The mechanism studies of ethanol oxidation on PdO catalysts by TPSR techniques

Rui Lin[a,b], Meng-fei Luo[a], Qin Xin[b,*], and Gong-Quan Sun[b]

[a] *Institute of Physical Chemistry, Zhejiang Normal University, P.O. Box 36, Jinhua 321004, China*
[b] *DMFC and SKLC, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

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The paper studies the direct oxidation of ethanol and CO on PdO/$Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.75}Zr_{0.25}O_2$ catalysts. Characterization of catalysts is carried out by temperature-programmed desorption (TPD), temperature-programmed surface reaction (TPSR) techniques to correlate with catalytic properties and the effect of supports on PdO. The simple $Ce_{0.75}Zr_{0.25}O_2$ is in less active for ethanol and CO oxidation. After loaded with PdO, the catalytic activity enhances effectively. Combined the ethanol and CO oxidation activity with CO-TPD and ethanol-TPSR profiles, we can find the more intensive of CO_2 desorption peaks, the higher it is for the oxidation of CO and ethanol. Conversion versus yield plot shows the acetaldehyde is the primary product, the secondary products are acetic acid, ethyl acetate and ethylene, and the final product is CO_2. A simplified reaction scheme (not surface mechanism) is suggested that ethanol is first oxidized to form intermediate of acetaldehyde, then acetic acid, ethyl acetate and ethylene formed going with the formation of acetaldehyde, acetic acid, ethyl acetate; finally these byproducts are further oxidized to produce CO_2. PdO/$Ce_{0.75}Zr_{0.25}O_2$ catalyst has much higher catalytic activity not only for the oxidation of ethanol but also for CO oxidation. Thus the CO poison effect on PdO/$Ce_{0.75}Zr_{0.25}O_2$ catalysts can be decreased and they have the feasibility for application in direct alcohol fuel cell (DAFC) with high efficiency.

KEY WORDS: catalytic oxidation of ethanol; PdO/$Ce_{0.75}Zr_{0.25}O_2$ catalyst; CO-TPD; ethanol-TPSR; conversion; mechanism.

1. Introduction

Environmental concerns and the need for improvement the efficiency of vehicles had spurred the development of direct alcohol fuel cell (DAFC). Liquid fuels, such as low-molecular weight alcohols, have advantages compared to pure hydrogen, because they can be easily handled, stored and transported. Ethanol is a promising liquid fuel for direct-fueled systems because of its low cost, easy storage, transportation and high-energy content. Furthermore, the most attractiveness of ethanol used in DAFC is due to its low permeability across the polymer electrolyte membrane [1]. So ethanol oxidation can be taken as a representative model system for the electrochemical reaction of an organic compound containing two or more C-atoms [2,3]. There have many excellent catalysts used in DAFC but the intermediates, which formed during the oxidation, will poison and decrease the activity of catalyst [1–4]. So the work of finding a novel catalyst that has much higher activity of deep oxidization ethanol to CO_2 is quite important.

The use of Pd-based catalysts, for the complete oxidation of ethanol has increased considerably by a number of groups. There are two major reasons for this renewed interest in palladium. First, PdO is by far the cheapest noble metal in the market for its ability to catalyze VOCs at significantly low temperature; second, to achieve faster light-off performance, Pd-based catalyst offer significant advantages over the traditional three-way catalysts [5–12].

The electronic conductivity of PdO in correlation with its cost puts it in a competitive position against the widespread used Pt catalysts. In recent years, it has been found that cerium oxide containing zirconium oxide is much better than pure ceria for catalytic oxidation, due to the doping of Zr into CeO_2 increasing the oxygen mobility in the bulk of mixed oxide thus improving its oxygen storage capacity, enhancing its redox properties as well as thermal stability [13–17]. It is shown that $Ce_{0.75}Zr_{0.25}O_2$ solid solution, which was derived by sol–gel route, released oxygen at much lower temperature than that prepared by the solid-state reaction [15]. As the improvement in the oxygen release property at lower temperature will promote the oxidation of VOCs, thus in this study, the supports are all prepared by sol–gel method.

As the principle of the electro-oxidation and direct oxidation is the same, through the study of direct oxidation of ethanol and CO can shed light on its future use in DAFC. In this paper, the direct oxidation of ethanol and CO on PdO catalyst is discussed. Temperature-programmed surface reaction (TPSR) and temperature-programmed desorption (TPD) techniques are used to support the catalytic activity and understanding the role of PdO in the catalytic combustion of ethanol

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* To whom correspondence should be addressed.
E-mail: xinqin@dicp.ac.cn

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and CO. The aim of this work is to have more information on the reaction mechanism of ethanol oxidation and to make preparation for its future use in DAFC.

2. Experimental

2.1. Preparation of catalysts

The supports employed for the preparation of PdO catalysts are $Ce_{0.75}Zr_{0.25}O_2$. The detailed description for $Ce_{0.75}Zr_{0.25}O_2$ preparation is similar with the method of preparing $Ce_xZr_{1-x}O_2$ solid solution, which had been described in detail elsewhere [16,17]. Briefly, $Ce_{0.75}Zr_{0.25}O_2$ is prepared by using citric acid sol–gel method. $Ce(NO_3)_3$, $ZrO(NO_3)_2$ and citric acid, in calculated amounts, are dissolved in ethanol to form a solution. The solution is then slowly heated up to 100 °C until a viscous gel is obtained. Then, the gel is evaporated to dryness and the obtained powder is calcined in air at 900 °C for 4 h to obtain $Ce_{0.75}Zr_{0.25}O_2$ solid solution. $PdO/Ce_{0.75}Zr_{0.25}O_2$ catalysts were prepared by impregnation of $Ce_{0.75}Zr_{0.25}O_2$ supports in a H_2PdCl_6 solution for 1 h, and then dried and calcined in air at 650 °C for 4 h. The PdO content (calculated in Pd) of $PdO/Ce_{0.75}Zr_{0.25}O_2$ employed in the present study is variably from 0.1 to 5 wt%.

2.2. Activity measurements for ethanol oxidation and CO oxidation

The Catalytic activity for the oxidation of ethanol and CO oxidation are carried out in a fixed bed reactor (0.6 cm i.d.) in the temperature range of 100–400 °C (the heating rate is 20 °C/min) at ambient pressure at steady state. They are compared keeping fixed the catalyst weight of 150 mg supported by quarts wool and all sieved at 20–60 mesh size (in order to avoid mass or heat transfer effects). The reaction temperature is measured inside the catalytic bed with a thermocouple. The catalysts are directly exposed to the reaction mixture as the reactor temperature stabilized at reaction temperature without any pretreatment. The total gas flow rate is set at 80 ml/min in all tests.

The employed experimental set up for ethanol oxidation is similar to that of Blasin-Aubé *et al.* [18]. The feed gas is composed of ethanol vapor (5000 ppm) in air. In order to adjust the concentration of ethanol, two streams of air are employed: one is introduced into a regulated bubble saturator to carry out a constant flow rate of organic vapor, and the other is used to balance the overall concentration. Reactants and organic products are analyzed by a gas chromatograph (Agilent GC6890A), equipped with a flame ionization detector (FID), using HP-5 (cross linked 5% PE ME siloxane) capillary column. The chromatograph, equipped with a thermal conductivity detector (TCD), is used to analysis the production of CO_2 and CO employing a Porapak Q and molecular sieves 13X columns respectively.

Equipments and procedure involved in CO oxidation are almost identical to ethanol oxidation except that the reactor gas consists of 2.4%CO and 1.2%O_2 in N_2. CO_2 and CO is analyzed with a TCD as the same as the former.

2.3. TPSR and TPD

A 100 mg catalyst was fixed in the middle of a quartz tubular reactor by packing quartz wool at both ends. Reactants and products were analyzed by an on-line mass spectrometer (Balzers Omnistar MS200). All measurements were carried out with a heating rate of 20 °C/min and a He flow rate of 20 ml/min. Prior to the experiment, the samples was cleaned by oxidation in an O_2 flow (20 ml/min) at 500 °C for 10 min then evacuated in He at room temperature for 0.5 h. After that pretreatment, the catalysts were named "oxidized" [6].

Ethanol-TPSR test was carried out on a detecting system using CH_3CH_2OH/He gas under steady flow conditions. After the catalysts pretreated to the "oxidized" state, the vapor of ethanol was consecutively purged into until the amount of ethanol of effluent stream is constant. Excess of adsorbate was removed by allowing the sample to remain in He flow until no significant amount of adsorbate could be detected (approximately 1 h). Finally, the temperature was raised up to 900 °C. The mass spectrometer was operated to detect all possible products: CH_3CH_2OH ($m/e = 45$), CH_3CHO ($m/e = 43$), C_2H_4 ($m/e = 27$), $CH_3COOC_2H_5$ ($m/e = 76$) and CO_2 ($m/e = 44$) simultaneously.

The procedure for CO-TPD is almost identical to ethanol-TPSR except that the purged adsorbate is CO and to detect the desorbed CO ($m/e = 28$) and CO_2 ($m/e = 44$) species.

3. Results and discussion

3.1. Activity of CO oxidation on $PdO/Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.75}Zr_{0.25}O_2$ catalysts

So for, the best catalyst for the electro-oxidation and complete oxidation of ethanol has been found to be platinum. Many problems arise when using platinum as an electrode or catalyst for the oxidation of ethanol as it is poisoned by intermediates such as CO. So, if the catalyst has higher activity toward CO oxidation, it will decrease the CO poison effect on catalysts. Taking these into account, we studied about CO oxidation activity on $PdO/Ce_{0.75}Zr_{0.25}O_2$ catalyst in more detail.

Figure 1 shows the effect of Pd loading for CO oxidation on $PdO/Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.75}Zr_{0.25}O_2$ catalysts. None of these catalysts were pretreated before running the reaction. From figure 1, it can be seen that the oxidation of CO over single $Ce_{0.75}Zr_{0.25}O_2$ is quite

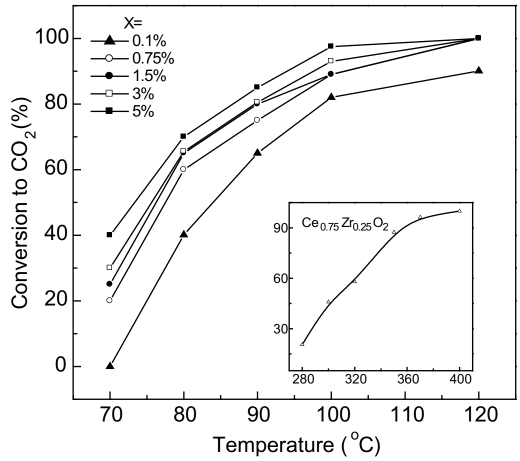

Figure 1. CO activity of $Ce_{0.75}Zr_{0.25}O_2$ and PdOx%/$Ce_{0.75}Zr_{0.25}O_2$ catalysts.

low, which reaches 100% conversion at 400 °C. After loaded with PdO, the catalytic activity enhances with increasing PdO loading, the higher the loading of PdO, the higher its catalytic activity. But we can also find with increasing the loading of PdO from 0.1% to 0.75% the catalytic activity enhances raptly, further increasing the loading of PdO, the activity only has a little increase. PdO 0.75%/$Ce_{0.75}Zr_{0.25}O_2$ reaches 100% conversion only at about 120 °C, which is about 280 °C lower than that of single $Ce_{0.75}Zr_{0.25}O_2$. It is clearly that the synergistic interaction between PdO and $Ce_{0.75}Zr_{0.25}O_2$ can greatly improve the catalytic activity of CO. In other words, the interaction between PdO and support is the main reason responsible for the higher activity of CO oxidation at low temperature.

3.2. CO-TPD of PdO/$Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.75}Zr_{0.25}O_2$ catalysts

CO-TPD profiles observed for PdO/$Ce_{0.75}Zr_{0.25}O_2$ (the loading of PdO is 1.5%) and $Ce_{0.75}Zr_{0.25}O_2$ following CO adsorption are shown in figure 2. They are in the amount of 150 mg. Almost no CO ($m/e = 28$) is observed during CO-TPD on PdO/$Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.75}Zr_{0.25}O_2$ catalysts. There are two CO_2 desorption peaks (α and β) on PdO/$Ce_{0.75}Zr_{0.25}O_2$ (at 110 and 320 °C). But none of CO_2 desorption peak is observed on $Ce_{0.75}Zr_{0.25}O_2$. As the CO adsorption amount of the catalysts is consistent with the CO_2 desorption amount, it indicates that the adsorption of CO is quite easy to occur and the adsorbed CO is also easy to be oxidized to CO_2 on the surface of PdO/$Ce_{0.75}Zr_{0.25}O_2$; but CO is quite difficult to be adsorbed on the surface of $Ce_{0.75}Zr_{0.25}O_2$, thus we cannot observe the desorbed CO_2. It may be the main reason of the large difference of CO oxidation activity between them. It indicates the combination of PdO and $Ce_{0.75}Zr_{0.25}O_2$ favors to the adsorption of CO and desorption of CO_2, so the CO oxidation activity of PdO/$Ce_{0.75}Zr_{0.25}O_2$ catalysts is greatly enhanced.

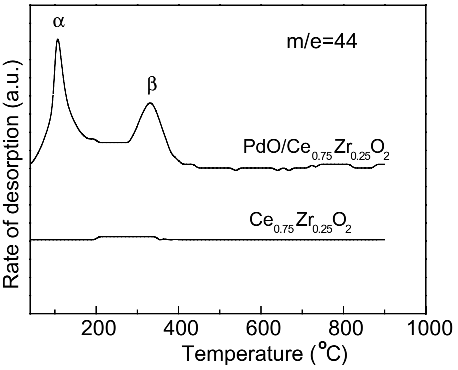

Figure 2. CO-TPD profiles of $Ce_{0.75}Zr_{0.25}O_2$ and PdO/$Ce_{0.75}Zr_{0.25}O_2$ catalysts, PdO in the loading of 1.5%.

3.3. Ethanol oxidation over PdO/$Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.75}Zr_{0.25}O_2$ catalysts

Figure 3 shows the ethanol oxidation activity as a function of temperature over PdO/$Ce_{0.75}Zr_{0.25}O_2$ catalysts and blank $Ce_{0.75}Zr_{0.25}O_2$. It is noticed that ethanol only began to be oxidized at 270 °C and converted completely at 400 °C on $Ce_{0.75}Zr_{0.25}O_2$. But after PdO supported on $Ce_{0.75}Zr_{0.25}O_2$, the catalytic activity enhances greatly with increasing the loading of PdO. When the loading of PdO is higher than 3%, the activity has a little decrease. PdO3%/$Ce_{0.75}Zr_{0.25}O_2$ reaches 100% conversion only at 170 °C. Combined with figure 1, it is evidence that the interaction between PdO and $Ce_{0.75}Zr_{0.25}O_2$ plays a promotional role in the ethanol oxidation as well as CO oxidation. We suppose one of the reasons may be due to the excellent redox cycling catalytic process of $Ce_{0.75}Zr_{0.25}O_2$ favors oxygen to form active O^{2-} and leads to the easy interaction of ethanol with oxygen. Moreover, PdO weakens the Ce—O bond thus increasing the mobility of the lattice oxygen, which may be involved in the ethanol oxidation [9,13]. This supposition needs to be identified using labeled oxygen for the oxidation of ethanol in further study. But now, it is limited by our laboratory limitation. Combined with the oxidation activity of CO (figure 1) and ethanol (figure 3), we can find there has a little difference between the oxidation of ethanol and CO. The catalytic activity of ethanol increases with increasing the loading of PdO from 0.1% to 3%, then having a little decrease when the loading of PdO is higher than 3% (from 3% to 5%). But the catalytic activity of CO oxidation enhances with increasing the loading of PdO, the higher the loading of PdO, the higher its catalytic activity. We conclude the suitable loading of PdO is 3% for ethanol and CO oxidation. Why the activity of ethanol and CO oxidation has some little difference may to due to the different reactant act differently on the surface of

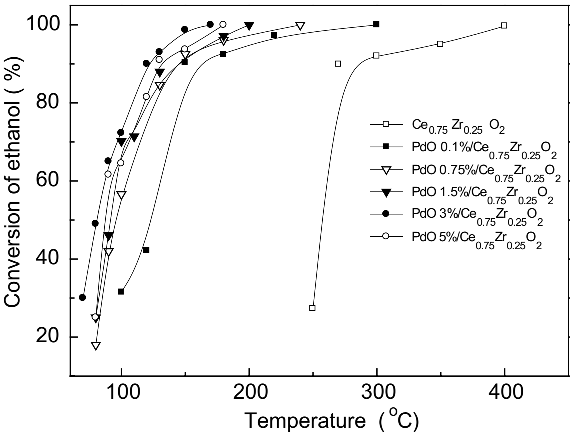

Figure 3. Ethanol oxidation activity as a function of temperature over $PdO/Ce_{0.75}Zr_{0.25}O_2$ catalysts and blank $Ce_{0.75}Zr_{0.25}O_2$.

catalyst, which needs further research. $PdO/Ce_{0.75}Zr_{0.25}O_2$ catalysts have much higher activity not only for ethanol oxidation but also for CO oxidation. So it has the potentiality used in DAFC.

3.4. *TPSR profiles of $PdO/Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.75}Zr_{0.25}O_2$*

Temperature-programmed surface reaction is a useful technique to identify the adsorbed intermediates on the catalyst and elucidate the reaction mechanism. We perform the ethanol-TPSR profile to have proof to identify the intermediates may be formed at un-steady state and to correlate with the catalytic activity of ethanol oxidation. Figure 4 shows ethanol-TPSR profiles of $PdO/Ce_{0.75}Zr_{0.25}O_2$ (the loading of PdO is 1.5%) and $Ce_{0.75}Zr_{0.25}O_2$ catalysts. On the $PdO/Ce_{0.75}Zr_{0.25}O_2$ catalyst, the adsorption particles are mainly focused at two temperature period (50–150, 150–350 °C). It indicates ethanol may have two adsorption states. In the low temperature stage (50–150 °C), the desorption species are mainly acetaldehyde and ethylene. It indicates in the low temperature, the capability of support to supply oxygen is not enough, thus does not favor to the deep oxidation of ethanol. But in the higher temperature stage (150–350 °C), the desorption specie is CO_2, at 190 °C (of relative small size) and 290 °C. It may be come from the further oxidation of acetaldehyde and ethylene to CO_2 as temperature rose. On $Ce_{0.75}Zr_{0.25}O_2$, almost no signals of ethanol, acetaldehyde and ethylene are detected, and the intensity of CO_2 is very weak. It can be deduced that it is difficult for ethanol to be adsorbed on the surface of $Ce_{0.75}Zr_{0.25}O_2$ and the desorbed CO_2 is quite less, which is in weak intensity. Combined the activity of ethanol oxidation with ethanol-TPSR, we can find the stronger the intensity of desorbed CO_2, the higher its ethanol oxidation activity.

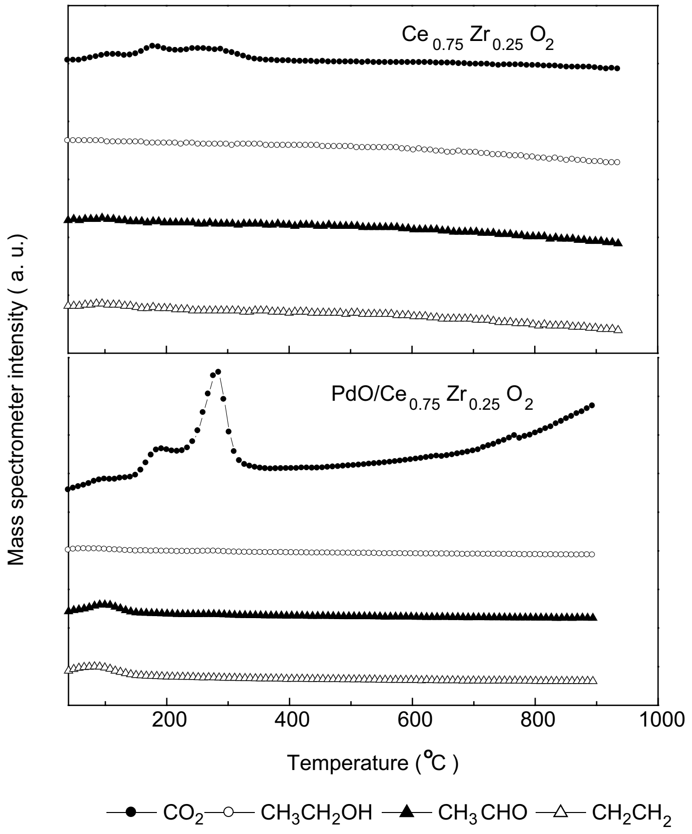

Figure 4. Ethanol-TPSR profiles of $Ce_{0.75}Zr_{0.25}O_2$ and $PdO/Ce_{0.75}Zr_{0.25}O_2$ catalysts.

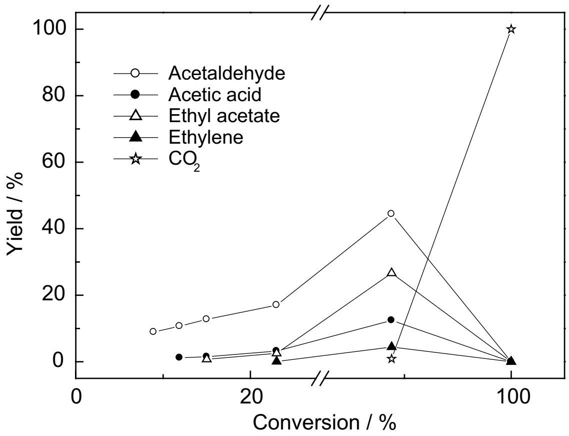

Figure 5. The plot of conversion versus yield of ethanol oxidation on $PdO/Ce_{0.75}Zr_{0.25}O_2$ catalyst.

3.5. *Mechanism studies of ethanol oxidation over $PdO/Ce_{0.75}Zr_{0.25}O_2$ catalyst*

Figure 5 plots the conversion versus yield. From it, we can see clearly that there is no direct route from ethanol to CO_2. It is noticed that on $PdO/Ce_{0.75}Zr_{0.25}O_2$ catalyst, acetaldehyde formed firstly at the conversion at about 9%. With enhancing the conversion, acetic acid, ethyl acetate and ethylene formed gradually. Finally, CO_2 formed and reached the yield of 100% at the temperature at about 200 °C (the temperature is not shown in the figure). It seems likely that ethanol is first oxidized to acetaldehyde, and then some of acetaldehyde further oxidized to acetic acid, which then reacts with ethanol to form ethyl acetate. Furthermore, some of ethanol dehydrates to form ethylene as conversion raised. CO_2 appeared after all these intermediates (acetic acid, ethyl acetate and ethylene) had formed. At the end, the intermediates are all oxidized to form CO_2, which is the final product of one or more pathways [19]. It is clearly that acetaldehyde is the primary product, and acetic acid, ethyl acetate and ethylene are the secondary products, and CO_2 is the final product. From the results figure 5, we can find one of the major by-produces is ethyl acetate and acetic acid, but it cannot be observed from the profiles of ethanol-TPSR (figure 4). A plausible explanation is that ethyl acetate and acetic acid are cracked into smaller organic molecular and subsequently oxidized to CO_2 on the surface of PdO and supports during ethanol TPSR [20].

Combined with ethanol-TPSR, we can deduce the mechanism of ethanol oxidation on PdO catalyst is as following: the first step of ethanol oxidation probably involves the formation of acetaldehyde, furthermore acetic acid is formed through the oxidation of acetaldehyde; then acetic acid reacts with ethanol to produce ethyl acetate and ethylene produced through dehydration of ethanol. With increasing temperature, these intermediates are further oxidized to CO_2.

4. Conclusions

This work studies the ethanol and CO oxidation over $PdO/Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.75}Zr_{0.25}O_2$ catalysts. The catalytic activity of ethanol over single $Ce_{0.75}Zr_{0.25}O_2$ is very low. But after $Ce_{0.75}Zr_{0.25}O_2$ loaded with PdO, the catalytic activity enhances greatly. The complementary character of the catalytic function of PdO and $Ce_{0.75}Zr_{0.25}O_2$ enhances the catalytic oxidation of ethanol and CO. A moderate content of PdO favors the catalytic oxidation of ethanol and CO. CO-TPD and ethanol-TPSR of $PdO/Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.75}Zr_{0.25}O_2$ reveal the more intensive of CO_2 desorption peaks, the higher it is for the oxidation of CO and ethanol. The mechanism of ethanol oxidation over PdO catalyst can be induced from the conversion versus yield and the ethanol-TPSR: ethanol reacts with the adsorbed oxygen and forms acetaldehyde. Then some of acetaldehyde is oxidized to acetic acid. Furthermore, acetic acid reacts with ethanol to produce ethyl acetate. Some of ethanol is dehydrated to form ethylene. At the end, these intermediates are further oxidized to CO_2 at much higher temperature. Conclusively, $PdO/Ce_{0.75}Zr_{0.25}O_2$ catalyst not only has much higher catalytic activity for the oxidation of ethanol but also for CO oxidation. Thus, it has the feasibility for application in DAFC.

Acknowledgments

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