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Superior activity of Rh₁/ZnO single-atom catalyst for CO oxidation

Bing Han ^{a,b}, Rui Lang ^a, Hailian Tang ^a, Jia Xu ^c, Xiang-Kui Gu ^{d,#}, Botao Qiao ^{a,e,*},
Jingyue(Jimmy) Liu ^{c,\$}

^a CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

^c Department of Physics, Arizona State University, Tempe, Arizona 85287, United States

^d Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202, United States

^e Dalian National Laboratory for Clean Energy, CAS, Dalian 116023, Liaoning, China

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ABSTRACT

CO oxidation is of great importance in both fundamental study and industrial application. Supported noble metal catalysts are highly active for CO oxidation but suffer from the scarcity and high cost. Single-atom catalysts (SACs) can maximize the metal atom efficiency. Herein, ZnO nanowire (ZnO-nw) supported Rh, Au, and Pt SACs were successfully developed to investigate their CO oxidation performance. Interestingly, it was found that Rh₁/ZnO-nw showed much higher activity than the other noble metals which are usually regarded as good candidates for CO oxidation. In addition, the Rh SAC possessed high stability in high-temperature CO oxidation under simulated conditions in the presence of water and hydrocarbons. The high activity and stability make Rh₁/ZnO-nw promising for practical applications, especially in the automotive exhaust emission control. Theoretical calculations indicate that the CO oxidation proceeds via the Mars-van Krevelen mechanism and the lowest barrier for the rate-limiting O₂ dissociation at a surface oxygen vacancy site is a key factor in determining the observed highest activity of Rh₁/ZnO-nw amongst the studied SACs.

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CO oxidation is one of the most widely investigated reactions in heterogeneous catalysis because of its significance in both fundamental research [1] and practical applications such as elimination of a trace amount of CO from automotive exhaust [2,3], or purification of hydrogen stream for polymer electrolyte membrane fuel cells [4,5]. A few metal oxides or composite oxides are highly active for CO oxidation even at ambient temperature [1,6,7] but suffer from the low thermal stability and

high susceptibility to poisons (e.g., sulfur and water) [8,9]. Therefore, supported noble metals, such as Au, Pt and Pd, are generally used as the highly active and/or stable catalysts for CO oxidation [8,10–13]. However, supported Rh catalysts are less regarded as good candidates for CO oxidation.

Single-atom catalysts (SACs), with isolated individual atoms dispersed on various supports, are emerging as a new frontier in heterogeneous catalysis and have gained increasing interest

* Corresponding author. Tel: +86-411-84379416; Fax: +86-411-84685940; E-mail: bqiao@dicp.ac.cn

Corresponding author. E-mail: xkgu@wayne.edu

\$ Corresponding author. E-mail: jingyue.liu@asu.edu

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due to their unique catalytic properties [14–20]. SACs have demonstrated superior performance in many reactions including CO oxidation [21–23], water gas shift reaction [24–26], selective hydrogenation [27,28] and selective oxidation [29]. Especially, supported Rh catalysts were found to be highly active for CO oxidation when dispersed in the form of subnanometer clusters or single atoms [30–33]. For example, TiO_2 supported subnanometer Rh clusters were proved to be highly active in CO oxidation even at cryogenic temperatures [31]. Moreover, Rh atoms dispersed over CeO_2 [30], phosphotungstic acid [32,34], and $\gamma\text{-Al}_2\text{O}_3$ [33] were also considered as effective catalysts. These studies suggested that supported Rh SACs may possess the characteristics of a highly active CO oxidation catalyst.

In the previously published works, we successfully developed ZnO nanowire (denoted as ZnO-nw) supported Au, Pt and Rh SACs for various applications [35–37]. Herein, we thoroughly investigated their catalytic performance for CO oxidation and surprisingly discovered that the Rh_1/ZnO SAC possessed the highest activity. It also exhibited good stability under high working temperature and a simulated condition, making the Rh_1/ZnO SAC suitable for CO oxidation under practical conditions. DFT calculations provided the possible reaction mechanism and the nature of the observed high activity for CO oxidation.

ZnO nanowires which mainly expose {10-10} facets were used as the support to minimize the structural effects of the support surfaces. About 0.01 wt% loading of Rh, Au and Pt precursors were separately deposited on the ZnO-nw surfaces to fabricate the ZnO-nw supported SACs, denoted as Rh_1/ZnO -nw, Au_1/ZnO -nw and Pt_1/ZnO -nw, respectively [35,37]. Increasing the Rh loading to about 0.4 wt% generated the Rh/ZnO-nw nanocluster catalyst (denoted as $\text{Rh}_{\text{NC}}/\text{ZnO}$ -nw). Moreover, ZnO nanoflakes supported Rh SAC was also synthesized for comparison (denoted as Rh_1/ZnO -nf). The actual metal loadings of the above catalysts are listed in Table S1, and the detailed preparation method is provided in the Supporting Information (SI).

The representative scanning electron microscopy (SEM) images of ZnO-nw and ZnO-nf are shown in Fig. S1. The average diameter of the ZnO-nws is ~ 80 nm with lengths ranging 5–50 μm , while the average diameter of the ZnO-nfs is ~ 1.2 μm with lengths in the range of 200–350 nm. The total surface area of the {0001} facets is negligible for the ZnO-nws while it dominates for the ZnO-nfs (Figs. S1e and S1f). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of various catalysts are presented in Fig. 1. As shown in Figs. 1a and S2a, Rh clusters with an average diameter of ~ 1.1 nm were deposited on the surfaces of ZnO-nws (Fig. S2b). When the actual Rh loading was decreased to 0.007 wt%, no Rh clusters were found in the low-magnification STEM images (Fig. S3a) but isolated Rh atoms became observable (Figs. 1b and S3b). The Au_1/ZnO -nw and Pt_1/ZnO -nw SACs were also successfully synthesized with only Au or Pt atomic species anchored onto the surfaces of the ZnO-nw support (Figs. 1c, 1d, S4 and S5), similar to those reported previously [35].

Fig. 1. HAADF-STEM images of (a) $\text{Rh}_{\text{NC}}/\text{ZnO}$ -nw, (b) Rh_1/ZnO -nw, (c) Pt_1/ZnO -nw and (d) Au_1/ZnO -nw. Single atoms are highlighted by the orange circles.

CO oxidation reaction was performed under the CO/O_2 gas flow with a space velocity (SV) of 40 000 $\text{mL g}_{\text{cat}}^{-1} \text{h}^{-1}$. The light-off curves of ZnO-nw and the corresponding SACs are shown in Fig. 2. The CO conversion of ZnO-nws alone was only 40% at 400 $^{\circ}\text{C}$, which is much lower than that of iron oxide or other highly reducible oxides [38]. The Au_1/ZnO -nw showed much higher activity than the bare ZnO-nws, suggesting that Au single atoms are active for CO oxidation. The activity of the Au_1/ZnO -nw was much lower than that of other Au SACs [39–41] owing to the low redox capability of the ZnO-nws [42]. Even though the Pt_1/ZnO -nw was more reactive than the Au_1/ZnO -nw, the Rh_1/ZnO -nw exhibited the best performance among these SACs because CO oxidation started at 160 $^{\circ}\text{C}$. Moreover, the T_{100} (temperature for total CO conversion) of the Rh_1/ZnO -nw was 210 $^{\circ}\text{C}$, much lower than that of the Pt_1/ZnO -nw (300 $^{\circ}\text{C}$) and Au_1/ZnO -nw (400 $^{\circ}\text{C}$). Although CO

Fig. 2. CO oxidation on Rh_1/ZnO -nw (black), Pt_1/ZnO -nw (red), Au_1/ZnO -nw (blue) and ZnO-nw (pink). Reaction conditions: 1 vol% CO, 1 vol% O_2 , He balance, total flow rate = 33.3 mL/min , 50 mg catalyst, weight hourly space velocity (WHSV) = 40 000 $\text{mL g}_{\text{cat}}^{-1} \text{h}^{-1}$.

was fully eliminated at ~ 160 °C on the Rh nanocluster catalyst (Fig. S6), isolated Rh atoms still exhibited superior activity considering the fact that the Rh usage of the nanocluster catalyst is ~ 60 times higher than that of the Rh₁ SAC. The CO conversion curve of the Rh₁/ZnO-nf almost coincides with that of the Rh₁/ZnO-nw (Fig. S6), suggesting that the high activity mainly originates from the singly dispersed Rh atoms, regardless of the facets of the ZnO support. In the three-way-catalysts (TWCs), NO_x and CO are eliminated by Rh and Pt/Pd components, respectively [2]. The capability of the Rh₁/ZnO SAC for low temperature CO conversion makes it a promising candidate to replace Pt/Pd in practical TWCs.

The specific rate and turnover frequency (TOF) of the Rh- and Pt-based catalysts in this work were compared with those reported in the literature (Table 1). The TOF of the Rh₁/ZnO-nw at 180 °C was 0.63 s⁻¹, higher than those of Rh_{NC}/ZnO-nw, Pt/θ-Al₂O₃ SAC [43], and Pt/zeolite SAC [44], demonstrating the good performance of the Rh₁/ZnO-nw SAC. However, the Rh/SBA-15 nanoparticle catalyst with a TOF of 1.69 s⁻¹ showed higher reactivity [45]. The E_a of the Rh₁/ZnO-nw and Rh_{NC}/ZnO-nw was calculated to be 85.6 and 80.5 kJ/mol, respectively (Fig. S7), much lower than those of the reported Rh nanocatalysts such as Rh/SiO₂ (104 kJ/mol) [46] and Rh/SBA-15 (124.8 kJ/mol) [45]. The lower activation barrier of the Rh/ZnO-nw catalysts might be the main cause for their better CO oxidation performance. To obtain deeper insights into the CO oxidation reaction mechanisms of the ZnO-nw supported noble metal SACs, we performed the density functional theory (DFT) calculations to understand the underlying factors governing the different activities of ZnO-nw supported Rh₁, Pt₁, and Au₁ SACs.

According to our previous results [35], the single Rh, Pt, and Au atoms were prone to substitute in a surface lattice Zn position on ZnO{10-10} surface since these single metal atoms can be stabilized by the lattice oxygen (O_{L}^{X}), resulting in partially positively charged Rh, Pt, and Au. The most stable structures of the intermediates involved in CO oxidation on the Rh₁/ZnO, Pt₁/ZnO, and Au₁/ZnO are shown in Fig. S8 and the corresponding binding energies are listed in Table S2. We found that

CO tends to adsorb on top of these single noble metal atoms; the single Au atom exhibits a lower CO binding strength than that on the single Pt and Rh atom. For O₂ adsorption, the two O atoms prefer to respectively adsorb on the single metal atom and the adjacent surface Zn atom. The bridge site, composed of one single metal atom and the neighboring surface Zn atom, is most favorable for atomic O adsorption. It was found that the Rh₁/ZnO shows the strongest binding for O₂ and O while the Au₁/ZnO shows the weakest. Table S2 indicates that these single noble metal atoms exhibit significantly stronger binding for all the intermediates than that of the bare ZnO{10-10}, suggesting that the single noble metal atoms are the important active sites for CO oxidation. Moreover, the stronger binding of CO than O₂ on these single noble metal atoms implies that the Eley-Rideal mechanism is not favorable for CO oxidation on these systems because the active site is prone to be occupied by CO. On the other hand, the high barriers of O₂ dissociation on the Au₁/ZnO (2.49 eV), Pt₁/ZnO (1.49 eV), and Rh₁/ZnO (0.97 eV) make CO oxidation via the Langmuir-Hinshelwood mechanism challenging (Table S3). Thus, the alternative Mars-van Krevelen mechanism was investigated. Such a process involves CO reaction with a surface lattice O to generate a surface O vacancy (V_0) first, followed by the dissociation of O₂ at the V_0 site and the subsequent formation of an O adatom on the surface that can be removed by another CO.

The Gibbs free energy diagrams for CO oxidation via the Mars-van Krevelen mechanism are shown in Fig. 3 and the calculated barriers and reaction energies of the elementary steps are listed in Table S3. The entropic contribution of the gas-phase species in the reaction energy at 250 °C at standard pressure was considered in this calculation [48]. The energy losses (exothermic process) for the gas-phase CO and O₂ adsorption onto the surface were determined to be 0.88 and 0.89 eV, respectively, while the desorption of the adsorbed CO₂ into the gas phase would gain an energy of 0.91 eV (endothermic process). The calculated barrier to generate surface V_0 , via CO (adsorbed onto the noble metal atom) reaction with a surface lattice O (of ZnO {10-10}), follows Au₁/ZnO (0.07 eV) < Pt₁/ZnO (0.55 eV) < Rh₁/ZnO (0.77 eV) and an opposite trend was observed for their exothermicity (Fig. 3a). The factors that determine these trends are mainly affected by the bonding strength between the lattice O and the single noble metal atom, which can be evaluated by the surface V_0 formation energy. The calculated surface V_0 formation energies with respect to an O of the gas phase O₂ are 0.70, 1.60, and 2.28 eV on Au₁/ZnO, Pt₁/ZnO, and Rh₁/ZnO, respectively, indicating that the Au–O bond exhibits the weakest bonding strength while the Rh–O the strongest. The weakest bonding strength implies the most favorable removal of lattice O by CO, resulting in the highest exothermicity and lowest barrier for this reaction. In addition, the weakest Au–O bonding strength gives rise to the weakest binding energy of –0.58 eV for O₂ adsorption on the surface V_0 (Table S2), resulting in the highest barrier (1.03 eV) for O₂ dissociation at this surface V_0 site of the Au₁/ZnO (Fig. 3b). Among these systems, Rh₁/ZnO showed the lowest barrier (0.83 eV) and the highest exothermicity (–1.50 eV) for O₂ dissociation at the V_0 site owing to the strongest Rh–O bond. Upon dissociative

Table 1
Activity comparison of Rh/ZnO-nw catalysts with the previously reported catalysts for CO oxidation.

Catalyst	Loading (wt%)	T (°C)	Specific rate (mol h ⁻¹ g _M ⁻¹)	TOF (s ⁻¹)	E_a (kJ mol ⁻¹)	Note
Rh ₁ /ZnO-nw	0.007	180	22.0	0.63	85.6	This work
Rh _{NC} /ZnO-nw	0.43	180	7.3	0.21	80.5	This work
Pt ₁ /ZnO-nw	0.0125	250	6.9	0.37	—	This work
Pt/θ-Al ₂ O ₃	0.18	200	0.24 ^a	0.013	—	[43]
Pt/zeolite	1	150	0.22 ^a	0.012	—	[44]
Rh/CeO ₂	1.6	110	0.098 ^a	0.056	68 ± 3	[47]
Rh/SiO ₂	0.5	120	2.59 ^a	0.074	104	[46]
Rh/SBA-15	0.78	170	38.4 ^a	1.69	124.8	[45]

TOFs were calculated based on the metal dispersion. For SACs, dispersion = 100%; for Rh_{NC}/ZnO-nw, the dispersion was estimated by the metal particle size according to $D = 1.08/d_{\text{Rh}} = 1$. ^a Reaction rate was calculated from the given TOFs based on the dispersion.

Fig. 3. (a) and (b) are the free energy diagrams for CO oxidation via the Mars-van Krevelen mechanism on Rh₁/ZnO, Pt₁/ZnO, and Au₁/ZnO SACs, respectively. (c) Optimized transition states of the elementary steps involved in CO oxidation. The green, blue, red, orange, and gray balls represent Zn, Rh, Pt, Au, O, O from O₂, and C atoms, respectively.

adsorption of the gas phase O₂ at the V₀ site, one O atom fills in the oxygen vacancy on the ZnO {10-10} surface while the other O adsorbs as an adatom, readily to react with another CO molecule. The CO reaction with an O adatom is an exothermic process on all these systems and the Au₁/ZnO showed the highest exothermicity and lowest barrier (0.25 eV) because of the weakest binding of the O adatom (Table S2).

In the catalytic cycle for CO oxidation via the Mars-van Krevelen mechanism, we found that the O₂ dissociation on a surface V₀ is the rate-limiting step for all the SAC systems we investigated. For this specific step, the calculated barriers were 0.83, 0.93, and 1.03 eV on the Rh₁/ZnO, Pt₁/ZnO, and Au₁/ZnO, respectively, suggesting that the activity of CO oxidation is in the order Rh₁/ZnO > Pt₁/ZnO > Au₁/ZnO, consistent with our experimental results. Furthermore, the barrier of 0.83 eV on the Rh₁/ZnO is comparable with the experimental value (Fig. S7).

The sintering resistance is vital for practical car-exhaust catalysts because they usually experience high temperatures (~750 °C) [49]. On the other hand, the catalysts can also be deactivated by impurities in the exhausting gas [50–52]. Therefore, as shown in Fig. 4a, the 100-h stability test of the Rh₁/ZnO-nw SAC was carried out at 300 °C under standard conditions (1 vol% CO, 1 vol% O₂ and He balance) as well as the simulated car-exhaust gas mixture (1.6 vol% CO, 1 vol% O₂, 0.01 vol% propylene, 0.0087 vol% toluene, 10 vol% H₂O and He balance). The CO conversion was maintained for 100 h without any deactivation, demonstrating the excellent stability of the Rh₁/ZnO-nw SAC even in the presence of water and hydrocarbon contaminants. The high temperature stability was further tested at 800 °C (Fig. 4b). However, during the second cycle, the activity of the catalyst obviously decreased, probably due to the aggregation or oxidation of the isolated Rh species. Regeneration of the catalyst by in situ reduction at 200 °C in 10

Fig. 4. (a) The stability test of the Rh₁/ZnO-nw SAC (1) under standard conditions and (2) in simulated CO emission control tested at 300 °C. Reaction conditions: (1) 1 vol% CO, 1 vol% O₂, He balance, total flow rate = 49.3 mL/min, 4.4 mg catalyst diluted with 120 mg SiO₂, WHSV = 6.7×10⁵ mL g_{cat}⁻¹ h⁻¹; (2) 1.6 vol% CO, 1 vol% O₂, 0.01 vol% propylene, 0.0087 vol% toluene, 10 vol% H₂O, He balance, total flow rate = 87.4 mL/min, 2.9 mg catalyst diluted with 150 mg SiO₂, WHSV = 1.8×10⁶ mL g_{cat}⁻¹ h⁻¹. (b) CO oxidation performance of Rh₁/ZnO-nw over three high temperature cycles. Reaction conditions: 1 vol% CO, 1 vol% O₂, He balance, total flow rate = 33.3 mL/min, 50 mg catalyst, WHSV = 40 000 mL g_{cat}⁻¹ h⁻¹; the third cycle was tested after in situ reduction.

vol% H₂/He, however, almost completely recovered the activity. To confirm the state of the Rh species after the first reaction run, AC-HAADF-STEM imaging and EDS mapping were carried out (Fig. S9). These results show that most of the Rh single atoms were stable and remained isolated although a small amount of small Rh nanoclusters were also observed. When we consider the fact that the activity can almost be restored by a mild reduction treatment, we can deduce that the Rh₁/ZnO-nw SAC was stable and the observed deactivation mainly originated from the oxidation of the Rh atoms during the CO oxidation reaction.

In summary, we have successfully fabricated ZnO-nw supported Rh, Au, and Pt SACs, catalysts among which the Rh₁/ZnO-nw SAC showed the highest activity for CO oxidation. DFT calculations revealed that the reaction probably undergoes via Mars-van Krevelen mechanism and the O₂ dissociation at the surface oxygen vacancy sites is the rate-determining step. Among the three noble metals investigated, the Rh₁/ZnO-nw SAC possesses the lowest barrier for the rate-limiting step and thus provides the highest CO oxidation activity. Furthermore, the resistance of Rh₁/ZnO-nw SAC to poisoning and sintering at high temperatures makes it a potential candidate for practical applications.

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Graphical Abstract

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Superior activity of Rh₁/ZnO single-atom catalyst for CO oxidation

Bing Han, Rui Lang, Hailian Tang, Jia Xu, Xiang-Kui Gu*, Botao Qiao*, Jingyue(Jimmy) Liu*
 Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China; University of Chinese Academy of Sciences, China; Arizona State University, USA; Wayne State University, USA; Dalian National Laboratory for Clean Energy, China

The ZnO nanowires supported Rh single-atom catalyst exhibits the highest activity for CO oxidation among the Pt and Au single-atom catalysts with extremely low metal loading.

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铈/氧化锌单原子催化剂的优异CO氧化反应性能

韩冰^{a,b}, 郎睿^a, 唐海莲^a, 徐嘉^c, 顾向奎^{d, #}, 乔波涛^{a, e, *}, 刘景月^{c, S}

^a中国科学院大连化学物理研究所中国科学院应用催化科学与技术重点实验室, 辽宁大连116023, 中国

^b中国科学院大学, 北京100049, 中国

^c亚利桑那州立大学物理系, 坦佩, 亚利桑那州85287, 美国

^d韦恩州立大学化学工程与材料科学系, 底特律, 密歇根州48202, 美国

^e大连洁净能源国家实验室, 辽宁大连116023, 中国

摘要: 一氧化碳(CO)低温氧化因其在基础研究和实际应用中的重要意义和价值, 成为多相催化领域中研究最多的反应之一。特定氧化物和复合氧化物均具有优异的CO氧化活性, 但其高温稳定性较差, 且易被水和硫化物毒化, 严重限制了其实际应用。贵金属具有较高的CO氧化活性, 但是资源稀缺、价格较高。减小贵金属尺寸至纳米尺度能够提高反应活性并有效提高金属利用效率, 但由于只有纳米粒子表面的原子能够提供吸附反应活性位, 因此金属原子利用率仍有待提高。

单原子催化是多相催化领域的新概念。单原子催化剂的活性组分以原子级分散在载体上, 能够实现原子利用率最大化, 降低贵金属使用量。活性位点的高度非饱和配位环境使得单原子催化剂在多种反应中具有优异的反应性能, 如CO氧化、水汽变换、选择性加氢和选择性氧化等反应。单原子催化剂具有相对简单和均一的化学环境, 可以作为较好的系统来研究化学反应的本质, 如反应活性位点和金属与载体的相互作用等。贵金属如金、铂、钯在CO氧化中具有较高活性, 但是一般认为铈金属活性较差。最近几年研究表明, 铈基单原子、亚纳米催化剂在CO氧化反应中可具有优异活性, 表明负载型铈单原子催化剂可能是一种潜在的CO氧化高活性催化剂。

氧化锌作为CO反应催化剂载体的研究不多, 因为其不可还原性使得催化剂活性不高。氧化锌纳米线(ZnO-nw)主要晶面为{10-10}, 作为载体使得催化剂活性位点更为均一。本文在前期研究工作基础上成功制备了氧化锌纳米线负载的铈、金、铂单原子催化剂, 并研究了其CO氧化性能。采用氧化锌载体一是因为其不可还原性, 可以最大程度降低载体的影响, 二是其单一暴露晶面{10-10}可以使催化剂均一程度最大化。研究发现, 在所制备的催化剂中Rh₁/ZnO-nw具有最高反应活性和良好的反应稳定性。CO完全转化温度为210 °C, 明显低于其它氧化锌负载的单原子催化剂。进一步测定其反应速率, 得

到Rh₁/ZnO-nw在180 °C时单位活性位点转化数(TOF)为0.63 s⁻¹, 是已报道的单原子催化剂中最高值之一, 为相同氧化锌负载Rh纳米粒子的3倍(0.21 s⁻¹). 密度泛函理论计算揭示了氧化锌负载Rh单原子催化剂上CO氧化的反应机理和高活性原因. 计算表明反应机理为Mars-van Krevelen, 氧气在表面氧空位的解离是速控步骤, 计算得到的能垒为Rh₁/ZnO < Pt₁/ZnO < Au₁/ZnO, 表明CO氧化活性顺序为Rh₁/ZnO > Pt₁/ZnO > Au₁/ZnO, 与实验结果相符. 此外, 测试了两种反应条件下Rh₁/ZnO-nw单原子催化剂的稳定性. 在300 °C反应温度、反应气氛为CO/O₂和模拟汽车尾气的反应条件下, 即反应气氛为1.6% CO、1% O₂、0.01%丙烯、0.0087%甲苯、10%水、He平衡, 在100 h的测试中其活性保持稳定. 高温循环测试中, 经过800 °C反应后, 活性有所下降, 但是在经过原位还原后, 其反应活性可以基本恢复, 表明Rh₁/ZnO-nw单原子催化剂不仅具有优异的高温抗烧结性能, 同时在水分和碳氢化合物存在的条件下, 具有优异的抗毒化能力, 展现出在实际应用中的潜力.

关键词: 单原子催化; 一氧化碳氧化; 铑; 氧化锌纳米线; 密度泛函理论计算

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*通讯联系人. 电话: (0411)84379416; 传真: (0411)84685940; 电子信箱: bqiao@dicp.ac.cn

#通讯联系人. 电子信箱: xkgu@wayne.edu

^S通讯联系人. 电子信箱: jingyue.liu@asu.edu

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