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Ignition of methanol partial oxidation over supported platinum catalyst

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Abstract

Supported platinum catalysts were prepared by precipitation of H_2PtCl_6 on powders of different metal oxides. Catalytic activity of the prepared catalysts was tested with reaction of partial oxidation of methanol (POM) for hydrogen production. Most of the prepared catalysts can ignite POM at the ambient temperature. The conversion of methanol and the selectivity of hydrogen and carbon monoxide, however, increased with the reaction temperature and varied with the kind of support and platinum loading. A 1 wt% Pt/ZnO catalyst exhibited optimized methanol conversion and selectivity at a low reaction temperature of 150 °C. The reactor may reach this temperature within 2 min after a start of the exothermic reaction.

Keywords: Hydrogen production; Methanol; Oxidative steam reforming; Ignition

1. Introduction

Fuel cell is an efficient device for the conversion of chemical energy into electric power. Among different types of fuel cells under development, the proton exchange membrane fuel cell (PEMFC) distinguishes itself by low operating temperature of around 70 °C [1–3]. Accordingly, PEMFC has a potential application to automobiles, and certain stationary applications to replace the internal combustion engine and lithium battery as the power source. However, PEMFC uses hydrogen gas as a fuel. The storage and the transportation of hydrogen gas are difficult problems upon a wide application of PEMFC in future. In order to avoid these delivery difficulties, reforming of liquid hydrocarbon fuels to hydrogen on site for PEMFC application has been suggested [4].

Methanol is a cheap, abundant and active liquid feed to reform for hydrogen production. Three different reforming processes, i.e., steam reforming of methanol [5–7] (SRM), partial oxidation of methanol (POM) [8–13] and oxidative steam reforming (OSRM) [14–16], can be used to convert methanol into hydrogen. These reactions are shown in Eqs. (1)–(3).

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2, \quad \Delta H^0 = 49\,\mathrm{kJ\,mol^{-1}} \qquad (1)$$

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow 2H_2 + CO_2, \quad \Delta H^0 = -192\,\mathrm{kJ\,mol^{-1}} \qquad (2)$$

$$5CH_3OH + \tfrac{1}{2}O_2 + 4H_2O \rightarrow 14H_2 + 5CO_2, \quad \Delta H^0 \sim 0\,\mathrm{kJ\,mol^{-1}} \qquad (3)$$

Among them, SRM has the highest hydrogen yield (number of hydrogen produced from each methanol, $Y_{H_2} = 3$) and is a widely studied reaction. However, it is endothermic in nature and needs external power supply to be operated at a required reaction temperature over 250 °C. On the contrary, the POM reaction has the lowest hydrogen yield of $Y_{H_2} = 2$. However, POM is exothermic in nature and, therefore, can be catalyzed at low reaction temperatures.

Copper based catalysts have been extensively studied and widely used for reactions of methanol reforming. However, a long start-up time ($t_s > 4$ min) has prevented practical utilization of the reforming on vehicle applications [17]. High ignition temperature ($T_i \sim 180$ °C for POM) is one of the major reasons for the long t_s. In a previous communication, a low $T_i = 100$ °C for POM was reported from noble metal catalyst of Ag/Ce-Zn [11] Herein, we report that POM reaction can generally be ignited at ambient temperature by supported Pt catalysts and that 1 wt% Pt/ZnO catalyst exhibits good methanol conversion (C_{MeOH}) and hydrogen selectivity (S_{H_2}) in POM at a low reaction temperature of $T_R = 150$ °C.

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2. Experimental

2.1. Catalyst preparation

Pt crystallites were dispersed on supports of ZnO [20 m^2/g, prepared by decomposition of $Zn(NO_3)_2$], CeO_2, ZrO_2 (Merck) and Al_2O_3 (Degussa) by the precipitation method. In preparation of 2 wt% Pt/ZnO, 1 M $NaOH_{(aq)}$ was added to a 250 mL solution containing 0.31 g of $PtCl_4$ until pH ~ 8. After stirring at the room temperature for 2 h, the resulting slurry was filtered and washed with deionized water until free of Cl^- (checked with $AgNO_3$ solution). The precipitates were further dried overnight at 100 °C, calcined in air at 400 °C, crushed and sieved into particles of 60–80 mesh. The particles were then reduced in pure hydrogen flow at 200 °C for 1 h and then stored as fresh Pt/ZnO catalysts.

2.2. POM activity

The catalytic activity of 0.1 g of prepared Pt catalysts on POM was tested in a fixed bed reactor (4 mm in i.d.). The temperature of the reactor was measured by a thermocouple directly in contact with the studied catalyst. Normally, a 100 mL min^{-1} flow composed of 12.2 mol% CH_3OH (metered by a liquid pump with a variation of ~10%) and preheated to 100 °C), 6.1 mol% O_2 and 81.7 mol% Ar (controlled by a mass flow controller) was fed as reactant. The flow was cooled down to ambient temperature before feeding into the reactor. Condensation of methanol was not observed at the cooling. Reaction products were analyzed by a downstream TCD-gas chromatograph equipped with Porapack Q column to separate CH_3OH, H_2O and CO_2 and Molecular Sieve 5A to separate H_2 and CO. Argon flow was used as the purging gas for the separation.

3. Results and discussion

Platinum catalysts supported on different oxides have been prepared for this study. Table 1 lists a series of 2 wt% Pt catalysts prepared. Negligible Pt (1 1 1) diffraction was found from their XRD examinations. The absence of significant diffraction peaks for Pt suggested that platinum crystallites were finely dispersed in all of the fresh catalysts. Column 3 of Table 1 lists average size of Pt particles (d_{Pt}) found from TEM characterization of 2% Pt catalysts dispersed on different supports. A size of $d_{Pt} = 2.0 \pm 1.0$ was generally found.

Table 1
Physicochemical properties and catalytic activities of supported Pt catalysts in POM reaction at 150 °C

Catalysts	Pt (wt%)	d_{Pt} (nm)[a]	C_{MeOH}[b]	S_{H_2}[c]	S_{CO_2}[d]
2%Pt/ZnO	1.9	1.5	80	72	90
2%Pt/CeO_2	2.0	–	84	73	81
2%Pt/ZrO_2	1.8	3.2	40	52	74
2%Pt/Al_2O_3	1.9	1.7	43	42	>99

[a] Estimated by TEM.
[b] $C_{MeOH} = (n_{MeOH,in} - n_{MeOH,out})/n_{MeOH,in} \times 100\%$.
[c] $S_{H_2} = n_{H_2}/2(n_{MeOH,in} - n_{MeOH,out}) \times 100\%$.
[d] $S_{CO_2} = n_{CO_2}/(n_{MeOH,in} - n_{MeOH,out}) \times 100\%$.

Prepared 2 wt% Pt catalysts are generally active for POM reaction. The reaction can be ignited at ambient temperature ($T_i < 25$ °C) by all of them except 2%Pt/ZrO_2 ($T_i = 50$ °C). Fig. 1 presents time profiles of reactor temperature measured in the catalytic bed using 2%Pt/ZnO catalyst. After an incubation time of ~20 s, temperature of the bed increased due to a start-up of the exothermic POM. The reactor temperature rose up to a plateau of T ~ 110 °C in 80 s in the absence of any heat insulation (Fig. 1a). With a decent insulation, initial ascending rate of the reactor temperature remained about the same but the plateau temperature would raise to $T \geq 200$ °C (Fig. 1b). Evidently from Fig. 1, a long reaction time of the exothermic POM reaction is required for its reactor to be heated to a high steady state temperature.

H_2, H_2O, CO and CO_2 were products detected by TCD-GC from POM at a feed ratio of $n_{MeOH}/n_{O_2} = 2$. In this study, a high methanol conversion (C_{MeOH}) and selectivity of H_2 (S_{H_2}, instead of oxidization to H_2O) and CO_2 (S_{CO_2}, instead of partially oxidized CO) were pursued. To compare the activity and selectivity (S_{CO_2} and S_{H_2}) of various catalysts supported on different oxides, the reactor bed was preheated and maintained at $T_R = 150$ °C by a heating tape. Methanol conversion and product selectivity of POM were found significantly affected by kinds of Pt catalyst studied. Column 4 of Table 1 compares the C_{MeOH} of POM reaction over different Pt catalysts studied. The prepared 2%Pt catalysts showed the following trend on increasing C_{MeOH}:

$$\mathrm{Pt/CeO_2}\,(84\%) > \mathrm{Pt/ZnO}\,(80\%) > \mathrm{Pt/Al_2O_3}\,(43\%),\quad \mathrm{Pt/ZrO_2}\,(40\%) \tag{I}$$

It is noteworthy that trend (I) is in good agreement with the size of Pt (d_{Pt} column 3 of Table 1) as determined from TEM measurements. The difference in C_{MeOH} of different catalysts therefore reflected their ability to decompose methanol. Fig. 2 introduces the effect of reaction temperature on C_{MeOH}. C_{MeOH} increased with the temperature of POM reaction.

Fig. 2 also presents effects of reaction temperature on selectivities of hydrogen and CO_2 over 1%Pt/ZnO. Other than

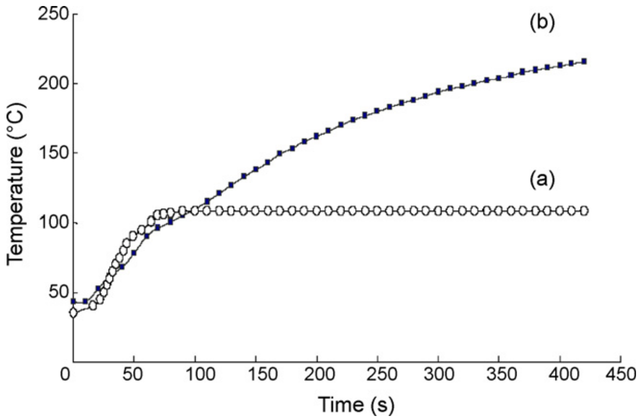

Fig. 1. Temperature changing after starting up POM reaction over 2%Pt/ZnO; (a) without insulation; (b) with insulation.

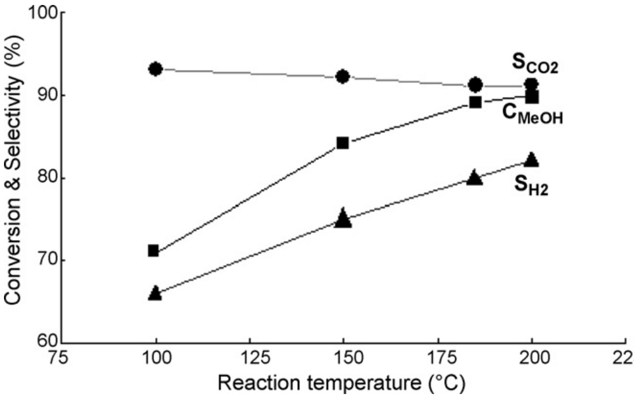

Fig. 2. Effect of reaction temperature on POM reaction over 1%Pt/ZnO.

CO_2, some anomalous CO was found co-produced. Conceivably, the CO should have been produced through an unwanted side reaction of direct decomposition of methanol (DDM):

$$CH_3OH \rightarrow 2H_2 + CO, \quad \Delta H^0 = 92\,\text{kJ mol}^{-1} \tag{4}$$

This endothermic side reaction might have occurred on hot Pt spots generated by the exothermic POM. Fig. 2 displays that S_{CO_2} remain high (>90%) in the reaction temperature range studied.

Fig. 2 also indicates that C_{MeOH} and S_{H_2} were concomitantly increased on increasing the reaction temperature. In this series of experiments, oxygen in the feed (with a stoichiometry of $n_{O_2}/n_{MeOH} = 0.5$) was completely consumed ($C_{O_2} \sim 100\%$). Oxygen molecules fed into but not consumed by POM would oxidize hydrogen of the POM product into water and decreased the S_{H_2},

$$2H_2 + O_2 \rightarrow 2H_2O \tag{5}$$

According to the experimental results, the fraction of oxygen spent in reaction (2) increased with the temperature. Accordingly, both the C_{MeOH} and the S_{H_2} of POM increased with the relative rate of reactions (2) and (4). A high activity to reaction (2) would increase not only C_{MeOH} but also S_{H_2}.

Table 2 compares POM activities of Pt/ZnO catalysts with different Pt loadings at $T_R = 150$ °C. Desired C_{MeOH} and S_{H_2} were found to increase with the Pt loading until 1 wt%. The 1%Pt/ZnO catalyst exhibited the highest C_{MeOH} (84%) and S_{H_2} (75%). Above this loading, the catalytic performance gradually decreased. The decrease of C_{MeOH} and S_{H_2} at high Pt loading may be explained by d_{Pt}. Size of Pt particles on ZnO has been examined by TEM. Pt particles in low loading Pt/ZnO (1% or less) were too small to be prominently noticed by TEM. On highly loaded samples, deposited Pt particles became noticeable and showed an average size of $d_{Pt} = 1.6$ and 2.5 nm for 2 and 3%Pt/ZnO. Conceivably, POM activity of Pt catalysts depended on size of Pt particles dispersed. The activity should decrease on increasing d_{Pt}.

Table 2
Effect of Pt loading on the physicochemical properties and catalytic activities of Pt/ZnO catalyst in POM reaction 150 °C

Catalysts	Pt (wt%)	d (nm)[a]	C_{MeOH}	S_{H_2}	S_{CO_2}
0.3%Pt/ZnO	0.3	–	67	42	88
0.8%Pt/ZnO	0.8	–	72	50	86
1%Pt/ZnO	1.2	–	84	75	93
2%Pt/ZnO	1.9	1.5	80	72	90
3%Pt/ZnO	3.2	2.7	54	61	84

[a] Estimated by TEM.

Table 3
Comparison of the POM performance (with $n_{O_2}/n_{MeOH} = 0.5$) of different metal catalysts dispersed on ZnO prepared by impregnation

Sample	T_i[a] (°C)	T_R (°C)	C_{MeOH}	S_{H_2}	S_{CO_2} (%)
30%Cu/ZnO	175	200	77	67	98
2%Au/ZnO	150	175	80	70	>99
5Ag/ZnO	100	175	75	60	90
1%Pt/ZnO	RT	150	84	75	93

The C_{MeOH}, S_{H_2} and S_{CO} represent data at T_R temperature.

[a] T_i: temperature required for ignition of POM.

Performance of POM varies with the kind of metal catalysts used. Table 3 summarizes performance of different metal catalysts supported on ZnO. Noble metal catalysts are generally more active for POM than Cu catalyst and can be ignited at low temperatures. The prepared catalysts showed following trend of decreasing ignition temperature (T_i):

$$\begin{aligned}&\text{Cu/ZnO}\,(175\,^\circ\text{C}) > \text{Au/ZnO}\,(150\,^\circ\text{C})\\ &> \text{Ag/ZnO}\,(100\,^\circ\text{C}) > \text{Pt/ZnO}\,(25\,^\circ\text{C})\end{aligned} \tag{I$'$}$$

The Pt/ZnO is the only catalyst that can ignite POM at room temperature (25 °C). However, the catalyst Au/ZnO exhibits the highest selectivity (99%) of CO_2 (instead of CO) among these metal catalysts.

In conclusion, supported Pt catalysts were able to ignite methanol in POM reaction at ambient temperature. The low T_i of these catalysts renders a fast start-up for the POM reaction without preheating. Besides, Pt catalysts may also be used to produce hydrogen through POM at a low temperature of 150 °C. Kind of catalyst support significantly affected the selectivity of H_2 and CO_2 from POM. Among prepared catalysts, Pt/ZnO showed the highest selectivity.

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