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Probing the catalytic behavior of ZnO nanowire supported Pd₁ single-atom catalyst for selected reactions

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ABSTRACT

We have dispersed individual Pd atoms onto ZnO nanowires (NWs) as single-atom catalysts (SACs) and evaluated their catalytic performance for several selected catalytic reactions. The Pd₁/ZnO SAC is highly active, stable, and selective towards CO₂ for steam reforming of methanol to produce hydrogen. This catalyst system is active for oxidation of CO and H₂ but performs poorly for preferential oxidation of CO in hydrogen-rich stream primarily due to the strong competitive oxidation of H₂ on ZnO supported Pd₁ atoms. At ambient pressure, reverse water-gas-shift reaction occurs on the Pd₁/ZnO SAC. This series of tests of catalytic reactions clearly demonstrate the importance of selecting the appropriate metal and support to develop SACs for catalytic transformation of molecules.

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1. Introduction

Single-atom catalysts (SACs) have proved to be active for many catalytic reactions and are proposed to significantly increase atom efficiency, which is important for sustainability and for lowering the cost of manufactured goods [1–10]. Among all of these SACs, the superior catalytic performance can be attributed to the synergistic effect and the strong-metal support interactions between the highly dispersed metal atoms and the surfaces of the support materials. For example, single Pt atoms (Pt₁) dispersed onto FeO_x nanocrystallites showed excellent activity and stability for both CO oxidation and preferential oxidation of CO (PROX) [6]. The metal (Pt₁)-support interaction weakens the adsorption strength of a CO molecule on Pt₁, facilitates the generation of oxygen vacancies on the FeO_x surface, and subsequently reduces the activation barriers for CO oxidation [6]. The catalytic behavior of Pt₁ and Au₁ an-

chored onto the {10-10} surfaces of ZnO nanowires (NWs) was investigated for steam reforming of methanol (SRM) [8]. Both the activity and selectivity, for SRM reaction, over the Pt₁/ZnO and Au₁/ZnO SACs are different, primarily due to the intrinsic differences in the chemical nature of different elements as well as the different degrees of metal-support interactions [8]. As one of the most catalytically active metals, the catalytic properties of Pd₁ SACs have been investigated for various catalytic reactions [7,9,11–18]. For example, atomically dispersed Pd atoms supported on Al₂O₃ were reported to be highly stable and achieved high activity for CO oxidation at low temperatures [9]. Highly dispersed Pd on ZnO powders have been reported to possess excellent catalytic activity and selectivity for chemoselective hydrogenation of acetylene [11]. Single Pd atoms supported on various types of supports such as metal oxides [7,13], carbon [15] and metal particles [12] were also reported to exhibit excellent catalytic performance for hydrogenation reac-

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tions.

Among various supported Pd catalysts, ZnO supported Pd catalysts have attracted broader scientific interest because of its potential applications for SRM to produce hydrogen [19]. Onboard reforming of methanol to produce hydrogen has been suggested to alleviate the problems of hydrogen storage and can be implemented for onboard feed of hydrogen to polymer electrolyte membrane fuel cells (PEMFCs) to produce electricity [20,21]. For SRM reaction, Pd nanoparticles (NPs) supported on ZnO powders, after appropriate reduction treatment, showed high activity and selectivity towards CO₂ [19] while on other supports, decomposition of methanol to CO predominates [22,23]. The superior CO₂ selectivity of the Pd/ZnO system is attributed to the formation of the intermetallic compound PdZn [19], which is proposed to possess a similar valence density of states to that of Cu. The Cu/ZnO systems are used commercially for SRM and methanol synthesis reactions. Methanol synthesis through hydrogenation of CO₂ under high, or even atmospheric, pressures have been tested on Pd/ZnO catalytic systems [24,25]. The formation of PdZn alloy NPs is again proposed to be responsible for the experimentally observed high activity and selectivity. Study of reverse water-gas-shift (RWGS) reaction on Pd/ZnO systems demonstrated that the rate of CO₂ conversion was strongly dependent on the size of the PdZn NPs [26]. Investigations of PROX on metal oxides supported Pd NPs suggested that these systems provided poor activity and selectivity although the Pd/ZnO system was most active and selective among all the oxides supports [27]. Modifications of the Pd/ZnO system can significantly enhance its PROX activity by suppressing H₂ oxidation [27]. Recent studies reported that for CO oxidation on PdZn systems the initial rates depend on the composition of the Pd-Zn bimetallic phases. The enhanced rate of CO oxidation on the PdZn over the Pd systems is proposed to originate from the weakening of the CO adsorption and easier binding of oxygen to Pd sites modified by Zn. The interaction of Pd with Zn or the isolation of neighboring Pd sites may play a major role in modulating the adsorption and catalytic reactivity of Pd-based catalysts [28].

In this work, we report the successful synthesis of Pd₁/ZnO SACs and the investigations of their catalytic performance for SRM, CO oxidation, hydrogen oxidation, PROX, and RWGS reactions. We further conducted structural characterization of both the as-synthesized and the used Pd₁/ZnO SACs and correlated the structural observations with their catalytic performance. The Pd₁/ZnO SAC yields excellent activity and selectivity for SRM reaction, is active for H₂ and CO oxidation, but gives poor activity and/or selectivity for PROX, WGS and RWGS reactions. This work highlights the importance of selecting the right combinations of single metal atoms and the support materials for desired catalytic reactions.

2. Experimental

2.1. Catalyst preparation

The ZnO NWs were synthesized by a one-step, non-catalytic,

and template-free physical vapor deposition process [29]. Briefly, mixed ZnO and carbon powders, in a 1:1 ZnO/C weight ratio, were heated to about 1100 °C in a high temperature tube furnace. The ZnO NWs were formed inside the tube furnace, transported, by a carrier gas, out of the tube, and collected.

The ZnO NWs supported Pd₁ SACs were synthesized by a modified adsorption method. Typically, the preformed ZnO NWs were dispersed into deionized water under rigorous stirring and a calculated amount of aqueous solution (Pd(NO₃)₂) precursor was then added dropwise to the ZnO solution at room temperature. After continuously stirring and aging for 2 h, the suspension was filtered and washed with deionized water for several times to remove the salt residuals. The resultant solid was dried at 60 °C for 12 h without any treatment hereafter. The nominal loading of Pd was kept at 0.05 wt%. We used such low level of Pd loading in order to make sure that all the Pd atoms adsorbed onto the ZnO NWs and that no Pd clusters or NPs formed during the synthesis processes.

2.2. Characterization

The morphologies of the freshly prepared Pd₁/ZnO SACs were characterized by scanning electron microscopy (SEM, JEOL JXA-8350F). High-angle annular dark-field (HAADF) images, which provide information on the spatial distribution of the individual Pd atoms, were obtained on a JEM-ARM200F aberration-corrected scanning transmission electron microscope (AC-STEM) with a guaranteed spatial resolution of 0.08 nm. Before AC-STEM examination, the Pd₁/ZnO SACs were ultrasonically dispersed in ethanol and then a drop of the solution was transferred onto a transmission electron microscopy (TEM) copper grid coated with a thin lacey carbon film.

2.3. Evaluation of catalytic performance

The SRM reactions were carried out in a fixed-bed reactor with 50 mg of Pd₁/ZnO. Methanol (CH₃OH) and deionized water were premixed, pumped to a He carrier gas, and vaporized at 160 °C. The gas feed lines were maintained at 160 °C in order to avoid any condensation of CH₃OH and H₂O. The final feed gas composition was 8 vol% CH₃OH + 12 vol% H₂O and He balance. The total gas flow rate was 37 ml/min, providing a gas hourly space velocity (GHSV) of 44400 ml·h⁻¹g⁻¹_{cat}. The reaction products were on-line analyzed by a gas chromatograph (Agilent 7890A). Quantitative analysis of CO, CO₂, and methanol was realized by calibrating with standard samples. The methanol conversion was calculated based on the carbon balance. The selectivity of CO₂ formation was determined as moles of CO₂ per mole of (CO₂ + CO) in the products.

The WGS tests were conducted in a fixed-bed reactor with 50 mg of Pd₁/ZnO and a reaction feed gas of 2 vol% CO + 10 vol% H₂O balance with He. The total flow rate is 40 ml/min, providing a GHSV of 48000 ml·h⁻¹g⁻¹_{cat}. The reaction feed gas mixture was preheated to 160 °C to vaporize water. For the RWGS reaction, the feed gas composed of 5 vol% H₂ + 0.6 vol% CO₂ balance with helium with a GHSV of 96000 ml·h⁻¹g⁻¹_{cat}. The CO (CO₂) conversion rate was calculated based on the differ-

ence between the inlet and outlet CO (CO_2) concentrations.

The catalytic tests for CO oxidation, hydrogen oxidation and PROX were conducted with 50 mg of Pd_1/ZnO and a GHSV of $39600 \text{ ml} \cdot \text{h}^{-1} \cdot \text{g}^{-1}_{\text{cat}}$. The feed gas composition was 1 vol% CO + 1 vol% O_2 for CO oxidation, 1 vol% H_2 + 1 vol% O_2 for hydrogen oxidation, and 1–40 vol% H_2 + 1 vol% CO + 1 vol% O_2 for PROX. The outlet gas composition was on-line analyzed by a gas chromatograph (Agilent 7890A). The stability tests were conducted at 185 °C. The H_2 or CO conversion rate was calculated based on the inlet and outlet H_2 or CO concentrations.

3. Results and discussions

3.1. Structural characterization of Pd_1/ZnO catalysts

Fig. 1(a) is a typical SEM image of the as-prepared Pd_1/ZnO SACs. The average diameter of the ZnO NWs was estimated to be $\sim 50 \text{ nm}$ with an average length of ~ 10 micrometers, resulting in a high aspect ratio of about 200. The total surface-area of the ZnO NWs ranges from about 15 to about $20 \text{ m}^2/\text{g}$. The general morphology of the ZnO NWs did not change after catalytic evaluations. These ZnO NWs, with the length along the ZnO [0001] direction, are primarily enclosed by the {10-10} nanoscale facets and their surfaces are flat and smooth. Because of the extremely large aspect ratio of these NWs the support surface of the Pd_1/ZnO SACs can be considered to be ZnO {10-10}.

HAADF-STEM imaging was used to characterize the spatial distribution and dispersion of the deposited Pd atoms as well as the change of these Pd atoms after catalytic tests. This imaging technique can detect atoms of heavy elements dispersed onto high-surface-area light-element supports: The image intensity is approximately proportional to the Z^2 (atomic number) of the probed species [30]. Representative HAADF images of the Pd_1/ZnO SACs are shown in Fig. 1(b) and (c), where the ZnO NWs were tilted close to the ZnO [10-10] zone axis. After analyses of many low- and high-magnification HAADF images, we did not find any Pd clusters/particles in the as-prepared Pd_1/ZnO SACs. In Fig. 1(c), the brighter dots represent single Pd atoms (indicated by the yellow arrows) which are located on

the Zn cation sites of the ZnO NWs. These isolated Pd_1 single atoms were relatively stable under electron beam irradiation, implying that they were most probably anchored onto the Zn vacancy or other types of defect sites on the ZnO {10-10} surfaces. Based on the previous density functional theory (DFT) calculations [8], at these low loading levels of Pd, the Pd_1 single atoms act as surface dopants of the ZnO to be stabilized at the Zn cation vacancy sites. These Pd dopant atoms are most probably positively charged, resulting in the weakening of the CO adsorption strength and the activation of the nearby oxygen atoms of the ZnO support. Unfortunately, at such low levels of metal loading the XPS and other spectroscopic techniques cannot provide reliable data to exclusively determine the oxidation states of these Pd_1 single atoms. The HAADF-STEM images (e.g., Fig. 1(c)) unambiguously confirm that the Pd_1 single atoms are located at exactly the Zn positions of the ZnO NW.

3.2. Catalytic testing of Pd_1/ZnO SACs

3.2.1. Methanol steam reforming, water gas shift and reverse water gas shift

Pristine ZnO NWs, Pd_1/ZnO NWs and Pd NP/ZnO NWs were evaluated for the SRM reaction. Only H_2 , CO, CO_2 and H_2O were detected at the outlet of the tubular reactor. The methanol conversion rates as a function of temperature are displayed in Fig. 2(a) and the stability test on the Pd_1/ZnO SAC at 380 °C is shown in Fig. 2(b). Since ZnO is a catalyst for SRM reaction the conversion rates for both the ZnO NWs and Pd_1/ZnO NWs increased with reaction temperature. Fig. 2(a), however, clearly demonstrates that even a minute amount of Pd single atoms (0.05 wt%) anchored onto the ZnO NWs significantly increased the activity of the SRM reaction. Specifically, the methanol conversion rate reached 68% at 380 °C and almost full conversion at 400 °C on the Pd_1/ZnO while the conversion rates on the pristine ZnO NWs reached only 15% and 27%, respectively. We previously reported that the calculated turn-over-frequency (TOF) at 380 °C on pristine ZnO NWs was 0.018 s^{-1} [8]. For the Pd_1/ZnO SAC, the corresponding TOF (per Pd_1 site) for the SRM reaction was estimated to be 3.2 s^{-1} , about two orders of magnitude higher than that of the pristine ZnO NWs. On the pristine

Fig. 1. (a) SEM image of the as-prepared Pd_1/ZnO nanowire SAC shows the general morphology and the high aspect ratio of the ZnO nanowires which were used to support Pd single atoms; (b) low magnification HAADF image of the as-prepared Pd_1/ZnO nanowire SAC clearly reveals the smooth and flat ZnO surfaces and the absence of Pd clusters or nanoparticles; and (c) atomic resolution HAADF image reveals the presence of only Pd single atoms (indicated by the yellow arrows) at the Zn cation positions of the ZnO NW.

Fig. 2. Methanol conversion and CO selectivity for the SRM reaction over Pd₁/ZnO SAC (a), specific rates of ZnO NW supported Pd single atoms, clusters and particles (b), and a stability test at 380 °C (c). For the SRM reaction, both the activity and the selectivity did not change appreciably after 800 min stability test.

ZnO NWs, the selectivity toward CO is very low (~ 3%) and it seems to be independent of reaction temperature. The CO selectivity on the Pd₁/ZnO SAC started relatively high (25%) at 260 °C but it decreased rapidly with reaction temperature and reached a level as that of the pristine ZnO NWs for reaction temperatures above 340 °C.

Our experimental results and literature reports suggest that ZnO supported Pd NPs or clusters catalyze methanol decomposition ($\text{CH}_3\text{OH} \rightarrow \text{CO} + \text{H}_2$) and yield CO [19,31] while PdZn alloy NPs, which can be formed by reducing ZnO supported Pd NPs at temperatures > 300 °C, direct the reaction towards CO₂ production [32]. The initial high CO selectivity on the Pd₁/ZnO SAC is probably due to the presence of residuals since the as-prepared Pd₁/ZnO SAC was directly used without any further treatment. Upon the second cycle run (Fig. 2(a)), the CO conversion did not change appreciably from that of the first cycle run but the CO selectivity was low (close to that of the pristine ZnO) and kept constant with reaction temperature. The ZnO supported Pd single atoms yielded excellent CO₂ selectivity (over 97% at temperatures > 360 °C), much higher than the ZnO supported Pd NP catalysts and comparable to those of the

supported PdZn alloy NPs [32]. The catalytic behavior of the Pd₁/ZnO SAC seems to be drastically different from that of the ZnO supported Pd clusters or NPs but similar to those of the PdZn alloy catalysts. Fig. 2(b) displays the specific rates of a series of ZnO NW supported Pd catalysts for the SRM reaction at 300 °C. Our characterization data showed that for Pd loading levels < 0.05 wt% the Pd/ZnO NW catalyst consisted of only Pd single atoms. With increasing levels of Pd loading, Pd clusters and Pd NPs are formed. In terms of specific rate, Fig. 2(b) clearly demonstrates that the Pd₁/ZnO SAC possesses the highest activity for the SRM reaction. The detailed discussions on the size-dependent selectivity for the SRM reaction on ZnO supported Pd clusters and NPs will be reported separately.

As clearly shown in Fig. 2(c), the Pd₁/ZnO SAC was very stable for the SRM reaction at 380 °C even after the 800 min run. The HAADF images of the used Pd₁/ZnO SAC (Fig. 5(a) and (c)) show that both Pd single atoms (indicated by the yellow arrows) and two-dimensional clusters of sizes ~ 1 nm (indicated by the red arrows) were present after the 800 min run. Detailed analyses revealed that the two-dimensional clusters consisted of one or, at most, two layers of Pd atoms (Fig. 5(c)). The

number density of these Pd rafts was low in the used catalyst. Since we did not observe any drop of the SRM activity or the change of CO selectivity we propose that for the SRM reaction these two-dimensional clusters, which were tightly bound to the ZnO surfaces, may catalytically behave similar to those of the supported Pd single atoms or they did not contribute appreciably because of their small amount in the used catalyst.

Recent calculations suggest that for the SRM reaction the reaction pathway towards CO₂ can be accomplished via two different routes: (1) association of formaldehyde (from methanol) with hydroxyl (from water) and (2) decomposition of formaldehyde to CO followed by WGS reaction [8]. We previously reported that for the SRM reaction on the Pt₁/ZnO and Au₁/ZnO SACs, complete dehydrogenation of formaldehyde rather than its association with hydroxyl is favored [8]. In order to evaluate the catalytic processes on the Pd₁/ZnO SACs, we conducted WGS and RWGS tests on the as-prepared Pd₁/ZnO SACs at temperatures ranging from 260 to 440 °C. As shown in Fig. 3, this catalyst did not yield any observable activity for WGS reaction while CO₂ can be partially reduced during the RWGS reaction. These results suggest that under the SRM condition the Pd₁/ZnO SAC was not able to convert CO to CO₂ below 400 °C, implying that it possesses a different pathway from those on the Pt₁/ZnO and Au₁/ZnO SACs. We propose that the SRM reaction process over the Pd₁/ZnO SAC is similar to that on the PdZn system: the association of formaldehyde with hydroxyl eventually leads to the formation of CO₂ [9].

Although the Pd/ZnO systems were reported to be active for methanol synthesis via hydrogenation of CO₂ under atmospheric pressure [24], we have not detected any methanol product during our catalytic tests. The CO₂ reaction on ZnO could be structure sensitive. For example, it was reported that CO₂ could be activated and hydrogenated on the ZnO {10-10} during methanol synthesis on Cu/ZnO catalysts with the main products of CO and H₂O instead of methanol while methanol predominantly forms on the ZnO (0001) surface [33]. From this perspective, our Pd₁/ZnO SAC, with predominantly ZnO

{10-10} surfaces and a catalytic behavior similar to the Cu/ZnO catalytic system, may have a low selectivity to methanol during the RWGS reaction. Further work is needed to understand the fundamental processes of the WGS and RWGS reactions on ZnO NW supported noble metal SACs.

3.2.2. CO oxidation

The catalytic performance of the Pd₁/ZnO SAC for CO oxidation is displayed in Fig. 4. The CO conversion started at about 140 °C, increased gradually with temperature and achieved full conversion at about 196 °C. The pristine ZnO NWs, on the other hand, were totally inactive for CO oxidation. The Arrhenius plot, shown in the inset of Fig. 4(a), suggests an apparent activation energy (*E_a*) of ~ 69 kJ/mol. Our previous data showed that for CO oxidation on the M₁/ZnO SACs (M = Pd, Pt, Rh, Ir) the Pd₁/ZnO SAC possessed the highest activity [34].

The stability test of the Pd₁/ZnO SAC at 185 °C is shown in Fig. 4(b). The conversion rate dropped significantly with run time, ~25% after 150 min and > 50% after 800 min. Such deactivation behavior during CO oxidation is in stark contrast to that of exactly the same catalyst for the SRM reaction (cf. Fig. 2(b)). The deactivation of supported Pd catalysts, such as Pd/graphene [35] and Pd₁/Al₂O₃ [9] has been investigated. It has been suggested that the Pd²⁺ is being reduced during the CO oxidation process, significantly weakening the interaction between the Pd single atoms and the support surface and the subsequent clustering of Pd₁ to form Pd clusters. In our catalyst, after the 800 min run, we observed aggregation of Pd single atoms into clusters or particles with an average size of ~ 3 nm (Fig. 5(b) and (d)), causing the deactivation of the Pd₁/ZnO SAC during the CO oxidation reaction.

3.2.3. Hydrogen oxidation

The hydrogen oxidation reaction was conducted with a feed gas composition of 1 vol% H₂ + 1 vol% O₂ and balance with He. As shown in Fig. 6, the hydrogen conversion increased with reaction temperature and complete conversion was reached at

Fig. 3. CO conversion for WGS (a) and CO₂ conversion for RWGS (b) reactions over the Pd₁/ZnO SAC. The Pd₁/ZnO SAC was not active for the water-gas-shift reaction at all and showed only slight activity at high reaction temperatures for the reverse water-gas-shift reaction.

Fig. 4. CO conversion (a) and stability test at 185 °C (b) over the Pd₁/ZnO SAC. The Arrhenius plot and the calculated activation energy are shown in the inset in (a). For CO oxidation, the Pd₁/ZnO SAC deactivated significantly after 800 min run at 185 °C.

140 °C. The TOF values are calculated to be 0.03 and 0.93 s⁻¹ at 60 and 120 °C, respectively, which is 1–2 orders of magnitude higher than those reported on Pd/Al₂O₃ [36] and Au₁/CeO₂ catalysts [37]. The high activity of H₂ oxidation is proposed to be a result of the good capability of supported Pd₁ atoms to dissociatively absorb H₂ and the Pd₁-induced activation of ZnO surface to provide activated oxygen species. Although there have been reports in literature that at least two contiguous Pd atoms are required for H₂ activation [38] recent density functional theory calculations indicated that Pd monomers can activate H₂ [39]. Isolated Pd single atoms supported on Ag [40],

Au [12] and Cu [41,42] surfaces have demonstrated superior capability in activating H₂. Our results unambiguously prove that isolated Pd single atoms supported on metal oxides can facilely activate H₂.

3.2.4. Preferential CO oxidation in hydrogen

PROX reactions with 40 vol% H₂ + 1 vol% CO and 1 vol% O₂ were conducted on Pd₁/ZnO SACs in the temperature range of 100–200 °C. Fig. 7(a) shows that the CO conversion rate increased with temperature, reached the maximum of 19% at 160 °C, and then decreased with further increase of the reaction temperature. Such behavior can be understood if we consider the competitive H₂ oxidation on the same Pd₁ active sites as discussed in the last section. During the PROX reaction, the O₂ conversion on the Pd₁/ZnO SAC (Fig. 7(b)) was relatively low at temperatures below 140 °C, increased significantly at ~160 °C and then increased slowly at higher temperatures.

In order to understand the competitive oxidation reactions of CO and H₂ on the Pd₁/ZnO SAC a series of PROX reactions

Fig. 5. Low magnification (a,b) and atomic resolution (c,d) HAADF images of the Pd₁/ZnO SAC after 800 min run for the SRM (a,c) and CO oxidation (b,d) reactions. Small Pd clusters with sizes ranging 1–2 nm (a) and 2–3 nm (b) are observable in the used Pd₁/ZnO SAC. The high resolution HAADF images show that both Pd atoms (indicated by the yellow arrows in (c)) and small two dimensional clusters (indicated by the red arrows in (c)) were present in the Pd₁/ZnO SAC after the SRM reaction for 800 min. Three-dimensional Pd nanoparticles (indicated by the green arrow in (d)) were formed after 800 min CO oxidation reac-

Fig. 6. Conversion rate for oxidation of hydrogen over the Pd₁/ZnO SAC.

Fig. 7. (a) CO conversion for the PROX and CO oxidation over the Pd₁/ZnO SAC with different H₂ concentrations. At reaction temperatures < 160 °C, the presence of H₂ slightly enhanced CO oxidation rate but at reaction temperatures > 180 °C, the presence of H₂ significantly hindered the oxidation of CO to CO₂. (b) Oxygen conversion rates for H₂ oxidation, CO oxidation and PROX reactions over Pd₁/ZnO SAC. At reaction temperatures < 140 °C, CO adsorption on the Pd single atoms drastically poisoned the hydrogen oxidation reaction.

were conducted in the temperature range of 180–200 °C with varying H₂ concentrations. Fig. 7(a) clearly demonstrates that at reaction temperatures < 160 °C the presence of H₂, even if a small amount, slightly enhances CO conversion on the Pd₁/ZnO SAC. At reaction temperatures > 190 °C, the presence of H₂, however, significantly inhibits CO oxidation on the Pd₁/ZnO SAC. Without the presence of any CO the O₂ conversion reached ~50% (the highest O₂ conversion value for hydrogen oxidation on the Pd₁/ZnO SAC) at ~120 °C while there were hardly any O₂ conversion under the PROX reaction condition at this temperature (Fig. 7(b)). This observation suggests that at low reaction temperatures the presence of CO significantly inhibited the oxidation of H₂ while at higher reaction temperatures the presence of H₂ significantly inhibits CO oxidation. These results clearly imply that at low temperatures CO binds to Pd₁ sites and blocks the adsorption and activation of H₂. Similar results

have been reported for Au and Cu supported Pd₁ SACs where CO selectively binds to isolated Pd₁ atoms and blocks the Pd sites for H₂ adsorption/dissociation [12,43]. When the reaction temperature increases, the CO binding strength is weakened which allows the competitive H₂ adsorption/dissociation. At higher reaction temperatures, the H₂ activation process becomes competitively dominant and thus the CO oxidation on the Pd₁ sites is significantly suppressed.

4. Conclusions

ZnO NW supported Pd₁ SACs were successfully prepared and their catalytic properties were evaluated for selected catalytic reactions. For the SRM reaction, the Pd₁/ZnO SAC demonstrated excellent activity, selectivity towards CO₂, and stability at high reaction temperatures. The Pd₁/ZnO SAC was active but not stable for CO oxidation. The CO adsorption induced movement of Pd atoms may play a role in determining the stability of the Pd₁/ZnO SAC. The strong dissociative activation of H₂ on supported Pd₁ atoms makes this catalyst less useful for PROX but may be utilized for hydrogenation reactions. For oxidation of H₂, however, the Pd₁/ZnO SAC was very active even though CO poisoning, especially at low reaction temperatures, persisted. These results help the fundamental understanding of the catalytic properties of the Pd₁/ZnO SACs. Since the approach of this study is general it can be broadened to the investigation of catalytic properties of other types of supported metal SACs for a plethora of catalytic reactions.

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Graphical Abstract

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Probing the catalytic behavior of ZnO nanowire supported Pd₁ single-atom catalyst for selected reactions

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ZnO nanowire supported Pd single-atom catalysts (SACs) were synthesized and evaluated for selected catalytic reactions and the Pd₁/ZnO SAC demonstrated excellent activity and selectivity for steam reforming of methanol to produce hydrogen.

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ZnO纳米线负载Pd₁单原子催化剂催化若干反应性能的考察

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摘要: 将孤立的Pd原子分散到ZnO纳米线(NWs)上作为单原子催化剂(SACs), 并考察了它们在若干反应中的催化性能. Pd₁/ZnO SAC对甲醇蒸汽重整制氢反应表现出高的活性、稳定性和CO₂选择性. 该催化剂体系对CO和H₂的氧化也具有高活性, 但在富氢物料中CO优先氧化反应中的催化剂性能较差, 这主要是由于在ZnO负载的Pd₁原子上H₂氧化的强竞争反应所致. 常压下在Pd₁/ZnO SAC上就可发生逆水汽变换反应. 该系列催化反应测试结果清楚地表明, 选择合适金属与载体对开发分子催化转化用单原子催化剂至关重要.

关键词: 单原子催化剂; 钯; 氧化锌纳米线; 甲醇蒸汽重整; 一氧化碳氧化; 加氢

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