# Environmental TEM Study of the Dispersion of Au/ $\alpha$ -MoC: From Nanoparticles to Two-Dimensional Clusters

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Cite This: Nano Lett. 2023, 23, 10367-10373 **Read Online** ACCESS III Metrics & More Article Recommendations Supporting Information ABSTRACT: The synthesis of highly dispersed Au nanoclusters that are stable under elevated temperatures in heterogeneous catalysis is challenging. Here, we directly observe a strong metalsupport interaction (SMSI)-induced dispersion of Au nanotering Au 2D clusters Au NPs particles (NPs) on  $\alpha$ -MoC using an environmentally atomically Elevated resolved secondary imaging technique. Under a realistic environtemperatures

ment, Au NPs flatten and spread out on the  $\alpha$ -MoC to form twodimensional atomic layered clusters. The formed highly dispersed Au/ $\alpha$ -MoC catalyst shows excellent stability at 600 °C for 160 h in the reverse water-gas shift reaction. The X-ray photoelectron spectrum and extended X-ray absorption fine structure results show that Au NPs gradually become low-coordination-number cluster species and lose electrons to become Au<sup> $\delta$ +</sup>; these form



chemical bonds with the  $\alpha$ -MoC support and are responsible for the dispersion behavior. This work provides an insightful understanding of dispersion behavior and promotes the rational design and synthesis of reverse sintering catalysts.

**KEYWORDS:** environmental TEM, second electron imaging, dispersion, strong metal-support interaction

n contrast to bulk Au, supported Au NPs have attracted L increasing interest due to their high catalytic activity in various important reactions.<sup>1-5</sup> Extensive research has highlighted the size dependence of catalytic performance, demonstrating that relatively larger Au clusters exhibit enhanced activity compared to larger NPs or single atoms.<sup>9,7</sup> However, a major obstacle in the application of Au nanocatalysts is their low thermal stability since supported Au NPs tend to irreversibly sinter into larger NPs at elevated temperatures, resulting in catalyst deactivation.<sup>8-10</sup> To improve the thermostability of Au nanocatalysts, various supports have been utilized to modulate the size and coordination environment of the deposited Au species through metal-support interactions, thereby stabilizing highly dispersed Au species. Carbides have recently attracted considerable attention among different support materials due to their strong metal-support interaction (SMSI) and intrinsic catalytic activity. 11-13 It has been reported that highly dispersed Au clusters or even atomically dispersed single atoms can form on carbides, leading to unique catalytic performances. The structural evolution of Au catalysts supported on carbides has been monitored using in situ techniques, such as X-ray diffraction (XRD) and extended Xray absorption fine structure (EXAFS), confirming the dynamic destruction process of the supported Au NPs during preparation.<sup>14</sup> However, detailed atomic-scale information regarding the evolution of the supported Au species and the atomic configurations of the final Au species remains unknown,

impeding a comprehensive understanding of the structureactivity relationship of these novel catalysts. Although in situ transmission electron microscopy (TEM) is a state-of-the-art technique for visualizing the atomic-scale evolution of nanomaterials,<sup>15–17</sup> the high mass density and irregular shape of carbide materials pose challenges for in situ TEM observation. Therefore, the development of a new microscopic approach is required to directly visualize the structural evolution of molybdenum-carbide-supported Au NPs, enabling a comprehensive understanding of the reversible sintering process, irrespective of the properties of the supports.<sup>15,18-2</sup> In our previous work,<sup>21</sup> we successfully utilized in situ atomically resolved secondary electron (SE) imaging techniques to directly visualize the topographic surface structure of Mo<sub>2</sub>N-supported Ni NPs under a realistic chemical environment; our results provided dynamic information regarding the dispersion of Ni atoms induced by SMSI. This study further examines the application of this advanced microscopic method in studying unique systems, which have not been previously accomplished.

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**Figure 1.** (a) STEM-SE image of an  $\alpha$ -MoC nanobelt. (b) HRSTEM-ADF image of a selected area from the nanobelt (marked by a dashed line). (c) STEM-SE image of the precursor; the inset shows the diameter distribution of supported Au NPs (based on 214 NPs). EDX mapping of (d) Au and (e) overlap of Mo and Au. (f) STEM-SE images of Au/ $\alpha$ -MoC after activation. (g) HRSTEM-ADF image of a selected area from the activated nanobelt is shown in (f) (marked by a dashed line). (h) Corresponding EDX mapping overlap of Mo and Au and integrated X-ray spectra of Au extracted from two selected areas marked as area 1 and area 2 in (g and h).<sup>24</sup>

In this study, we synthesized  $\alpha$ -MoC-supported Au nanocatalysts and used atomically resolved SE imaging to investigate the dispersion process of the Au NPs under realistic carbonation conditions. Aberration-corrected environmental TEM (AC-ETEM) observations showed that Au NPs gradually flattened and spread out on  $\alpha$ -MoC at elevated temperatures, ultimately forming epitaxially aligned 2D atomiclayered clusters (2D ALCs) that exhibit a high lattice match with  $\alpha$ -MoC. Furthermore, EXAFS results showed a gradual decrease in coordination numbers (CNs) and bond distances of Au-Au during the carbonation process, confirming the dispersion behavior of the Au NPs. Notably, the CNs of Au-Mo significantly increased, indicating the spreading and bonding of Au NPs with  $\alpha$ -MoC supports. The decreased bond distance of Au-Mo verified the tighter coverage of the 2D ALCs on the  $\alpha$ -MoC support. X-ray photoelectron spectroscopy (XPS) analysis demonstrated that as Au redispersed on  $\alpha$ -MoC it underwent electron loss, resulting in the formation of Au<sup> $\delta$ +</sup>. Importantly, the formed 2D Au ALCs exhibited excellent structural stability, showing no sintering at 600 °C even after 160 h during the high-temperature reverse water-gas shift (HTRWGS) reaction. Our results showed the dispersion nature of Au supported on  $\alpha$ -MoC and the characteristic atomic configuration of the formed Au clusters, providing valuable insights into the rational design of highly active Au catalysts with exceptional stability and sintering resistance.

 $\alpha$ -MoC with a nanobelt shape was prepared via carburization of MoO<sub>3</sub>, following the methodology described in the literature.<sup>22,23</sup> Scanning transmission electron microscopesecond electron (STEM-SE) images (Figure 1a) confirmed the successful synthesis of belt-like  $\alpha$ -MoC. The STEMannular dark field (STEM-ADF) image (Figure 1b) and the corresponding larger view high-resolution STEM-SE (HRSTEM-SE) image (Figure S1) indicated that the surface of  $\alpha$ -MoC is dominantly exposed to the (100) plane. Subsequently, the  $\alpha$ -MoC-supported Au NP (Au/ $\alpha$ -MoC) catalyst was prepared using the impregnation reduction method (see Supporting Information for details). The XRD pattern of the prepared Au/ $\alpha$ -MoC catalyst exhibited excellent agreement with the diffraction profile of  $\alpha$ -MoC (Figure S2), while no diffraction peak corresponding to metallic Au was observed. This absence was attributed to the low loading amount and small size of the Au NPs. The STEM-SE image (Figure 1c) shows that the Au NPs were dispersed on the surface of the nanobelts and were primarily loaded on the (100) planes, as also shown in the low-magnification image of the Au/ $\alpha$ -MoC catalyst (Figure S3a-d), HRSTEM-SE image (Figure S1), and energy-dispersive X-ray (EDX) mapping results (Figure 1d,e). The average diameter of the Au NPs was ~6.9 nm (see the inset in Figure 1c).

Upon carburization of the as-prepared Au/ $\alpha$ -MoC catalyst in a 20% CH<sub>4</sub>/80% H<sub>2</sub> atmosphere at 550 °C, the STEM-SE image (Figure 1f) showed that no Au NPs were observed on the nanobelt, and the belt-like shape of the  $\alpha$ -MoC support did not change. The XRD spectrum confirmed that the structure of the  $\alpha$ -MoC remained unchanged (Figure S2). Lower magnification STEM images (Figure S3e-h) further confirmed the absence of Au NPs on the  $\alpha$ -MoC nanobelts. However, different from the EDX elemental mapping results of Au/ $\alpha$ -MoC (Figure 1d,e), the EDX elemental mapping of the carburized sample showed the uniform dispersion of Au species throughout the  $\alpha$ -MoC nanobelt (Figure S4), indicating the disintegration of Au NPs into smaller clusters or even single atoms. Notably, in comparison to the  $\alpha$ -MoC support, the HRSTEM-ADF image of the activated sample



**Figure 2.** In situ SE observation of the dispersion process of the Au NPs supported on  $\alpha$ -MoC. The activation gas is 20% CH<sub>4</sub>/80% H<sub>2</sub>, and the partial pressure around the catalysts is ~1.9 Pa. (a–d) STEM-SE images of the Au NPs at different temperatures. (e–h) STEM-SE images of the dispersion processes of Au NPs at 550 °C at different times.



**Figure 3.** (a) HRSTEM-SE image of the P2 region from Figure 2e. FFT patterns from area 1 and area 2 (marked by dashed line) indicate the presence of  $\alpha$ -MoC (100) and fcc Au (111) planes, respectively. (b) HRSTEM-SE image of the P2 region from Figure 2h; the inset shows the EDX line scan of Au. FFT patterns from area 1 and area 2 show identical features, corresponding to  $\alpha$ -MoC (100) planes. (c) Filtered HRSTEM-SE image based on area 2 in (b). (d) Schematic illustration of the dispersion process of a Au NP supported on  $\alpha$ -MoC.

(marked by a white dashed box in Figure 1f) exhibited inhomogeneous contrast distributions that were even more pronounced (Figure 1g). Nevertheless, the FFT pattern displayed characteristics identical to those of  $\alpha$ -MoC (Figure S5), indicating the preservation of its crystal structure. To investigate the distribution of the Au species, EDX mapping analysis was conducted (Figure 1h) and showed that inhomogeneous distributions of Au species correlated well with the observed contrast variations. Furthermore, the integrated EDX spectrum from the selected brighter area (area 1 in Figure 1g,h) confirmed the enrichment of the Au species in the brighter area compared with the darker area (area 2 in Figure 1g,h). This result indicated that the Au NPs dispersed into ALCs with an identical structure to that of  $\alpha$ -MoC. The comparison of the Au/ $\alpha$ -MoC catalyst before and after carburization confirmed the dispersion of larger Au NPs.

This observation highlighted the vital role of the support and rationalized the significance of the interaction between the support and Au NPs.

Additionally, *ex situ* characterizations may be influenced or even contaminated by exposure to the outer atmosphere and subsequent transferring processes. To visualize this unique process at atomic scales and under realistic *in situ* conditions, activation experiments were conducted using an AC-ETEM equipped with ADF and SE detectors, which enabled the spontaneous acquisition of STEM-ADF and STEM-SE images under realistic reaction conditions. The Au/ $\alpha$ -MoC catalysts were loaded onto heating chips, and a gas mixture of 20% CH<sub>4</sub>/80% H<sub>2</sub> was introduced into the ETEM column. An area of interest was carefully selected for *in situ* characterization, as indicated in the STEM-SE image shown in Figure 2a (also see Figure S6). A series of STEM-SE images were collected at



**Figure 4.** (a) Au 4f XPS spectra of the Au/ $\alpha$ -MoC catalyst that was as-prepared, activated for 30 min, and activated for 120 min. XPS fitting results of the samples that were (b) as-prepared and (c) activated for 120 min. (c) Au L<sub>3</sub> edge EXAFS (line) spectrum and curve fitting (hollow dotted line) for the samples of Au foil, as-prepared, activated for 30 min, and activated for 120 min. The fitting parameters are given in Table S1.

different temperatures (Figure 2a–d). Notably, these NPs remained unchanged before 450 °C. However, once the temperature reached 550 °C, the three smaller Au NPs vanished (Figure 2c,d), leaving behind a noticeably brighter area where the NPs had previously been present, which indicated that the temperature is the key factor in this phenomenon. Notably, sintering did not occur under these conditions since the diameters of the neighboring Au NPs did not increase. Since 550 °C represented the actual activation temperature, this temperature was maintained for further investigation of the dispersion process of the Au NPs, denoted as P1, P2, and P3 in Figure 2d.

Upon activation of the support surface, P1 and P2 underwent elongation and flattening processes after 13 min (Figure 2e). Subsequently, P1 and P3 almost disappeared after 23 min, while P2 exhibited a slight elongation (Figure 2f). By the 34th min, P1 and P3 had completely vanished, and P2 had significantly shrunk. After 45 min, all three Au NPs had disappeared, resulting in a uniformly distributed contrast throughout the area. The STEM-ADF image and corresponding EDX mapping results (Figure S7a-c, with respect to Figure 2a) confirmed the presence of Au NPs. However, following activation, the STEM-ADF image and corresponding EDX mapping results (Figure S7d-f, with respect to Figure 2h) exhibited a uniform distribution of Au species throughout the  $\alpha$ -MoC support. Both the *in situ* SE (Figure 2) results and EDX data (Figure S7) confirmed the irreversible dispersion of the Au NPs on the  $\alpha$ -MoC and demonstrated the uniform distribution of Au mass.

To gain insights into the dispersion process at the atomic scale, an area including P2 was selected for atomic-resolved STEM-SE imaging at 13 (Figure 3a) and 45 min (Figure 3b). At 13 min, P2 remained undispersed, and surface atom configuration analysis was performed on the  $\alpha$ -MoC support (area 1) and P2 (area 2). Clearly, a noticeable difference was observed between the fast Fourier transform (FFT) patterns of areas 1 and 2 (Figure 3a). The FFT pattern of area 1 corresponded to the  $\alpha$ -MoC (100) planes, while the FFT pattern of area 2 corresponded to the fcc Au (111) planes. At 45 min, P2 had vanished, and the FFT patterns of area 1 and area 2 appeared the same, both corresponding to the  $\alpha$ -MoC (100) planes. The filtered atomically resolved STEM-SE image (Figure 3c) based on area 2 in Figure 3b confirmed the wellordered surface atom configuration of the  $\alpha$ -MoC (100) planes, in agreement with both the FFT and XRD data. This result indicated that after the dispersion of the Au NP the surface atom configuration remained identical with that of the support. However, an EDX line scan across area 2 (the inset in Figure 3b) and corresponding X-ray spectra (Figure S8) indicated that this area was covered by Au,<sup>24</sup> providing evidence for the formation of epitaxial 2D ALCs on the  $\alpha$ -MoC (100) planes. Notably, the lattice parameters of Au (2.04) Å for (200)) closely resembled those of  $\alpha$ -MoC (2.11 Å for (200)), indicating that this could potentially be one of the driving forces behind the dispersion behavior of the Au NPs on  $\alpha$ -MoC. Furthermore, we observed that not only smaller Au NPs with high surface energy underwent dispersion but also relatively stable larger Au NPs (~12 nm in diameter) dispersed



Figure 5. (a) Catalytic performance of the 1% Au/ $\alpha$ -MoC catalyst in the HTRWGS reaction at 600 °C. The feed gas is composed of 23% CO<sub>2</sub>, 69% H<sub>2</sub>, and 8% N<sub>2</sub>, and the gas hourly space velocity is 900000 mL·g<sup>-1</sup>·h<sup>-1</sup>. (b) STEM-SE and (c) STEM-ADF images of the 1% Au/ $\alpha$ -MoC catalyst after 160 h of reaction. (d) HRSTEM-ADF and (e) HRSTEM-SE images of a selected area of the nanobelt shown in (c) and corresponding EDX mapping of (f) Au and (g) overlap of Mo and Au.

in reverse on  $\alpha$ -MoC, as illustrated in Figure S9 and Figure S10. Combining this with the atomically resolved STEM-ADF image in Figure 1g, we concluded that at elevated temperatures Au NPs underwent dispersion on  $\alpha$ -MoC, spreading throughout the support surface and ultimately forming 2D ALCs that lattice-matched with  $\alpha$ -MoC.

To obtain a comprehensive understanding of the dynamic structural evolution of supported Au NPs under activation conditions, spectroscopic tools were used to determine the chemical state and coordination environment of the Au catalysts. *Ex situ* XPS experiments were conducted (see Supporting Information for details) to characterize the chemical states of Au that were activated at different times. Figure 4a displays the normalized Au 4f spectra of the precursor, as well as the samples activated for 30 and 120 min. In the spectrum of the precursor, the binding energy of Au  $4f_{7/2}$  located at 84.4 eV corresponded to Au<sup>0</sup> species.<sup>25,26</sup>

However, after activation for different durations, the full width at half-maximum (fwhm) of the Au 4f peaks broadens, indicating a decrease in particle sizes and changes in the chemical states of the Au species<sup>27</sup> due to the activation treatment. Compared to the Au 4f peak, the deconvoluted Au 4f profiles of the activated samples show the presence of Au<sup> $\delta$ +</sup> species with a binding energy of 86.2 eV. The XPS results suggest that during the activation process Au loses a certain amount of electrons, leading to the formation of Au<sup> $\delta$ +</sup>. The spectroscopic evidence indicates a chemisorption-like interaction between clusters and supports,<sup>27</sup> which is likely the driving force behind the dispersion behavior of the Au NPs on  $\alpha$ -MoC. It is plausible that the Au atoms in the 2D ALCs strongly bond with the  $\alpha$ -MoC support, further preventing ALC sintering.

The Au L<sub>3</sub> edge *ex situ* EXAFS spectra of the Au/ $\alpha$ -MoC samples were analyzed to study the coordination environment

and bonding conditions of the Au atoms. Overall, with increasing activation time, the peak intensity in R-space associated with the average first shell Au-Au CNs decreased,<sup>14</sup> and the peak locations associated with average bond distances shifted to lower values (Figure 4c and Figure S11). For the precursor, the shape of the first shell peak was similar to that of the Au foil. The curve fitting results showed that the CNs and bond distance of the Au-Au first shell were 10.7 and 2.86 Å,<sup>1</sup> respectively. After 30 min of activation, the intensity of the spectrum significantly decreased and slightly shifted to the left. A reasonable fitting could not be achieved with only the path of the Au-Au first shell but could be obtained after the Au-Mo first shell path. The fitted CNs and bond distance of the Au-Au first shell were 6.2 and 2.85 Å, respectively. The reduction in the CNs indicated the formation of smaller Au species.<sup>14</sup> The corresponding values of the Au–Mo first shell were 1.9 and 2.66, respectively, indicating that the Au species began to bond with the  $\alpha$ -MoC support. After 120 min of activation, the CNs and bond distance of the Au-Au first shell further decreased to 5.6 and 2.82, respectively, indicating that Au NPs further spread out on the support. In contrast, the CNs of the Au–Mo first shell significantly increased to 2.5, and the bond distance decreased to 2.55 Å; additionally, the CNs of the Au–C were 0.8 and the bond distance was 2.22, which indicated that more Au atoms bonded with the  $\alpha$ -MoC support, forming stronger chemical bonds compared to the sample activated for 30 min.<sup>1,14</sup> The corresponding  $\chi(k) \cdot k^2$ spectra and fitting parameters are provided in Figure S12 and Table S1. These findings were consistent with the AC-ETEM results, where the gradual dispersion of Au NPs into the 2D ALCs was observed. The formation of chemical bonds between Au species and  $\alpha$ -MoC was responsible for the dispersion effect of the Au/ $\alpha$ -MoC catalyst.

The activity and stability of the activated Au/ $\alpha$ -MoC catalysts were further tested in the HTRWGS reaction.<sup>28</sup> From Figure 5a, the initial CO<sub>2</sub> conversion rate reached approximately 60%, and the selectivity and carbon balance remained at approximately 100%. After 160 h of reaction, the  $CO_2$  conversion rate dropped to ~22.5%, while the deactivation was likely attributed to surface oxidation of  $\alpha$ -MoC. Electron microscopy analysis was performed on the spent catalyst, as depicted in Figure 5b-e. The STEM-SE (Figure 5b) and STEM-ADF (Figure 5c) images showed that the morphology of the support remained intact and no Au NPs were observed. This result indicated that the Au species did not sinter into large NPs even after 160 h of reaction. The EDX elemental mapping results further confirmed the uniform distribution of Au throughout the support (Figure S13), without any concentrated signals. Furthermore, an area was selected (Figure 5d,e) for high-resolution EDX mapping which (Figure 5f,g) showed some concentrated Au signals, indicating the presence of Au 2D ALCs that resembled those shown in Figure 1g,h. This demonstrated that the highly distributed fine Au species could be maintained on the  $\alpha$ -MoC support even under harsh experimental conditions.

In conclusion, through the utilization of advanced microscopic tools, we have successfully determined the dispersion process of Au NPs supported on  $\alpha$ -MoC at atomic scales and rationalized the epitaxial 2D structure of the formed Au cluster. The SMSI-inducing process involves the gradual transformation of the Au NPs into low-coordination cluster species, which chemically bond with the  $\alpha$ -MoC support, accompanied by electron transfer from Au to Mo. This unique dispersion effect significantly enhances the stability of the formed Au clusters, even under harsh reaction conditions. These findings provide valuable insights into the dispersion behavior of Au catalysts supported on  $\alpha$ -MoC, clarifying the mechanisms underlying their exceptional stability and catalytic performance. Our study has the potential to facilitate the rational design and synthesis of various noble metals, transition metals, or alloy catalysts with  $\alpha$ -MoC as the support, leading to a superior performance in a wide range of catalytic reactions.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.3c02960.

Materials and synthesis sections describing the synthesis of catalysts studied in this work, detailed sample preparation processes for electron microscopy and spectroscopy testing, parameters of the instruments used for this work, and figures that provide additional information about the dispersion process of Au/ $\alpha$ -MoC catalysts (PDF)

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### Notes

The authors declare no competing financial interest.

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