%Au/ β -Mo $_2C$ catalysts (Fig. 2C and fig. S9). After purging with Ar (100 ml/min), the system was then switched to 2% CO/Ar (100 ml/min) at 303 K, and kept at that temperature for 10 min and then increased to 523 K at 5 K/min. For the Au/ SiO_2

catalyst, only water desorption was observed at ~ 403 K. In sharp contrast, CO_2 and H_2 were detected simultaneously on the 2%Au/ α -MoC catalyst at around 308 K and their intensities reached the maxima at 367 K. Thus, the reaction of CO with surface OH could occur at very low temperature (308 K) to form CO_2 and additional H_2 . The reforming reaction can also happen on α -MoC catalyst, but initiating at a much higher initialing temperature (347 K).

The co-existence of a low-temperature water dissociation center on α -MoC and the low-temperature reforming center over the 2% Au/ α -MoC catalyst is the key for the extraordinary activity of this catalyst. The Au L_3 edge extended x-ray absorption fine structure (EXAFS) fitting (table S2 and fig. S10) shows a low Au-Au first shell coordination number(CN) of 6.9 indicates that the average size of Au species is ~ 1.5 nm for a hemispherical morphology (16). The Au-Mo CN of 1.6 is particularly striking given that Au nanoparticles (NPs) tend to undergo sintering because of the low Tammann temperature (668 K) of bulk Au. (17, 18) Given that this sample was activated at 973 K for more than 2 hours, a strong metal-support interaction must exist between Au and α -MoC. X-ray photoelectron spectroscopy (XPS) (fig. S11) revealed that the Au 4f binding energy shifted 0.6 eV to higher energy with respect to bulk gold (19), indicating that the electronic structure of the Au species is perturbed by the substrate. The reaction order of CO of -0.16 (Fig. 1D), also indicated that CO was already relatively strongly adsorbed on the electronically modified Au surface.

Aberration-corrected scanning transmission electron microscopy (STEM) analysis on the 2%Au/ α -MoC catalyst showed that the catalyst supports were porous assemblies of small α -MoC NPs (3 to 20 nm in diameter, fig. S12). High resolution STEM Z-contrast imaging (Fig. 2, D and E) revealed two types of Au species on the surface of α -MoC, small Au layered clusters epitaxially grown on the α -MoC support and atomically dispersed Au. The epitaxial Au clusters had an average diameter of 1 to 2 nm and thickness of 2 to 4 atomic layers (<1 nm), as measured from edge-on clusters occasionally found in profile view (Fig. 2E and fig. S13). Detailed crystal structure analysis (fig. S12, C and D) also showed that these epitaxial Au clusters strongly aligned with the (111) planes of the α -MoC support, with some exposed (200) facets. There were no larger Au NPs present in this sample (fig. S14). No obvious structural difference was observed between the fresh and the used catalyst samples (Fig. 2F), and both types of Au species were retained in the tested sample, which is also consistent with the relatively good stability of the catalyst noted in the catalytic reaction.

We used NaCN solution to selectively leach the layered Au clusters from the 2% Au/ α -MoC catalyst (1, 20). The Au loading decreased to around 0.9 wt%, leaving predominantly the atomically dispersed Au atoms, which was confirmed

by both STEM and XAFS results (Fig. 2G; fig. S12, E to G; and table S2). The Au normalized WGS activity of 0.9% Au/ α -MoC (NaCN) at 393 and 423 K decreased to around 1/11 and 1/6 of their original values respectively, but was still higher than that of NaCN-leached α -MoC catalyst (with activation barrier similar to that of fresh α -MoC, Fig. 1E). This result indicated that atomically dispersed Au species were indeed catalytically active (I), but the catalytic efficacy of the layered Au clusters on α -MoC support for low temperature WGS was even higher than the atomically dispersed Au. Furthermore, the E_{app} increased to 41 kJ/mol after NaCN leaching (Fig. 1E), suggesting some degree blocking of the low-temperature reaction route after the removal of layered Au clusters. Thus, we attribute the low-temperature WGS activity mainly to the epitaxial Au clusters decorating the α -MoC support.

We carried out DFT calculations to investigate the WGS reaction path on the Au/ α -MoC catalyst. Three catalyst models (see fig. S15) of Au (111), monolayer Au/ α -MoC (111) and cluster Au₁₅/ α -MoC (111) were constructed to represent the different sites on Au/ α -MoC, in which Au (111) and monolayer Au/ α -MoC (111) simulate large Au NPs and electronic property modified Au NPs, respectively. Au₁₅/ α -MoC (111) represents the interface model of our atomic-layered Au cluster over α -MoC (111). Similar to experimental observations, the Au cluster in Au₁₅/ α -MoC has a layered structure, with (111) and (200) type exposed facets.

As shown in fig. S16, H₂O is hard to dissociate on Au (111) and monolayer Au/ α -MoC (111) thermodynamically and kinetically, with barriers of 1.91 and 1.66 eV, and the reactions are endothermic by 1.57 and 1.15 eV, respectively. In contrast, when we investigated the first step of WGS, namely water dissociation, on Au₁₅/ α -MoC (111), we found that at lower coverage (Fig. 3A), two H₂O molecules could be easily dissociated and form two H atoms and two OH species with the effective barrier of 0.77 eV ($\text{CO} + 2\text{H}_2\text{O} \rightarrow \text{CO} + 2\text{OH} + 2\text{H}$), and the two OH can immediately react (and without barrier), forming a surface O atom ($\text{CO} + 2\text{OH} + 2\text{H} \rightarrow \text{CO} + \text{H}_2\text{O} + \text{O} + 2\text{H}$, it is exothermic by 0.38 eV). These results indicate that some surface domains of α -MoC could be oxidized by water during the reaction, which has been confirmed by XPS and ¹⁸O nuclear magnetic resonance experiments (figs. S7 and S8). After the surface was partially decorated with oxygen (Fig. 3B), the calculations found that surface O atoms could further promote water dissociation. The successive O-assisted water dissociation ($\text{CO} + 3\text{O} + \text{H}_2\text{O} \rightarrow \text{CO} + 2\text{O} + 2\text{OH}$) on the boundary of Au₁₅ and α -MoC (111) had a much lower barrier of 0.22 eV, indicating that the first O-H bond of water could be easily broken at low temperature by this bifunctional catalyst.

The formed surface OH species on the Mo site was apt to react with CO adsorbed on the adjacent Au surface, which

has the right geometry (triangular) to enable a low reaction barrier. Indeed, at low CO coverage (Fig. 3A), the effective barrier for the reforming of CO on Au and OH on α -MoC (111) is 0.72 eV, including a migration barrier of 0.22 eV and the reaction barrier of 0.50 eV. At high CO coverage (Fig. 3C), the reforming barrier was even lower, *i.e.* 0.52 eV, demonstrating that the reaction between adsorbed CO and surface OH species on the peripheral interface of Au and α -MoC ($\text{CO} + \text{OH} = \text{CO}_2 + \frac{1}{2}\text{H}_2$) was apt to proceed. Although the reforming process was facile, it still had a higher barrier than the first step of the WGS reaction, *i.e.*, water dissociation on partially oxidized α -MoC. Thus, the rate-determining step of the WGS process over Au₁₅/ α -MoC is the reforming process, which is in good agreement with our TPSR observations (Fig. 2). The interfacial nature and optimum bonding of this α -MoC confined Au nanostructure that confers the catalyst with outstanding WGS reactivity at low temperature.

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ACKNOWLEDGMENTS

This work received financial support from 973 Project (2017YFB0602200, 2013CB933100, 2011CB201402), CAS Pioneer Hundred Talents Program, and the Natural Science Foundation of China (91645115, 21473003, 21222306, 21373037, 21577013 and 91545121). The electron microscopy work was also supported in part by the U.S. Department of Energy, Office of Science, Basic Energy Science, Materials Sciences and Engineering Division (W.Z.), and through a user project at ORNL's Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility. The XAS experiments were conducted in SSRF and BSRF. We also acknowledge National Thousand Young Talents Program of China, the CAS Hundred Talents Program, the Shanxi Hundred Talent Program and the Fundamental Research Funds for the Central Universities (No. DUT15TD49 and DUT16ZD224). The research done at Brookhaven National Laboratory (BNL) was financed under Contract No. DE-SC0012704 with the U.S. Department of Energy. Part of the theoretical calculations were done at the Center for Functional Nanomaterials in the BNL campus. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. YY acknowledges the support of the ALS Doctoral Fellowship. CJK gratefully acknowledges funding from the National Science Foundation Major Research Instrumentation program (GR# MRI/DMR-1040229). D.M thanks L. Peng and M. Wang for help in ¹⁷O NMR experiments. All data are reported in the main text and supplement. C. S. and X.Z. are inventors on patent application (ZL 2015 1 0253637.6) held by Dalian University of Technology that covers the preparation of Au/α-MoC. Author contributions: D.M, C.S., and J. A. R., designed the study. X. Z. and S. Y., performed most of the reactions. W. Z., L.L., C.J.K., and L.G. performed the electron microscopy study. R.G. X.-D.W., P. L., and Z. Z. finished the DFT calculation. S.Y., Q.W. and W.L. performed the X-ray structure characterization and analysis. S.Y., D.M., W.Z., and J.A.R. wrote the paper. Other authors provided reagents, performed the certain experiments and revised the paper.

SUPPLEMENTARY MATERIALS

www.sciencemag.org/cgi/content/full/science.aah4321/DC1
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26 June 2016; resubmitted 12 April 2017

Accepted 9 June 2017

Published online 22 June 2017

10.1126/science.aah4321

Table 1. Comparison of the activities over the representative catalytic systems for low-temperature WGS reaction.

	Temp (K)	Gas feed composition	Mass specific activity [$\mu\text{mol}_{\text{CO}}/(\text{g}_{\text{cat}}\cdot\text{s})$]	Metal normalized activity [$\text{mol}_{\text{CO}}/(\text{mol}_{\text{metal}}\cdot\text{s})$]	Apparent activation energy (kJ/mol)	Ref
Reducible oxide supports						
Au/CeO ₂	523	11%CO-26%H ₂ O-26%H ₂ -7%CO ₂ -He	4.8	0.13	37	(1)
Pt/CeO ₂	523	11%CO-26%H ₂ O-26%H ₂ -7%CO ₂ -He	22	0.17	75	(1)
Ir ₁ /FeO _x	573	2%CO-10%H ₂ O-He	1.2	2.32	50	(21)
Au/FeO _x	598	11%CO-26%H ₂ O-26%H ₂ -7%CO ₂ -He	11	0.31	49	(22)
Alkali promoted inert supports						
Au-Na/MCM41	423	11%CO-26%H ₂ O-26%H ₂ -7%CO ₂ -He	0.8	0.067	44	(5)
Pt-Na/SiO ₂	523	11%CO-26%H ₂ O-26%H ₂ -7%CO ₂ -He	12	0.24	70	(4)
Pt-Na/CNT	473	2%CO-10%H ₂ O-He	1.25	0.024	70	(23)
Molybdenum carbide supports (β-Mo₂C)						
Pt/Mo ₂ C	513	11%CO-21%H ₂ O-43%H ₂ -6%CO ₂ -N ₂	221	1.42	53	(11)
Pt/Mo ₂ C	393	7%CO-22%H ₂ O-37%H ₂ -8.5%CO ₂ -Ar	1.8	0.023	48	(12)
Au/Mo ₂ C	393	7%CO-22%H ₂ O-37%H ₂ -8.5%CO ₂ -Ar	1.6	0.021	44	(12)
Homogeneous catalysts						
Ru ₃ (CO) ₁₂	373	1 bar CO/NaOH solution	0.12	2.6 E-5	-	(24)
Our results						
2% Au/ α -MoC	313	3%CO-6%H ₂ O-20%N ₂ -Ar	1.22	0.012		
	333	5%CO-10%H ₂ O-20%N ₂ -Ar	5.91	0.06		
	353		13.06	0.13		
	393		103	1.05		-
	423	10.5%CO-21%H ₂ O-20%N ₂ -Ar	167	1.66	22†	
	473		325	3.19		
2% Au/ α -MoC	333	5%CO-10%H ₂ O-10%H ₂ -3%CO ₂ -N ₂	2.39	0.02		
	353		9.20	0.09		
	393		53	0.62		-
	423	11%CO-26%H ₂ O-26%H ₂ -7%CO ₂ -N ₂	106	1.05	27	
	473		213	2.02		
0.9% Au/ α -MoC (NaCN)	393	10.5%CO-21%H ₂ O-20%N ₂ -Ar	9.07	0.09		
	423		26.6	0.26	41	-
	473		73.1	0.72		
2%Au/ β -Mo ₂ C	393	11%CO-26%H ₂ O-26%H ₂ -7%CO ₂ -N ₂	2.06	0.02		
	423		4.29	0.04	38	-
	473		14.4	0.14		
α -MoC	393	11%CO-26%H ₂ O-26%H ₂ -7%CO ₂ -N ₂	2.05			
	423		8.57		64	-
	473		56.7			
2% Au/SiO ₂	673	10.5%CO-21%H ₂ O-20%N ₂ -Ar	0.24	2.4 E-3		
2% Au/CeO ₂	423	11%CO-26%H ₂ O-26%H ₂ -7%CO ₂ -N ₂	1.1	0.01		

*The operating pressure of the catalysts listed is 1 bar.

†The activation energy was also determined by another method, see fig. S17.

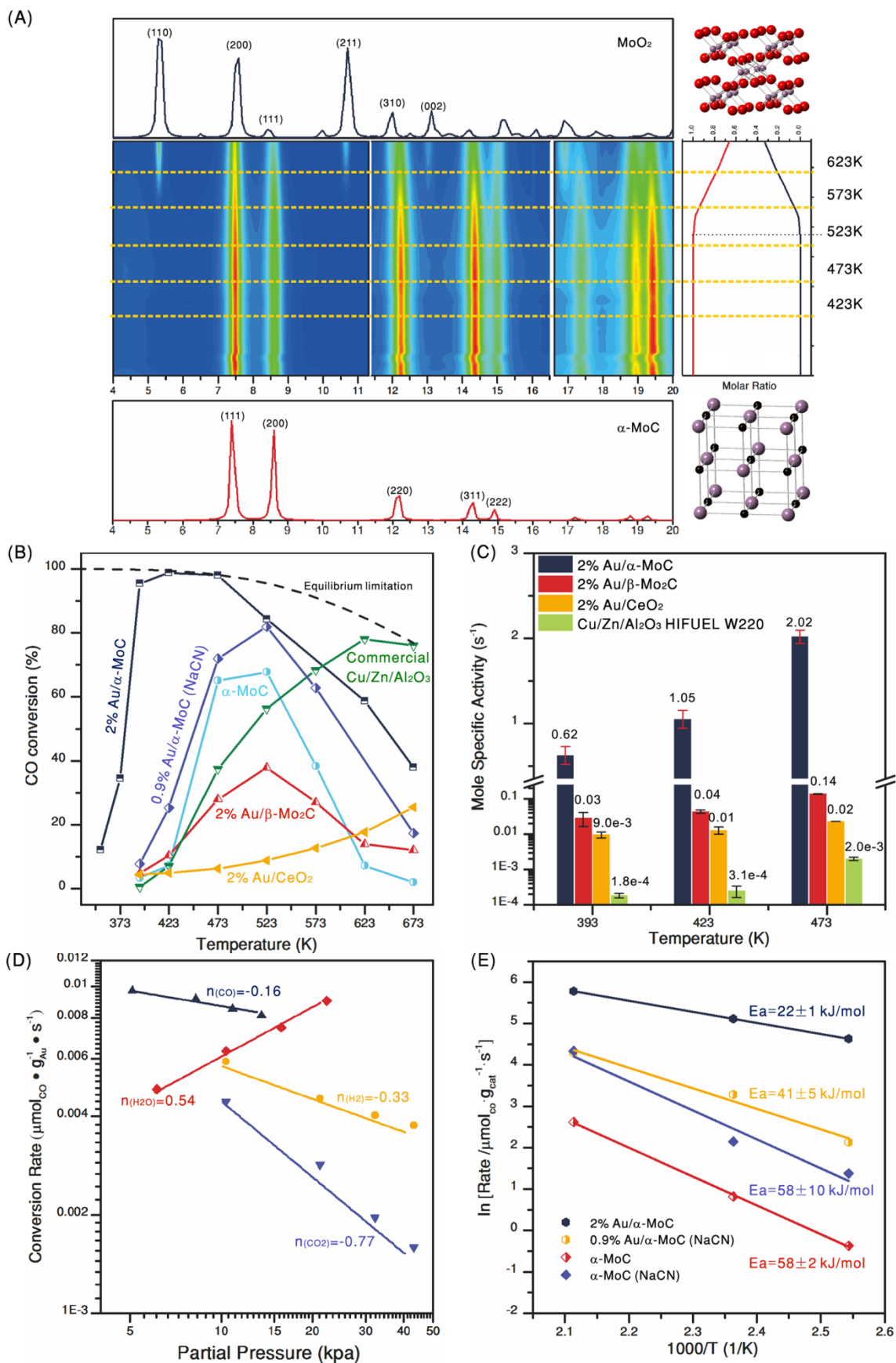


Fig. 1. Catalytic properties and structural characterization of 2% Au/ α -MoC catalyst. (A) In-situ XRD ($\lambda=0.3196$ Å) of 2% Au/ α -MoC catalyst under WGS reaction conditions at various temperatures. (B) CO conversion on different catalysts at various temperatures. (Reaction condition: 10.5% CO, 21% H₂O, 20% N₂ in Ar; GHSV: 180,000 hours⁻¹). (C) The activity of different catalysts (unit mol_{CO}/(mol_{metal}.s), (measured at CO conversion below 15% in 11% CO-26% H₂O-26% H₂-7% CO₂-30% N₂). (D) Kinetic orders of the reactants and products. (E) Apparent activation energy E_{app} of various catalysts in 10.5% CO-21% H₂O-20% N₂-Ar balance.

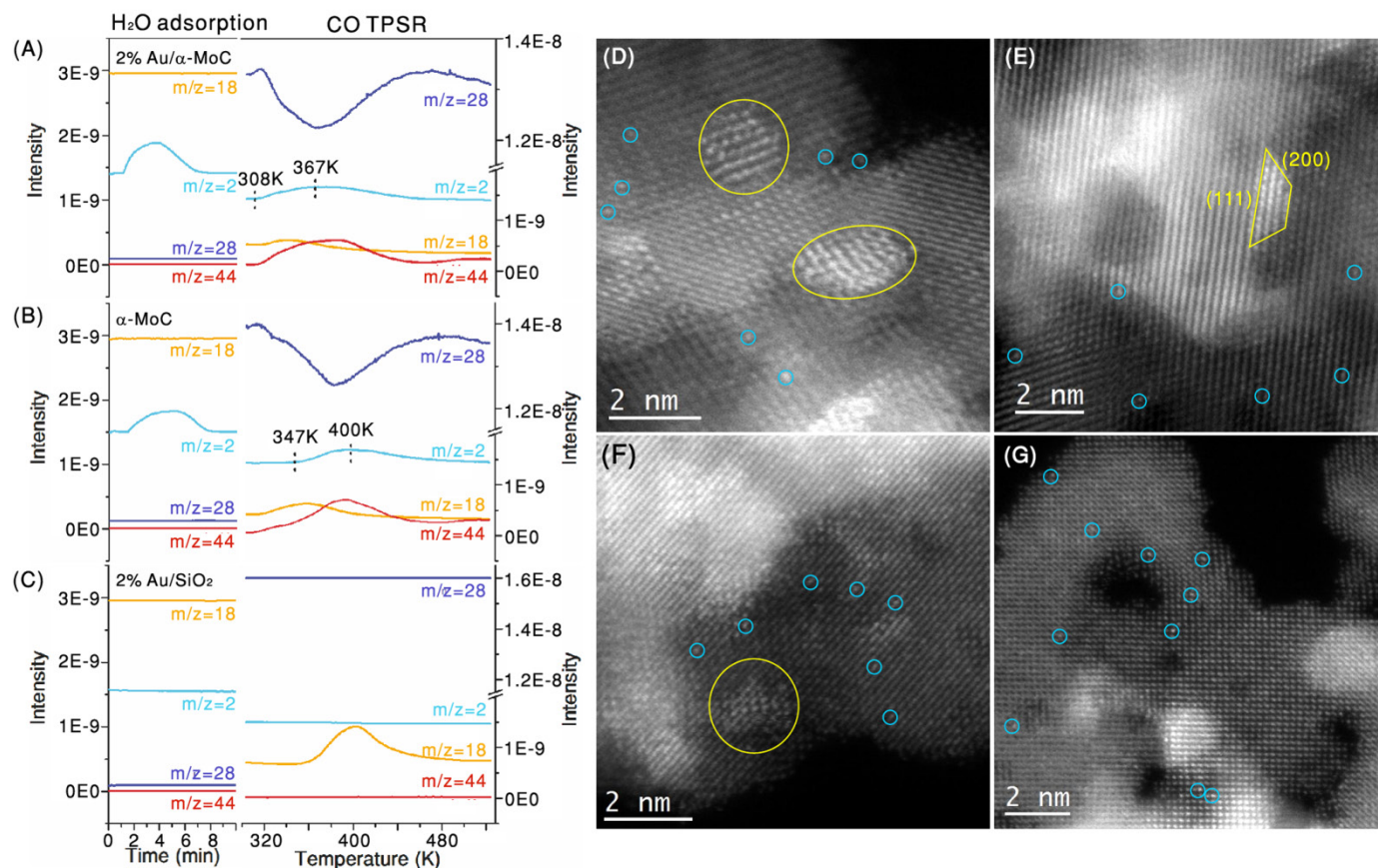


Fig. 2. Mechanism study and electron microscopy characterization. Water adsorption (at 303 K) followed by CO-TPSR on 2% Au/α-MoC (A), α-MoC (B) and 2% Au/SiO₂ (C). Signals of H₂ (m/z=2), H₂O (m/z=18), CO (m/z=28) and CO₂ (m/z=44) were detected. (D and E) High-resolution HAADF-STEM images of 2% Au/α-MoC fresh catalyst, with single atoms of Au marked in blue circles and Au layered-structures highlighted in yellow. The Au clusters were further identified by elemental analysis (figs. S18 and S19). (F) HAADF-STEM image of 2% Au/α-MoC catalyst after reaction in which sample still contains both single-atom Au and Au layered-clusters. (G) HAADF-STEM image of the NaCN leached 2% Au/α-MoC catalyst, showing predominantly single atom Au, most of which overlap with Mo sites in the support lattice. Note that the very bright features in this image are caused by overlapping MoC particles, as confirmed by elemental mapping (figs. S18 and S19).

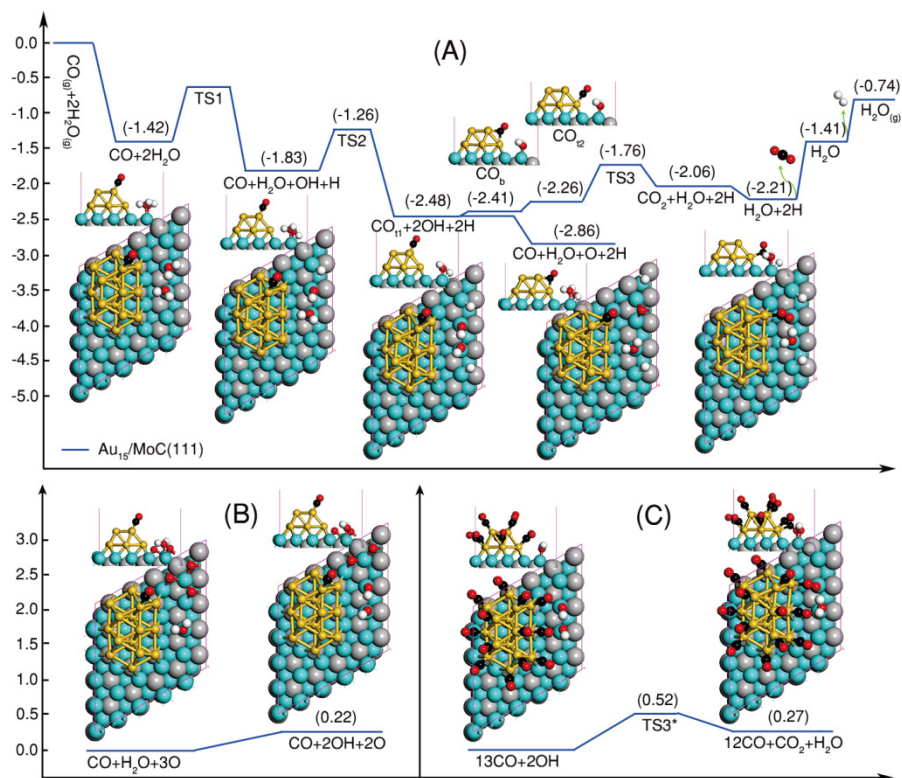


Fig. 3. The reaction paths for the water-gas shift reaction on $\text{Au}_{15}/\alpha\text{-MoC}(111)$. (A) H_2O dissociation and CO reforming at lower coverage, (B) O-assisted H_2O dissociation on the boundary oxidized by 3 O atoms and (C) CO reforming at high coverage. The energies of gaseous molecules have included the zero-point energy (ZPE) and entropy correction at 423 K. Au, Mo, C, O and H atoms are shown in gold, cyan, gray, red and white, respectively; while in order to make a distinction for the C atom from CO, it is represented by dark gray.

Atomic-layered Au clusters on α -MoC as catalysts for the low-temperature water-gas shift reaction

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published online June 22, 2017

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