Supported Single Pt$_1$/Au$_1$ Atoms for Methanol Steam Reforming

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ABSTRACT: The single Pt$_1$ and Au$_1$ atoms stabilized by lattice oxygen on ZnO{1010} surface for methanol steam reforming is reported. Density functional theory calculations reveal that the catalysis of the single precious metal atoms together with coordinated lattice oxygen stems from its stronger binding toward the intermediates, lowering reaction barriers, changing on the reaction pathway, enhancing greatly the activity. The measured turnover frequency of single Pt$_1$ sites was more than 1000 times higher than the pristine ZnO. The results provide valuable insights for the catalysis of the atomically dispersed precious metals on oxide supports.

KEYWORDS: single atom catalysis, methanol steam reforming, density functional theory, electron microscopy, activity, selectivity

In heterogeneous catalysis, metal particles are used to catalyze various industrially important chemical processes. To effectively utilize the desired, often expensive, precious metal, one usually disperses them onto high-surface-area supports with sizes ranging from a few nanometers down to subnanometers.$^{1−4}$ The presence of a large number of low-coordination sites on small particles is thought to be responsible for the enhanced catalytic activity.$^{5}$ To fully understand the structure-reactivity relationship of small particles or clusters, however, requires detailed knowledge of the active sites at the atomic level, which are often not available. Alternatively, metal species atomically dispersed onto oxide supports provide a well-defined system and have demonstrated excellent catalytic performance.$^{6}$ Moreover, such systems can provide a new platform to mimic homogeneous catalysis under heterogeneous environment.$^{7,8}$ Due to the recent advances of atomic resolution and in situ characterization techniques,$^{9}$ there is increasing interest in studying atomically dispersed catalysts. Furthermore, it is found that the active centers, responsible for the low-temperature activity of the water-gas-shift reaction$^{10,11}$ and CO oxidation,$^{12,13}$ can be attributed to the function of individual precious atoms strongly anchored onto the surfaces of oxide supports. Although the atomically dispersed catalysts may open a new and probably an efficient way to design novel classes of heterogeneous catalysts, it remains a challenge to fully uncover the nature of the active sites, to significantly improve their performance, and to develop strategies to prolong the stability of single-atom catalysts.

To address these questions, we report here a density functional theory (DFT) calculation, subangstrom resolution scanning transmission electron microscopy (STEM) character-

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nanowires with Au1 are thermodynamically stable and resistant to segregation observed. The stability of the Pt1/Au1 sites originates from the state.

0.86 eV lower than the reservoirs in equilibrium with in large metal counterparts, implying that the embedded Pt1 and the corresponding {10...} sites would raise the corresponding energies by 0.45 and 0.70 eV and is energetically less favorable. On the other hand, the Pt1 or Au1 atoms positioned on top of the surface Zn sites is unstable and would displace to the bridge sites between Zn and O atoms at the grooves of ZnO{1010}, which was not observed. The stability of the Pt1/Au1 sites originates from the strong chemical bonding between Pt1/Au1 and the coordinated lattice oxygen, as seen from the extensive charge redistribution during the synthesis and/or the catalytic reactions. Pt1 or Au1 substituted at the subsurface Zn lattice sites would raise the corresponding energies by 0.45 and 0.70 eV and is energetically less favorable. The Pt1 or Au1 atoms on the dehydrogenation of H2O* and CH3OH* toward OH*, CH2O*, and CH3O* (the initial elementary reaction steps in MSR) were calculated and plotted in Figure 3a (tabulated in Table S2). In terms of energetics, the sum of the binding energies of two reactants (H2O* and CH3OH*) on Pt1/ZnO is 0.26 eV lower than those on ZnO. Moreover, the reaction energetics ΔE for the O–H bond scission of H2O* and CH3OH* are exothermic (−0.27 eV).

![Figure 1. HAADF-STEM images of ZnO{1010} nanowires with embedded Pt1 (a) and Au1 (b) atoms (indicated by the yellow arrow), respectively. (c) Schematic structure for Pt1/Au1/ZnO{1010} (top view) and (d) Pt1/Au1/ZnO{1010} with adsorbed CH3O* (side view). The blue, green, red, gray, and white spheres represent Pt1/Au1, Zn, O, C, and H atoms, respectively.](image)

![Figure 2. Calculated binding energies of the reactants and intermediates involved in MSR on ZnO{1010}(shadow), Au1 (red solid), and Pt1 (blue solid) embedded ZnO{1010}.

![Figure 3. (a) Calculated potential energy surfaces for CH3OH* + H2O* → CH2O* + OH* + 2H* on ZnO, Au1/ZnO, and Pt1/ZnO. (b), (c), and (d) are the schematic structures for the transition state TS1, TS2, and TS3 on Pt1/Au1/ZnO(1010), respectively.](image)
and −0.25 eV) on Pt1/ZnO, respectively, in contrast to the endothermic (0.21 and 0.23 eV) on ZnO. For the subsequent C–H bond scission of CH3O* to HCHO*, the difference of ΔE between Pt1/ZnO and ZnO is however negligible. The stronger binding of the reactants and favorable reaction energetics on Pt1/ZnO than those on ZnO improve the overall energetics and therefore the corresponding reactivity. This has also been found for water dissociation on Pd-doped ZnO.19 On the other hand, the calculated reaction barriers $E_*$ for the above three reaction steps are 0.44, 0.49, and 1.05 eV with the corresponding transition states TS1, TS2, and TS3 in Figure 3b, 3c, and 3d, respectively, which are all higher than those on ZnO (0.28, 0.31, and 0.19 eV). Such a behavior suggests that the overall potential energy surface (PES) becomes corrugated. Nevertheless, as seen from Figure 3a, the downshift of PES on Pt1/ZnO, a consequence of the stronger binding of the reactants and improved ΔE for the O–H bond scissions, is so significant that the corresponding TSs (blue bar) remains energetically lower than those of TSs (black bar) of ZnO. This implies that Pt1/ZnO would have a higher reactivity than ZnO.

For Au1/ZnO, the overall binding of two reactants enhances modestly by ∼0.14 eV compared to ZnO. Reaction energetics ΔE in the subsequent O–H scissions remains endothermic (0.19 and 0.18 eV), similar to those of ZnO. However, the corresponding O–H scission barriers $E_*$ (0.65 eV for H2O* and 0.66 eV for CH3OH*) become even larger than those on Pt1/ZnO (0.44 and 0.49 eV). Namely, the Au1/ZnO does not possess appreciable improvement in binding the reactants or the reaction energetics than those of ZnO, whereas the corresponding overall PES becomes more corrugated than that of ZnO. As a result, the values of the TSs (red bar in Figure 3a) are energetically even higher than those of ZnO (black bar).

The MSR experiments were carried out in a fixed-bed reactor with 50 mg of catalyst in about 60–80 mesh size. Pristine ZnO, Pt1/ZnO, and Au1/ZnO NWs were tested. The products were H$_2$, CO, and CO$_2$ only within the detection limit, and the conversion was calculated based on the carbon balance. All three catalysts were very stable during the MSR reaction at 390 °C (Figure 4a). On the pristine ZnO NWs, the conversion was low (<10%), but the selectivity toward CO$_2$ approached 100%, which agrees well with the recent literature reports.20,21 The Pt1/ZnO catalyst was much more active than that of the pristine ZnO with the corresponding conversion of about 43% at the steady state. The selectivity toward CO$_2$ remained high, ca. 88%. The Au1/ZnO catalyst was also much more active than the pristine ZnO NWs with a conversion of about 28% and nearly 100% CO$_2$ selectivity.

Taking into account the extremely low levels of Pt and Au loading (only about 125 ppm), the differences in TOF values between these single-atom catalysts and the pristine surfaces of ZnO (measured in a kinetically controlled regime with methanol conversion less than 20%) will be huge. For the pristine ZnO NWs primarily exposing {1010} surfaces with a total surface area of ~10 m$^2$/g, the corresponding TOF for MSR was calculated by assuming that all the Zn sites in the topmost layer of the ZnO surface are active centers. The calculated TOF at 380 °C is 1.8 × 10$^{-2}$ s$^{-1}$. For the Pt1/ZnO and Au1/ZnO catalysts, after subtracting the contribution from the surface Zn sites of the ZnO NWs, the corresponding TOF solely from the embedded Au$_{1}$ and Pt$_{1}$ sites for MSR were estimated to be 4.7 and 18.9 s$^{-1}$, respectively, about two and three orders of magnitude higher than that of ZnO.

The TOF at different T varying from 340 to 420 °C were measured. The corresponding Arrhenius plots are shown in Figure 4b, from which the apparent activation energies $E_{app}$ and pre-exponential factors $A_{app}$ can be extracted. The $E_{app}$ from lower to higher values, are 1.05, 2.32, and 2.58 eV for Pt1/ZnO, ZnO, Au1/ZnO, respectively, with the corresponding $A_{app}$ of 2.4 × 10$^5$, 1.7 × 10$^6$, 3.2 × 10$^{20}$ s$^{-1}$. The remarkable different $A_{app}$ could be rationalized by the so-called compensation effect with respect to the corresponding $E_{app}$ of the Arrhenius law found from various activation processes.27 Namely, when the apparent activation energy changes, so does the pre-exponential factor. Among three catalysts studied here, Pt1/ZnO has the lowest $E_{app}$ and the smallest $A_{app}$ whereas Au1/ZnO has the highest $E_{app}$ and the largest $A_{app}$. It is likely that the much lower $E_{app}$ of the Pt1/ZnO and higher $A_{app}$ of the Au1/ZnO explains their three and two orders of magnitude higher TOF than that of ZnO. We note that the MSR on ZnO powder catalysts has been studied and the measured $E_{app}$ was found to be less than 100–200 kJ/mol.20,21 The smaller $E_*$ may have originated from the contribution of surfaces other than the {1010} surfaces, for example, polar surfaces, or defect sites present in ZnO powder catalysts.

To rationalize further the experimental findings on the trend variation of the MSR activity and selectivity toward CO$_2$ and gain more mechanistic insights, the complete PESs on ZnO, Au1/ZnO, and Pt1/ZnO were explored thoroughly, and the most favorable reaction pathways are shown in Figure 5 (detailed energetics, barriers, and TSs in Table S2). The reaction pathway toward CO$_2$ could be classified into two pathways: Path I, association of formaldehyde from methanol with hydroxyl from water, and Path II, decomposition of formaldehyde to CO followed by water gas shift (WGS) reaction.23 The pathway via methyl formate was not considered here because it was found to be of minor importance.24

First of all, we note that among all of the optimized TSs, only the order of the relative height of TS3 and TS4 in the optimized PES (Pt1/ZnO < ZnO < Au1/ZnO) follows the same order of the measured apparent activation energies. This indicates that either TS3 or TS4 could be the potential rate-determining state contributing to the measured apparent activation energy. Compared to TS4, the relative height of TS3 is higher, and would be more demanding to approach.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** (a) Methanol conversion (solid) and CO$_2$ selectivity (open) as a function of reaction time at 390 °C on Au$_1$/ZnO (red triangle), Pt$_1$/ZnO (blue square) catalysts, and the pristine ZnO nanowires (black diamond); (b) corresponding Arrhenius plots of the reaction rate $\ln$ (TOF) (s$^{-1}$) versus $1/T$ for the MSR reaction.

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Actually, TS3 represents the highest TS in the optimized PES, irrespective to the three catalysts studied. In the literature, the energetically highest transition state in the PES of a multistep reaction was suggested to be the rate-determining state closely related to the apparent activation energy. Accordingly, we attribute attentively TS3 (the dehydrogenation of methoxy to formaldehyde) as the rate-determining step of MSR for the three catalysts considered here.

For CO2 selectivity on ZnO, the association of CH2O* with OH* to form H2COOH* (Path I) has a modest reaction barrier $E_a$ of 0.51 eV and exothermic reaction energetics of $-0.62$ eV (TS4 in Figure S6). While for Path II, the dehydrogenation from CH2O* to CHO* has a considerably higher barrier $E_a$ of 1.51 eV and endothermic reaction energetics $\Delta E$ of 0.29 eV. Therefore, Path I is not only kinetically but also energetically more favorable than Path II. Once H2COOH* is formed, sequential dehydrogenation to HCOO* and CO2 are exothermic with $E_a$ of 0.57 and 1.10 eV (TS5 and TS6 in Figure S6), respectively. These results indicate that ZnO have a higher MSR selectivity toward CO2 as evidenced by experiments.

On Pt1/ZnO and Au1/ZnO, because the overall binding energy of formaldehyde and hydroxyl is at least 1.46 eV stronger than those on ZnO, their association (Path I) becomes energetically less favorable, as seen from the change of reaction energetics from exothermic ($-0.62$ eV for ZnO) to endothermic (larger than 0.65 eV). Kinetically, it also becomes less favorable because the corresponding barrier increases at least by 0.49 eV. On the other hand, the binding of formyl (CHO*) on Pt1/ZnO and Au1/ZnO is at least 1.83 eV stronger than that on ZnO. Therefore, the reaction energetics for dehydrogenation of CH2O* to CHO* (Path II) would be improved. Indeed, the calculated reaction energetics changes from endothermic (0.29 eV for ZnO) to exothermic (−0.72 eV at least), concurrently with a decrease of barrier by 0.20 eV for Pt1/ZnO and 0.11 eV for Au1/ZnO (TS4, Figure Sb). The subsequent dehydrogenation of CHO* to CO* remains facile (TS5, Figure Sc). These considerations suggest that on Pt1/ZnO and Au1/ZnO complete dehydrogenation of formaldehyde rather than its association with hydroxyl becomes favorable. To evaluate the overall processes of Path II, the WGS reaction was studied. The calculated barriers of CO* association with OH* for CO2 are 1.24 and 0.64 eV for Pt1/ZnO and Au1/ZnO, respectively (TS6, Figure Sd).

The calculations above show that although all the three catalysts have good selectivity toward CO2, the corresponding reaction pathways are different when single atoms of Pt1 or Au1 are embedded onto the ZnO {10\{10\} surfaces. Therefore, the Pt1 and Au1 do not act as promoters; together with the oxygen and Zn sites of ZnO, they form new active centers that are intrinsically different from the catalytic properties of ZnO.

In summary, isolated precious metal atoms including Pt1 and Au1 together with coordinated lattice oxygen embedded onto ZnO surfaces provide single yet stable active sites for methanol steam reforming. Such single active sites bind stronger toward the intermediates, have a more favorable reaction energetics and kinetics, and even change the reaction pathways. These lead to a great enhancement of the activity, and in particular, the single Pt1 sites embedded onto ZnO{10\{10\} surfaces were found to have a TOF of over 1000 times higher than that of the pristine ZnO. The results in this study for the function of the surface-embedded single precious metal atoms on supports provide valuable insights for the catalysis of the single precious metal atoms embedded on the oxide surfaces.

**ASSOCIATED CONTENT**

### Supporting Information

Computational and experimental details, optimized reaction conditions and tests, calculated binding energies and reaction barriers, optimized structures and calculated charge density conditions and tests, calculated binding energies and reaction barriers, optimized structures and calculated charge density differences, and transition states for TS4, TS5, and TS6. 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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### REFERENCES


