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 (CO + H₂O ↔ CO₂ + H₂) is an essential step in the purification process for on-board fuel reforming and hydrogen production. From thermodynamic points of view, WGS is an exothermal reaction, low temperatures favor this process. However, the current industrial CuO/ZnO/Al₂O₃ catalysts exhibit poor activities under working temperatures lower than 250°C. Therefore, considerable work has been focused on developing efficient catalysts for low temperature WGS reaction. Herein, we successfully synthesized layered gold (Au) clusters on a face centered cubic crystal (FCC) structured alpha-phase molybdenum carbide (α-MoC) substrate to create an interfacial catalyst system for the ultralow-temperature WGS reaction. In this paper, we firstly compared the substrate properties of α-MoC with beta-phase molybdenum carbide (β-Mo₂C) which has a hexagonal closed packed (HCP) unit cell. As shown in Figure 1A, β-Mo₂C exhibited very poor WGS activity at whole temperatures. While α-MoC substrate could effectively catalyze the WGS reaction, exhibiting 65% CO conversion at 473 K. Surprisingly, the 2% Au/α-MoC shows 98% CO conversion at only 423K in the product-free gas feed, reaching 1.05 molCO/molAu/s, which was 20 times higher than the best activity previously reported in literature. In a single-run reaction (more than 140 h) under the full reformate gas feed, the 2% Au/α-MoC catalyst shows an excellent total turnover number (TTN), reaching up to 385,400 molCO/molAu.

Structural characterizations of 2% Au/α-MoC catalyst were further performed. HR-STEM images revealed layered Au clusters epitaxially grown on the substrate (Figure 1B, average diameter of 1-2 nm; thickness of 2-4 atomic layers (<1 nm)), which were in good agreement with the EXAFS fitting results (Figure 1C). Detailed crystal structure analysis also showed that these epitaxial Au clusters strongly aligned with the (111) planes of the α-MoC support. More astonishingly, no obvious structural difference was observed when the catalyst undergoes the high temperature activation (700°C) process for 2h and the long-term reaction in WGS (more than 100h). Electron diffraction pattern proved that the contact angle of Au (200) and α-MoC (111) was calculated to be 42.7º, much smaller than Au particles over oxides surface, which implies the existence of strong Au-α-MoC interactions between the particles and the substrates. Benefiting from the strong metal-support interaction, water was activated over α-MoC at 30°C. Adsorbed CO on adjacent Au sites were apt to react with surface hydroxyl groups formed from the water dissociation, leading to the high WGS activity at low temperatures.

Figure 1. Catalytic properties and structural characterization of 2% Au/α-MoC catalyst. (A) The CO conversion of 2% Au/α-MoC and reference catalysts at various temperature. (condition: 10.5% CO, 21% H₂O, 20% N₂ in Ar; WHSV = 90,000 ml/g/h); (B) The HAADF-STEM images of 2% Au/α-MoC catalyst; (C) Fourier transformation (FT) EXAFS spectrum and fitting results of 2% Au/α-MoC catalyst.

References

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