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Hydrogen production by oxidative methanol reforming on Pd/ZnO: Catalyst preparation and supporting materials

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Abstract

Pd and Pd–Zn alloy were supported on various supporting materials using impregnation, co-precipitation and microemulsion methods, and their catalytic performances in oxidative methanol reforming (OMR) were investigated. Pd/ZnO exhibited much higher selectivity than either Pd/Al_2O_3 or Pd/ZrO_2 in the OMR for hydrogen production. This was attributed to the presence of Pd–Zn alloy on the ZnO support. Elemental Pd on Al_2O_3 or ZrO_2 promotes methanol decomposition reaction and increases CO formation. Using a microemulsion method, a highly selective Pd/ZnO can be obtained with much lower Pd loading than that in samples prepared by co-precipitation. Modification of Al_2O_3 with ZnO produced a $ZnAl_2O_4$ phase, which was found to be a good support for the Pd/ZnO catalyst. Highly active and selective Pd/ZnO/$ZnAl_2O_4$ catalysts for the OMR reaction, containing much lower Pd loadings have been developed by impregnation of the supports with an aqueous solution of $Pd(NO_3)_2 + Zn(NO_3)_2$.

Keywords: Hydrogen production; Oxidative steam reforming; Methanol; Pd; Pd–Zn alloy; ZnO; Al_2O_3; $ZnAl_2O_4$; ZrO_2

1. Introduction

The hydrogen fuel cell technologies are expected to achieve a cleaner and much more efficient, flexible and reliable energy system in the mid-to-late-21st century. As the indispensable partner to the fuel cell energy system, the production and storage of hydrogen in a more efficient and economic way is urgently required [1,2]. A widely studied process for on-site hydrogen production involves the oxidative methanol reforming (OMR) [3–5] as generally expressed in Eq. (1). By adjusting the molar ratios of $p(H_2O/CH_3OH)$ and $q(O_2/CH_3OH)$ one can make the reaction thermally neutral. The high selectivity (s) and low temperature of the reaction, together with the high energy density, zero sulfur content and ready availability of methanol, enable OMR to be among the most promising of processes for distributed power generation using proton-exchange membrane fuel cells (PEMFC).

$$CH_3OH + pH_2O + qO_2 \rightarrow sCO_2 + (1-s)CO + (2+p)H_2 \quad (\Delta H^\circ = 0) \qquad (1)$$

Literature studies of OMR mainly focus on Cu-ZnO based catalysts [6–13]. However, the rapid deactivation of Cu-ZnO based catalysts by sintering of the metal at temperatures above 300 °C, is a barrier to its practical application in the OMR process.

Another interesting catalyst for the OMR reaction is Pd/ZnO. It is highly active and selective for both the steam reforming of methanol (SRM, Eq. (2)) and partial oxidation of methanol (POM, Eq. (3)) [14–21]. It has been proposed that the high selectivity of Pd/ZnO towards SRM relates to the formation of Pd–Zn alloy on the catalyst. As the melting point of Pd is higher than that of Cu, better thermal stability is to be expected for Pd/ZnO at higher reaction temperatures.

We have investigated the catalytic performance of Pd/ZnO under realistic OMR conditions [22–25]. Both high activity and selectivity were obtained, and with the catalyst durability being much better than that of the Cu-ZnO based catalysts. However, the CO formation on Pd/ZnO was higher than that on Cu/ZnO catalyst. To achieve lower CO formation, which is a requisite for the PEMFC application, a higher Pd loading, often above 20%, is necessary when using conventional impregnation or co-precipitation methods. It is obvious that the high Pd loading and consequent high cost is a hurdle for the wide commercial application of this catalyst. A possible way to decrease the Pd loading is to disperse the Pd/ZnO on a supporting material

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having high surface area. Another issue in decreasing CO formation is related to the further modification of the catalyst with a third metal component. By doping with a small amount of Cr, Fe or Cu and increasing the water gas shift activity of Pd/ZnO, the CO formation can be effectively decreased [24]. But higher doping amount of these elements resulted in increased CO formation. Our previous results also revealed that the catalytic performance of Pd/ZnO can be greatly modified by doping with Mg, Al, Zr, Ce, La or Ru and other first row transition metal elements. The interaction of the doped component with ZnO and Pd-related species may finally lead to the formation of elemental Pd which promotes methanol decomposition reaction (Eq. (4)) and increases CO formation [12,26]. Clearly, in enhancing the activity and selectivity of Pd/ZnO by supporting it on a high surface area material, such as Al_2O_3, ZrO_2, TiO_2, MgO, etc., direct interaction of the Pd–Zn alloy with the supporting materials other than ZnO should be avoided. This report will discuss our efforts in reducing the Pd loading by dispersing the Pd/ZnO catalyst on several modified supporting materials, using impregnation and microemulsion techniques.

$$CH_3OH(l) + H_2O(l) \rightarrow CO_2 + 3H_2 \quad (\Delta H^\circ = +131\,\text{kJ/mol}) \tag{2}$$

$$CH_3OH(l) + \tfrac{1}{2}O_2 \rightarrow CO_2 + 2H_2 \quad (\Delta H^\circ = -154.8\,\text{kJ/mol}) \tag{3}$$

$$CH_3OH(g) \rightarrow CO + 2H_2 \quad (\Delta H^\circ = +92.0\,\text{kJ/mol}) \tag{4}$$

2. Experimental

2.1. Catalyst preparation

Co-precipitation (CP) and microemulsion (ME) methods were employed for the preparation of Pd/ZnO catalysts. The preparation of CP samples followed the procedure described in our previous paper [23]. The preparation of ME samples followed a procedure similar to that described by Agrell et al. [20]. Briefly, two kinds of microemulsion were prepared by adding aqueous solution of $Pd(NO_3)_2$ or $Pd(NO_3)_2 + Zn(NO_3)_2$ (Pd/Zn molar ratio = 0.2) into a solution of 20% NP-5 (Nonphenolethoxylate) surfactant in cyclohexane. The water/surfactant molar ratio (ω_0) was 6.0. The $Pd(NO_3)_2$ microemulsion was then reduced with hydrazine, followed by chemical destabilization with THF (tetrahydrofuran) and deposition of the Pd particles onto the ZnO support under vigorous stirring. The catalyst was then recovered by filtration and washing with methanol. In the case of the $Pd(NO_3)_2 + Zn(NO_3)_2$ microemulsion, an aqueous solution containing a suitable amount of hydrazine and Na_2CO_3 was added for a simultaneous reduction of Pd^{2+} and precipitation of Zn^{2+} in the microemulsion. The deposition of this reduced and precipitated microemulsion onto ZnO support and the catalyst recovery procedure were then the same as for the $Pd(NO_3)_2$ microemulsion. The samples were denoted as ME and MEM catalysts for the $Pd(NO_3)_2$ and the $Pd(NO_3)_2 + Zn(NO_3)_2$ microemulsion processes, respectively. The prepared Pd/ZnO catalysts were identified according to their preparation method and designated loading amount of Pd. For example, the sample prepared by MEM method with 6.5 wt.% Pd was identified as MEM6.5.

Pd/Al_2O_3 and Pd/ZrO_2 were prepared by conventional impregnation (IMP) of Al_2O_3 and ZrO_2 with an aqueous solution of $Pd(NO_3)_2$.

Two Al_2O_3-based supports were prepared. One was imp-$ZnAl_2O_4$, prepared by impregnation of Al_2O_3 with a stoichiometric quantity of $Zn(NO_3)_2$ to form $ZnAl_2O_4$, whilst the other was cp-$ZnAl_2O_4$, prepared by the co-precipitation method. Both precursors were dried at 80 °C overnight and then calcined at 600 °C for 2 h. cp-$ZnCr_2O_4$ was prepared by similar procedure to that of cp-$ZnAl_2O_4$. This dried precursor was also calcined at 600 °C for 2 h.

The supported Pd/ZnO catalysts with Pd loading of 2% and 6.5% were then prepared by impregnation of the prepared imp-$ZnAl_2O_4$, cp-$ZnAl_2O_4$ and cp-$ZnCr_2O_4$ with $Pd(NO_3)_2 + Zn(NO_3)_2$ aqueous solution having a Pd/Zn molar ratio of 0.2.

All the catalysts were finally calcined at 450 °C for 2 h, and crushed to a particle size of 0.15–0.25 mm for the activity test.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT1100 diffractometer with Cu Kα (λ = 0.15406 nm) radiation. Scanning 2θ angles ranged from 20° to 80°.

2.3. Activity test

The OMR reactions were carried out in a fully automated flow reaction system as described elsewhere [23] with 0.3 g catalysts at atmospheric pressure. Before the reaction, the catalyst was pre-reduced in situ at 500 °C in a 20% H_2 + 80% N_2 gas flow for 2 h, and then cooled to 250 °C for the reaction. The methanol weight hourly space velocity (W_MHSV) was 47 h^{-1}. N_2 was used as the carrier gas and as an internal standard for dry product gas flow calculations. The products were analyzed on-line using a Shimadzu GC-8A gas chromatograph automatic analysis system. Unless otherwise mentioned, the initial activity was evaluated from the data collected over reaction times of between 1 and 3 h on stream. The gas yield (moles of CO_2 + CO produced per mole of methanol feed) was used as a measure to compare the catalyst activity. The selectivity of CO formation was defined as moles of CO per mole CO_2 + CO formed in the products.

3. Results and discussion

3.1. Catalytic performances of Pd/ZnO, Pd/Al_2O_3 and Pd/ZrO_2

Literature studies of supported Pd catalysts for the SRM reaction [14,15] revealed that ZnO is superior to other materials such as Al_2O_3, ZrO_2 and SiO_2, etc. as the support. The unique supporting effect of ZnO for Pd is due to the metal–support interaction leading to Pd–Zn alloy formation, which exhibits high selectivity for SRM reaction towards hydrogen production. It was also revealed that the Pd/ZnO catalyst was very active and selective for the OMR reaction, and this high selectivity was attributed to the formation of Pd–Zn alloy on the ZnO support [22–25]. Nevertheless, similar data for OMR reaction when using other supported Pd catalysts are still limited in the literature. Thus, we prepared Pd/Al_2O_3 and Pd/ZrO_2 with 6.5%Pd loading by a conventional impregnation method and evaluated their catalytic performances in the OMR reaction under realistic conditions. The gas yield and CO selectivity on the Pd/Al_2O_3 and Pd/ZrO_2 are compared with Pd/ZnO in Fig. 1. It is clear that the Pd/ZnO is more active and produces much less CO than the Pd/Al_2O_3 or Pd/ZrO_2. The gas yield on Pd/Al_2O_3 was only about half of that on Pd/ZnO. The formation of CO was in minor quantities on Pd/ZnO, while it was dominant on Pd/Al_2O_3 and Pd/ZrO_2. XRD characterization (Fig. 2) of the spent catalysts after OMR test revealed the presence of Pd–Zn alloy on the Pd/ZnO. But elemental Pd was detected on the spent Pd/Al_2O_3 or Pd/ZrO_2, and this promotes the methanol decomposition reaction and results in higher CO formation. These results clearly indicate that the Pd–Zn alloy on ZnO is more active and selective than the elemental Pd on Al_2O_3 or ZrO_2 in the OMR reaction.

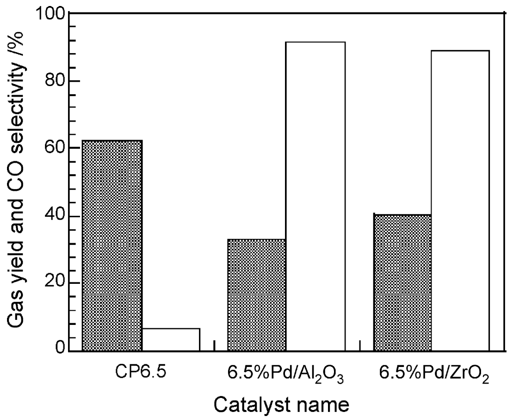

Fig. 1. Gas yield (filled bar) and CO selectivity (empty bar) of OMR on 6.5%Pd catalysts supported on different materials.

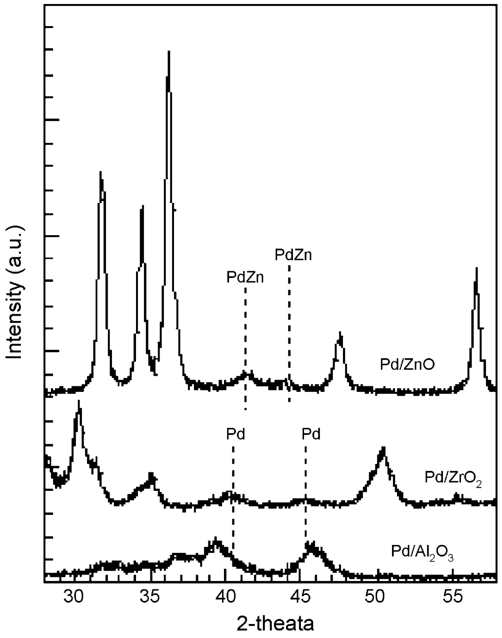

Fig. 2. Powder XRD patterns of the spent Pd/ZnO, Pd/ZrO_2 and Pd/Al_2O_3 with Pd loading of 6.5%.

3.2. Catalytic performances of Pd/ZnO prepared by microemulsion technique

Our previous studies [22,23] revealed that the catalytic activity and selectivity of Pd/ZnO for OMR both increase with increasing Pd loading at below 40%. Samples prepared by co-precipitation displayed better performance than those prepared by impregnation at Pd loadings above 5% when using $Pd(NO_3)_2$ aqueous solution as the starting material. Impregnation of ZnO with the commonly available $Pd(NO_3)_2$ aqueous solution resulted in larger Pd–Zn alloy crystallites due to the dissolution effects of ZnO in the acidic solution. More homogeneous catalysts with smaller Pd–Zn alloy crystallites can be obtained by the co-precipitation method. However, co-precipitation of Pd^{2+} and Zn^{2+} will inevitably result in the encapsulation of the expensive Pd into the bulk phase of the catalyst, which is inefficient for the surface catalysis reaction. Agrell et al. [20] employed a microemulsion method to prepare the Pd/ZnO catalysts. Nanosized PdO particles were obtained on the calcined samples. As the catalysts were prepared by deposition of the Pd nanoparticles onto the ZnO support, produced by reduction of Pd^{2+} in the microemulsion, the encapsulation of Pd into the bulk phase and the dissolution effects leading to heterogeneity of the catalysts could be mostly avoided.

Two Pd/ZnO catalysts with Pd loadings of 2% and 6.5% were prepared by using $Pd(NO_3)_2$ microemulsion (ME samples) method, and their catalytic performances are compared in Fig. 3 with those of the corresponding CP samples. Disappointedly, the ME samples produced lower gas yield and higher CO formation than the CP samples. In the preparation of ME samples, Pd particles were first produced by reduction of Pd^{2+} with hydrazine before depositing onto the ZnO support. It is reasonable to imagine that the alloying of the Pd particles with ZnO during the pre-reduction treatment and the following OMR reaction may not be as perfect as that between the well mixed PdO and ZnO as prepared by co-precipitation. More elemental Pd species may exist on the ME samples, promoting CO formation during OMR. This may explain why the ME samples exhibited higher CO formation than the corresponding CP samples.

To improve the mixing or contact conditions between the reduced Pd particles and ZnO, an aqueous solution containing both $Pd(NO_3)_2$ and $Zn(NO_3)_2$ was used for the microemulsion preparation (MEM samples). This microemulsion was then reduced and precipitated simultaneously by adding suitable amount of hydrazine and Na_2CO_3 aqueous solution, followed by deposition onto the ZnO support. The reaction results are also compared in Fig. 3. Concerning on the selectivity of CO

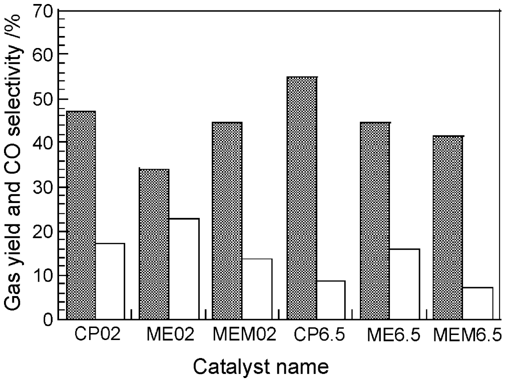

Fig. 3. Gas yield (filled bar) and CO selectivity (empty bar) of OMR on supported Pd catalysts prepared by the co-precipitation and microemulsion methods.

formation, it is clear that the MEM samples performed much better than the corresponding ME samples. The CO formation on MEM samples was even lower than that on the corresponding CP samples. The gas yield on MEM02 was higher than that on ME02 and similar to that on CP02. However, the gas yield on MEM6.5 was lower than that on CP6.5. It is presently not clear as to why the MEM6.5 has lower activity than the corresponding CP6.5 sample. Possible loss of Pd in washing procedure during preparation could not be excluded, as the precursor before washing was rather sticky due to a higher content of the surfactant.

Durability performances of the MEM6.5 and ME6.5 are compared with CP20, (one of the most active and selective CP samples), in Fig. 4. A slow decline in gas yield with a similar slope was observed for all the three samples. The decreases in gas yield are mainly attributed to a carbon deposition reaction during OMR, as has been discussed in our previous studies [25]. The gas yield on MEM6.5 was similar to that on ME6.5, but lower than that on CP20. The formation of CO on MEM6.5 was much lower than that on ME6.5 during all the 24 h reactions. At the commencement of the reaction, the CO formation on MEM6.5 was slightly higher than that on CP20, but it exhibited a common value after a prolonged reaction. Considering the much lower Pd loading of MEM6.5, it is significant that, by using the $Pd(NO_3)_2 + Zn(NO_3)_2$ microemulsion method, more selective Pd/ZnO catalysts can be prepared with lower Pd loadings. By varying the water/surfactant molar ratio of the microemulsion, the particle size of Pd–Zn alloy can be controlled [26] and thus is possible to improve the dispersion of Pd–Zn alloy and to further improve the catalyst activity. Additional experimental work is necessary to develop more active and selective catalysts by using this microemulsion method.

3.3. Al_2O_3, $ZnAl_2O_4$ and $ZnCr_2O_4$ as supports for Pd/ZnO

Previous results [24] have indicated that addition of a third metal component such as a small amount of Cr, Fe or Cu to the Pd/ZnO system enhances its activity and selectivity. However, it could not greatly decrease the Pd loading and enhance the catalytic performance. Actually, in most cases, CO formation was unexpectedly increased due to the interaction of the added component with Pd-related species. Therefore, in order to decrease the Pd loading, we focused on dispersing the Pd/ZnO on some commonly used high surface area materials, in an attempt to avoid the interaction of Pd–Zn alloy with a non-ZnO support.

Zn-modified γ-Al_2O_3 was selected for the first trial. Two samples, with Pd loadings of 2% and 6.5%, were prepared by simple impregnation of γ-Al_2O_3 with aqueous solution of $Pd(NO_3)_2 + Zn(NO_3)_2$. Their catalytic performances are compared in Fig. 5 with 6.5%Pd/Al_2O_3. Although the Pd loading was a factor of three lower, much less CO formation was obtained on 2%$Pd/ZnO/Al_2O_3$ at a similar gas yield. On 6.5%$Pd/ZnO/Al_2O_3$, the gas yield was greatly increased from 32% to 62%, whilst the selectivity of CO formation was significantly decreased from 45.3% to 10.3%. The catalytic performances of 6.5%$Pd/ZnO/Al_2O_3$ are comparable to that of CP6.5 but are quite different from that of 6.5%Pd/Al_2O_3.

XRD analysis of the 6.5%$Pd/ZnO/Al_2O_3$ after the OMR test indicated the presence of $ZnAl_2O_4$, ZnO and Pd–Zn alloy phases on the catalyst (Fig. 6). Also, regarding the reaction results (Fig. 5), it appears that the presence of ZnO and $ZnAl_2O_4$ phases on Al_2O_3 effectively screened any interaction between Pd–Zn alloy and Al_2O_3, and prevented the formation of elemental Pd species. These results prompted us, on the one hand, to further modify the Al_2O_3 with higher ZnO loadings and, on the other hand, to prepare $ZnAl_2O_4$ spinel as a

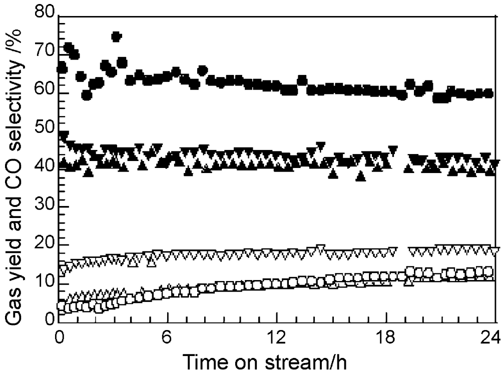

Fig. 4. Gas yield (solid) and CO selectivity (open) with reaction time on stream of OMR on MEM6.5 (▲, △), ME6.5 (▼, ▽) and CP20 (●, ○).

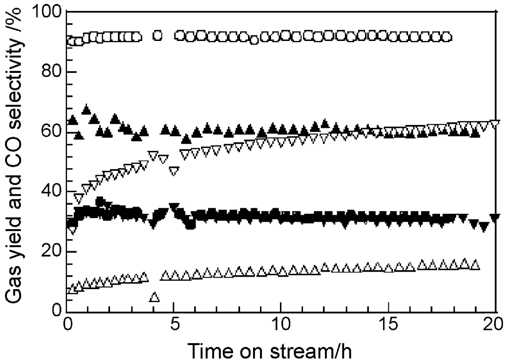

Fig. 5. Gas yield (solid) and CO selectivity (open) with reaction time on stream of OMR on 6.5%Pd/Al_2O_3 (●, ○) and $Pd/ZnO/Al_2O_3$ with Pd loading of 6.5% (▲, △) and 2% (▼, ▽).

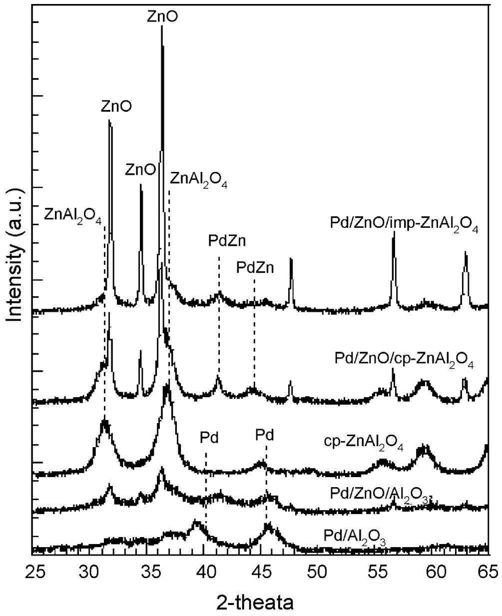

Fig. 6. Powder XRD patterns of the spent catalysts with Pd loading of 6.5%.

promising supporting material for the Pd/ZnO catalyst. XRD analysis of the prepared supports indicated that the imp-$ZnAl_2O_4$ contains the ZnO and $ZnAl_2O_4$ spinel phases, whilst the cp-$ZnAl_2O_4$ contains only $ZnAl_2O_4$ spinel phase (Fig. 6). XRD patterns of the spent catalysts with Pd loading of 6.5% are also shown in Fig. 6. It is clear that both catalysts contain Pd–Zn alloy, ZnO and $ZnAl_2O_4$ phases. The intensity of ZnO diffractions from imp-$ZnAl_2O_4$ are much stronger than that from cp-$ZnAl_2O_4$, indicating that more ZnO was present on the imp-$ZnAl_2O_4$. Both catalysts are essentially Pd/ZnO dispersed on $ZnAl_2O_4$ spinel supports.

The catalytic performances of Pd/ZnO on different supports with Pd loading of 2% are compared in Fig. 7. It can be seen that, in comparison with Al_2O_3, a higher gas yield and much lower CO selectivity were obtained when using imp-$ZnAl_2O_4$ or cp-$ZnAl_2O_4$ as the supports. Moreover, they also performed better than CP02. The CO selectivity was decreased from 17.4% for CP02 to 9.8% for the imp/cp-$ZnAl_2O_4$ supported catalysts at similar or even higher gas yields.

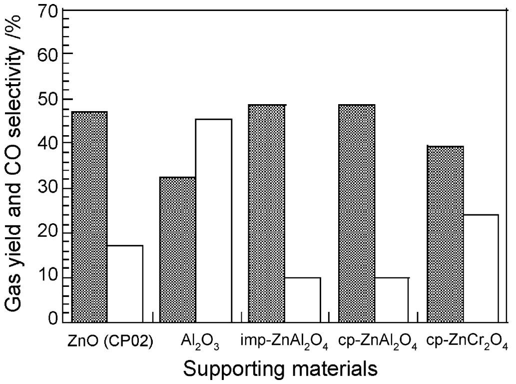

Fig. 7. Gas yield (filled bar) and CO selectivity (empty bar) of OMR on Pd/ZnO supported on different materials with 2%Pd loading.

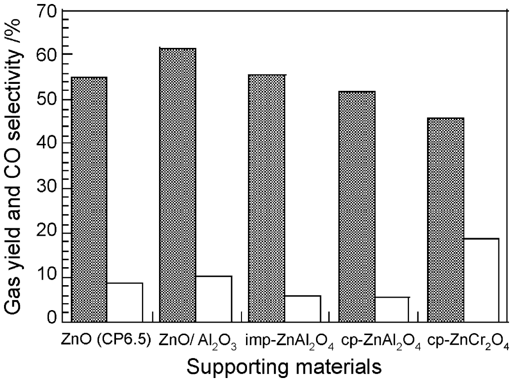

Fig. 8. Gas yield (filled bar) and CO selectivity (empty bar) of OMR on Pd/ZnO supported on different materials with 6.5%Pd loading.

The catalytic performances of Pd/ZnO on different supports with 6.5%Pd loading are shown in Fig. 8. Similar or slightly lower gas yield was obtained on the imp/cp-$ZnAl_2O_4$ supported catalysts. However, the CO formation was greatly decreased, compared with that on CP6.5 or 6.5%Pd/ZnO/Al_2O_3. A CO selectivity of 5.5% was obtained on 6.5%Pd/ZnO/cp-$ZnAl_2O_4$, about 37% and 47% lower than that on CP6.5 and 6.5%Pd/ZnO/Al_2O_3, respectively. Clearly, the modification of Al_2O_3 with ZnO greatly decreases the CO formation and $ZnAl_2O_4$ as support for the Pd/ZnO catalyst is superior to Al_2O_3.

Additionally, the catalytic performances of the cp-$ZnCr_2O_4$ supported Pd/ZnO with Pd loadings of 2% and 6.5% are also shown in Figs. 7 and 8, respectively. The performances were not as good as those of CP and imp/cp-$ZnAl_2O_4$ supported samples. But the 2%Pd/ZnO/cp-$ZnCr_2O_4$ did exhibit a higher gas yield and lower CO formation than the 2%Pd/ZnO/Al_2O_3.

The durability of imp/cp-$ZnAl_2O_4$ supported Pd/ZnO with 6.5%Pd loading for OMR reaction is compared with that of CP20 in Fig. 9. Quite stable performances were achieved with the imp/cp-$ZnAl_2O_4$ supported catalysts. For up to 50 h of reaction time on stream, no evident decrease in gas yield was observed with the 6.5%Pd/ZnO/cp-$ZnAl_2O_4$ catalyst. The lower CO formation on CP20 was maintained only for the first 5 h of reaction time on stream. After prolonged reaction, the CO formation progressively increased on CP20 but remained almost constant on the imp/cp-$ZnAl_2O_4$ supported Pd/ZnO.

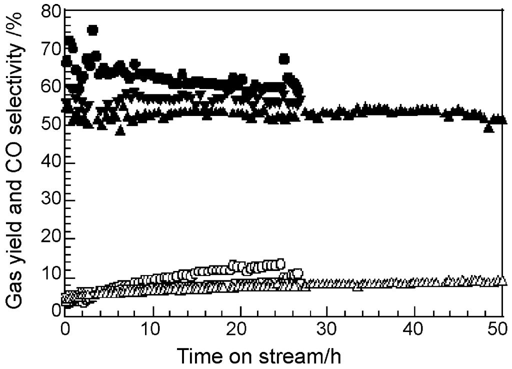

Fig. 9. Gas yield (solid) and CO selectivity (open) of OMR on CP20 (●, ○) and Pd/ZnO supported on cp-$ZnAl_2O_4$ (▲, △), imp-$ZnAl_2O_4$ (▼, ▽) with 6.5%Pd loading.

After 20 h of the reaction, the CO selectivity was held at about 8.2% on the imp/cp-$ZnAl_2O_4$ supported Pd/ZnO, whilst it reached 12.8% on CP20. $ZnAl_2O_4$ as the support for Pd/ZnO improved, not only the catalytic selectivity but also the catalyst durability. As has been revealed in our previous study [25], carbon deposition is a main reason for the Pd/ZnO catalyst deactivation. In case of using $ZnAl_2O_4$ instead of ZnO as the support for Pd–Zn catalyst, the carbon deposition reaction could be most probably inhibited. At the same Pd loading the surface area and metal dispersion for CP catalyst and cp-$ZnAl_2O_4$ supported Pd/ZnO are supposed to be quite different, which may also contribute to the different catalytic performances. However, careful characterization of the catalysts surface, including the amount of deposited carbon, the change of metal dispersion and surface area as well as the change in chemical states of the active Pd metal, before and after long-term OMR reaction is necessary to understand the different performances of CP and $ZnAl_2O_4$ supported catalysts.

4. Conclusions

Highly selective OMR catalysts can be prepared by stepwise co-impregnation of the supports, first with Zn^{2+} and then with $Pd^{2+} + Zn^{2+}$ solutions. A modified microemulsion method was developed to prepare Pd/ZnO with a lower Pd loading.

$ZnAl_2O_4$ and ZnO-modified Al_2O_3 were found to be good supports for the Pd/ZnO catalyst for the OMR reaction.

It was confirmed, once again, that elemental Pd promotes CO formation in the OMR reaction, and that the Pd–Zn alloy on ZnO is essential to the catalyst activity and selectivity.

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