Partial oxidation of methanol on Au-Pd/ceria

Qing-bo Chen, Lai-tao Luo, & Xiaomao Yang

Institute of Applied Chemistry, Nanchang University, Nanchang 330031, P.R. of China

Institute of Applied Materials, Jiangxi University of Finance & Economics, Nanchang 330013, P.R. of China

Email: luolaitao@163.com

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Partial oxidation of methanol over Au/CeO₂ and Au-Pd/CeO₂ catalysts is reported here. The catalysts have been characterized by using X-ray diffraction, temperature programmed reduction and temperature-programmed desorption of methanol. The studies show that the Au-Pd alloy particles are formed, and Au dispersion on CeO₂ support is promoted owing to the addition of Pd to the Au-Pd/CeO₂ bimetallic catalyst. Compared with Au/CeO₂ catalyst, the Au-Pd/CeO₂ catalyst has larger active surface area and stronger interaction between Au-Pd and support. The desorption temperature of methanol is low. The Au-Pd/CeO₂ catalyst reduced by H₂ before the reaction shows higher methanol conversion and hydrogen selectivity, which suggests that the metallic states of Au, Pd and Au-Pd play an important role in the partial oxidation of methanol.

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Methanol is suitable liquid fuel for producing hydrogen due to its high-energy, high hydrogen-to-carbon ratio and availability. Hydrogen may be produced directly from methanol by a number of different processes, such as methanol decomposition (MD), steam reforming (SR), partial oxidation or oxidative reforming (OSR). When used in engine and vehicle technologies, hydrogen produced by partial oxidation of methanol (POM) has some advantages, because this process requires air instead of steam. It is an exothermic reaction and does not require heat supply. It is, thus, suitable for supplying hydrogen for fuel cell since it is a fast reaction. CeO₂ is a very active support for oxidation reactions. Dispersion of the supported metal to cerium oxide has oxygen vacancies in the fluorite oxide structure and has a higher oxygen storage capacity (OSC). Producing hydrogen by POM was studied in detail over supported Cu and Pd catalysts. Unfortunately, Wang et al. found CO as by-product in POM over Cu/Cr catalysts. If the carbon monoxide level exceeds a few ppm, the precious metal-based anode electrocatalyst of the fuel cell deactivates. Haruta et al. found that gold catalysts exhibited high activity towards CO oxidation at low temperature. Au catalysts were used for POM, and the amount of CO was reduced. However, Au catalysts are sintered at high temperature. To avoid sintering, the second ingredient is added. Venezia et al. found that the conversion of CO was increased in CO oxidation over SiO₂-supported gold-palladium catalysts, and the conversion strongly depended on interaction between Au and Pd.

The addition of Pd to Au catalysts caused the change of the size of catalyst and the appearance of bimetallic clusters of Auₚₚ, and brought synergistic effect between Au and Pd. With the aim of developing new suitable systems for partial oxidation of methanol, Au/CeO₂ and Au-Pd/CeO₂ bimetallic catalysts have been prepared by alcohol-reduction method and characterized by X-ray diffraction (XRD), temperature programmed reduction (TPR) and temperature-programmed desorption (TPD).

Materials and Methods

Nanometer CeO₂ was prepared by deposition-precipitation method, using 0.1 mol/L Ce(NO₃)₃·6H₂O as precursor with polymer Polyethylene Glycol (PEG-4000) protection; 0.1 mol/L (NH₄)₂CO₃·H₂O was added into the above solution quickly and maintained at 313 K for 10 min under vigorous stirring (800 r/min). The molar ratio of (NH₄)₂CO₃·H₂O and Ce(NO₃)₃·6H₂O was 2:3. The precipitate was vacuum-filtered and washed with deionized water and ethanol thoroughly. The sample was dried in vacuum at 343 K for 12 h and calcined in air at 673 K for 1 h.
The Au-Pd/CeO₂ catalyst was prepared by an alcohol-reduction method. The appropriate quantities of HAuCl₄ (10² mol/L) and PdCl₂ (10² mol/L) were dissolved in 400 mL mixture solution of ethanol/water (1/1, v/v) containing the polymer poly-N-vinyl-2-pyrrolidone (PVP). The mole ratio of PVP and (HAuCl₄+PdCl₂) was 5:1. After adding CeO₂ support to the solution, the suspension was stirred and refluxed at 363 K for 5 h under N₂. The solvents were removed using rotary evaporator, and the solid was washed several times to eliminate superfluous PVP. Finally, the samples were dried in oven at 343 K and calcined in air at 673 K for 1 h. The result of inductively coupled plasma (ICP) indicated that load of the deposit noble metals was 2.0% (Au:Pd, 6:4 wt/wt).

The Au/CeO₂ catalyst was prepared by following the same method as Au-Pd/CeO₂ catalyst and the content of Au was 2.0 wt%.

X-ray diffraction measurements were carried out with German Bruker-AXS Corporation D8 Advence diffractometer equipped with a rotating anode, Cu Kα radiation. Operating voltage was 40 kV and current 30 mA, with a scanning rate of 1°/min from 20 =25° to 65°. Auₚdₚ alloy size was calculated by Scherrer formula \( d = \frac{k \lambda}{B \cos \theta} \).

Chemical compositions of the catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using Perkin-Elmer Optima 5300 DV instrument.

Temperature-programmed reduction (TPR) was carried out in-house apparatus over 0.1g catalysts. The samples were first heated from room temperature to 873 K in N₂ (40 mL/min) at a rate of 5 K/min in order to remove possible impurities contained in the samples. After cooling to room temperature in N₂, the gas mixture H₂/ N₂ (5:95, v/v) was introduced into the reactor. The gas composition was analyzed before and after the reaction by an on-line gas chromatograph with thermal conductor detector (TCD). The porapak Q column and 5 A molecule sieve column analyzed H₂O, CH₃OH, CO₂, HCOOCH₃ and H₂, CO, CH₄, respectively. The catalytic activities of the catalysts were expressed by CH₃OH conversion (%). Hydrogen selectivity was defined as follows:

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\text{H}_2 \text{ selectivity (\%)} = \left( \frac{\text{moles of H}_2 \text{ produced}}{\text{moles of methanol consumed} \times 2} \right) \times 100
\]

Results and Discussion

Structural characterization of Au/CeO₂ and Au-Pd/CeO₂ catalysts

The XRD patterns of Au/CeO₂ and Au-Pd/CeO₂ catalysts are shown in Fig. 1. The peaks observed at 2θ =28.5°, 32.8°, 47.5° and 57.5° were assigned to the diffraction patterns of CeO₂ (111), (200), (220) and (311); a weak diffraction signal of Au (111) in the spectra is observed at 2θ=38.18° in the sample. No Pd peak was observed in the XRD pattern of Au-Pd/CeO₂ sample because the content of Pd was little and the particle of Pd was too small to be detected. The peak observed at 2θ=40.46° was assigned to Auₚdₚ alloy, which indicated that there was interaction between Au and Pd and formed Auₚdₚ alloys of enriched gold model. The existence of the Auₚdₚ alloy could improve the performance of the Au-Pd/CeO₂ catalyst.

Activity measurements of the catalysts

The partial oxidation of methanol was performed in a continuous micro-reactor. The catalyst sample (100 mg) was reduced in situ first in H₂ flow (30 mL/min) at 623 K for 2 h, and then cooling to the reaction temperature. A gas mixture of CH₃OH (25.0 vol%), O₂ (7.5 vol%) and N₂ (balanced) was fed into the reactor. The gas composition was analyzed before and after the reaction by an on-line gas chromatograph with thermal conductor detector (TCD). The porapak Q column and 5 A molecule sieve column analyzed H₂O, CH₃OH, CO₂, HCOOCH₃ and H₂, CO, CH₄, respectively. The catalytic activities of the catalysts were expressed by CH₃OH conversion (%). Hydrogen selectivity was defined as follows:

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for POM. Using the Scherrer formula \( d = \frac{k\lambda}{B\cos\theta} \), the particle sizes of gold in Au/CeO₂ and Au-Pd/CeO₂ catalysts were 8.5 and 6.4 nm, respectively. The dispersion of gold in Au/CeO₂ was 0.138, and 0.183 in Au-Pd/CeO₂. Obviously, the dispersion of Au on CeO₂ support was promoted owing to the addition of Pd into Au/CeO₂ catalyst, which was advantageous to the POM reaction. It is worth noting that much Pd-Au-Ce was formed in the interface of Au-Pd/CeO₂ catalyst because of the interaction between Au and Pd, where oxygen transferred from CeO₂ to the precious metal. It was an important step for ceria-supported catalysts, and favourable for POM reaction.

**TPR studies**

The H₂-TPR can provide information concerning the reducibility of different chemical species presented in the catalyst as well as the degree of interaction between metal-metal and metal-support. The TPR profiles of CeO₂ support, Au/CeO₂ and Au-Pd/CeO₂ catalysts are shown in Fig. 2. The CeO₂ support exhibits a reduction peak at 720 K under the experiment conditions, which correspond to the reduction of superficial CeO₂ (Ce⁴⁺→Ce³⁺). The low temperature peak appearing at 455 K in the Au/CeO₂ catalyst could be attributed to the reduction of Au₂O₃, while the high temperature peak observed at 730 K corresponds to the reduction of superficial CeO₂. As reported, Au₂O₃ may completely transform into metallic Au when gold catalyst is calcined at the 673 K. However, the TPR peak of Au₂O₃ is found in Au/CeO₂ catalyst, and the reduced temperature is higher than that of pure Au₂O₃ (the reduced temperature of pure Au₂O₃ is 372K), suggesting that there is a strong interaction between Au₂O₃ and CeO₂.

No traces of any PdO phases could be found in the TPR patterns of Pd/CeO₂ and Au-Pd/CeO₂ catalyst, because PdO was reduced entirely in the calcined process. It is worth noting that the reduction peak areas of superficial CeO₂ in Au/CeO₂ and Au-Pd/CeO₂ catalysts decreased, owing to the formation of lots of Ce³⁺ on the surface of the catalysts. There was strong interaction between metal and CeO₂ support that resulted in its formation. As we observed in the XRD results, the metal Au and Au-Pd alloy appeared in Au-Pd/CeO₂ catalyst. A low temperature peak at about 368 K was assigned to the reduction of Au-Pd₂O and Au₂O₃ in the Au-Pd/CeO₂ catalyst. The reduction temperature of Au₂O₃ was lower than the Au-Pd/CeO₂, which possibly was attributed to dissociated H in palladium spillovered to the surface of Au₂O₃. The first ionization energy of Pd (804.3 KJ/mol) was lower than that of Au (890 KJ/mol). So, the electron could be transferred from Pd to the surface of Au₂O₃. It could also be seen that the low temperature peak area of the Au-Pd/CeO₂ catalyst was larger than that of Au/CeO₂ catalyst, because amounts of Au₂O₃ and Au₂Pd₂O in the Au-Pd/CeO₂ catalyst increased.

Defects of superficial CeO₂ and lots of oxygen vacancies were formed because of the strong interaction between Au-Pd and CeO₂. It was reported that noble metals like Pd can promote the oxygen mobility in CeO₂ lattice. In this situation, even if AuO and Au₄Pd₃O were reduced to metallic Au and Au₄Pd₃, the activated oxygen spillovered from CeO₂ might have re-oxidized Au⁰ and Au₄Pd₃O to AuO and Au₄Pd₃O through the opposite process:

\[
\text{Ce}^{4+}\text{O}_2^{+}\text{M}^0 (\text{Au}_3\text{Pd}_2\text{Au-Pd}) \rightarrow \text{Ce}^{3+}\text{O}_{1.5}^{1.5} + \text{MO}_{0.5} \\ 
\text{Ce}^{4+}\text{O}_2^{+} + \text{MO}_{0.5} \rightarrow \text{Ce}^{2+}\text{O}_{1.5} + \text{MO}
\]

**TPD characterization of the catalysts**

The CH₃OH-TPD profiles of the samples are shown in Fig. 3. Methanol desorption peak at about 665 K for the CeO₂ support was observed. Desorption peaks at about 611 and 688 K for the Au/CeO₂ catalyst might be attributed to the release of methanol in the CeO₂ support and the surface of metal, respectively. The desorption peak areas of CeO₂ were much larger than that of metal for Au/CeO₂ and
Au-Pd/CeO₂ catalysts, which shows that methanol is adsorbed on the surface of CeO₂ support mostly. Compared with pure CeO₂ support, it is clear that the desorption peak areas of CeO₂ are decreased for Au/CeO₂ and Au-Pd/CeO₂ catalysts, because a number of superficial CeO₂ particles are covered with the metals. The strong interaction between metal and CeO₂ support results in formation of a lot of Ce³⁺ on the surface of CeO₂, resulting in the decline of adsorbability of ceria for methanol and the reduction of desorption temperature. Desorption peak areas of metal are larger in Au-Pd/CeO₂ catalyst than that in Au/CeO₂ since the addition of Pd enhances the interaction between metals and supports and the dispersion of Au/CeO₂ catalyst. It is worth noting that the methanol desorption temperature on superficial CeO₂ is the lowest in Au-Pd/CeO₂ catalyst, which reveals that the interaction of CH₃OH-CeO₂ is the weakest. The activity of Au-Pd/CeO₂ catalyst towards POM is dominated by the adsorption of CH₃OH on Au, Pd and AuₙPdₙ surface. Methanol molecule is decomposed into methoxy species and H⁺:

\[ \text{CH}_3\text{OH}(g) \rightarrow \text{CH}_3\text{O}^-(a) + \text{H}^+(a) \quad \text{(1)} \]

where the symbols (g) and (a) represent the gas phase and the adsorbed state, respectively. The methoxy intermediate is converted to adsorbed formaldehyde by the abstraction of a hydrogen atom by a surface oxygen²⁰,²¹:

\[ \text{CH}_3\text{O}^-(a) + \text{O}^-(a) \rightarrow \text{CHO}^+(a) + \text{OH}^-(a) \quad \text{(2)} \]

HCHOₐ was converted into formate HCOOₐ through the surface reaction with adsorbed oxygen:

\[ \text{HCHO}^+_\text{(a)} + \text{O}^-\text{(a)} \rightarrow \text{HCOO}^\text{(a)} + \text{H}^\text{(a)} \quad \text{(3)} \]

Formate was an intermediate in the deep oxidation of methanol on the metal surface and the decomposition of formate resulted in CO₂ and H₂:

\[ \text{HCOO}^-\text{(a)} \rightarrow \text{CO}_2(g) + \text{H}^\text{(a)} \quad \text{(4)} \]

The important role of the surface oxygen was proposed for the selective production of formaldehyde. The adsorption of CH₃OH on the surface of metal dominated the activity of Au-Pd/CeO₂ catalysts. In addition, the weaker interaction between CH₃OH-CeO₂ was favourable for the adsorbed state CH₃OH transferring to the surface of metals from the surface of CeO₂. Abundant CH₃OH adsorbed on the surface of metal was propitious to POM reaction.

Figures 4 and 5 exhibit the methanol conversion and hydrogen selectivity of POM over Au/CeO₂,

\[ \text{CH}_3\text{OH}(g) \rightarrow \text{CH}_3\text{O}^-(a) + \text{H}^+(a) \]

\[ \text{HCHO}^+(a) + \text{O}^-(a) \rightarrow \text{HCOO}^-\text{(a)} + \text{H}^+(a) \]

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Pd/CeO\textsubscript{2} and Au-Pd/CeO\textsubscript{2} catalysts. With increasing temperature, a significant increase in methanol conversion and hydrogen selectivity could be observed. The methanol conversion increased from 75.1\% to 100\% by using Au-Pd/CeO\textsubscript{2} catalyst when reaction temperature varies from 523 K to 723 K. The increase in activity with increasing temperature of POM reaction is already reported\textsuperscript{9,10}. Further, the Au-Pd/CeO\textsubscript{2} catalyst exhibited higher hydrogen selectivity than the Au/CeO\textsubscript{2} and Pd/CeO\textsubscript{2} catalyst for most of oxidation reactions described in literature\textsuperscript{9,10}. The performance of the gold catalysts depended on the particle size of gold\textsuperscript{22-23}. The high hydrogen selectivity by using Au-Pd/CeO\textsubscript{2} catalyst could be explained since Au was highly dispersed on CeO\textsubscript{2} support, smaller Au particles are more active for hydrogen generation. In addition, the synergistic effect of Au and Pd in the Au-Pd/CeO\textsubscript{2} catalyst was favourable for improving the methanol conversion and hydrogen selectivity in POM\textsuperscript{11,12}. Feg-Wen Chang \textit{et al.}\textsuperscript{9} found that hydrogen selectivity was decreased significantly over Au/TiO\textsubscript{2} catalysts towards POM. The increase of the reaction temperature resulted in sintering of gold particles, and larger Au particles were more active for hydrogen oxidation. Figure 5 shows that hydrogen selectivity of the three catalysts increases with increasing reaction temperature, owing to the synergistic effect of Au and Pd.

It can be seen that hydrogen selectivity passed through some inflexion points. It is proposed that, for Pd-Au Pd- and Au-supported catalysts, several reactions such as methanol decomposition, steam reforming, water gas shift (WGS), reverse water gas shift (RWGS) and oxidation might be competing on the catalyst surface under partial oxidation conditions\textsuperscript{9,24}. According to the stoichiometry of POM (O\textsubscript{2}/CH\textsubscript{3}OH molar ratio of 0.3:1), complete consumption of oxygen should correspond to 60\% conversion of methanol. However, more than 60\% conversion of methanol was observed by using Au/CeO\textsubscript{2} and Au-Pd/CeO\textsubscript{2} catalysts between 623 and 723 K. It suggests that other methanol consumption reactions take place in the POM reactions. Different subordinate reactions occur at different temperatures. Initially, methanol quickly consumes oxygen and produces water and carbon dioxide (CH\textsubscript{3}OH+1.5O\textsubscript{2}→CO\textsubscript{2}+2H\textsubscript{2}O) between 523 and 757 K over Au/CeO\textsubscript{2} catalyst, which is highly exothermic reaction. However, POM reaction (CH\textsubscript{3}OH+0.5O\textsubscript{2}→CO\textsubscript{2}+2H\textsubscript{2}) happened at the same temperatures over Au-Pd/CeO\textsubscript{2} catalyst. As a result, the high hydrogen selectivity over Au-Pd/CeO\textsubscript{2} catalyst was obviously found between 523 and 575 K. Along with POM reaction, steam reforming reaction (CH\textsubscript{3}OH+H\textsubscript{2}O→3H\textsubscript{2}+CO\textsubscript{2}) occurred between 598 and 648 K over the two catalysts, showing that water was consumed and much hydrogen was produced. Little water was detected among the products, which may arose the steam reforming reaction occurred from 598 to 648 K. High temperature was unfavourable for Au/CeO\textsubscript{2} catalyst, and larger Au particles were more active for hydrogen oxidation. Thus, hydrogen selectivity decreased a little at high temperature (673-723 K). No decline of hydrogen selectivity was found over Au-Pd/CeO\textsubscript{2} catalyst at high temperature. It was considered that Au-Pd/CeO\textsubscript{2} catalyst was steady at high temperature. Furthermore, it could be seen that the conversion of methanol did not decline. Obviously, the catalyst activity was still higher than 90\% and the H\textsubscript{2} selectivity remained unchanged after reaction for 10 h. However, the deactivation for the industrial catalyst CuO/ZnO/Al\textsubscript{2}O\textsubscript{3} was quickly\textsuperscript{25}.

Haruta\textsuperscript{26} considered that metallic Au was active species for CO oxidation reaction over supported gold catalysts. However, some authors\textsuperscript{27} found that oxidized gold was also highly active. The effect of pretreatment for Au-Pd/CeO\textsubscript{2} catalyst on the methanol conversion and hydrogen selectivity in POM reaction are showed in Fig. 6. As compared with the unreduced Au-Pd/CeO\textsubscript{2} catalyst (A2), the reduced Au-Pd/CeO\textsubscript{2} catalyst (A1) (2 h in H\textsubscript{2}) shows high methanol conversion and hydrogen selectivity with a tipptop of 99\% and 40.66\% at 623 K. But, the
methanol conversion and hydrogen selectivity of A2 catalyst were only 91% and 19.99%, respectively. As shown in Figs 1 and 2, the A2 catalyst contained Au$_2$O$_3$ and Au$_x$Pd$_y$O, which were easy to be reduced in H$_2$ at 623 K. This implied that the reduction states of metals seem to be significant to improve activity of catalyst. The increased methanol conversion and hydrogen selectivity were caused by more metallic Au and Au-Pd alloy existing in A1 catalyst. The methanol conversion was almost equal in A1 and Au-Pd alloy existing in A1 catalyst. The methanol conversion was almost equal in A1 and A2 catalysts at high-temperature (above 623 K), which could be explained by most of AuO and Au$_x$Pd$_y$O species in A2 catalyst being reduced to Au and Au$_x$Pd$_y$ species by H$_2$ at high reaction temperature.

Conclusions
The PVP-stabilized Au-Pd/CeO$_2$ bimetallic catalyst, prepared by CH$_3$CH$_2$OH reductant method, was found to be active towards POM. The measured activity of POM over Au/CeO$_2$ and Au-Pd/CeO$_2$ catalysts decreased in the following order: Au-Pd/CeO$_2$> Au/CeO$_2$. Adding Pd to Au/CeO$_2$ catalyst could prevent the gold particles from sintering. As compared with Au/CeO$_2$ catalyst, the interaction between Au-Pd and CeO$_2$ support in Au-Pd/CeO$_2$ catalyst was stronger, the dispersion of metals and adsorption amount of CH$_2$OH were larger, and more Au$_x$Pd$_y$ alloy particles were formed. The different states of Au-Pd bimetal played a distinct role in POM reaction. The Au-Pd/CeO$_2$ catalyst reduced in H$_2$ before reaction showed higher methanol conversion and hydrogen selectivity, indicating that metallic Au, Pd and Au-Pd alloy were the active species towards POM reaction.

References