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Low-temperature mild partial oxidation of ethanol over supported platinum catalysts

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Abstract

Supported platinum catalysts containing 1.2% Pt loaded on Al_2O_3 (1.2% Pt/Al_2O_3) and 1.9% Pt loaded on ZrO_2 (1.9% Pt/ZrO_2) were prepared by incipient wetness impregnation and sol–gel method, respectively. The activity of these catalysts in the partial oxidation of ethanol (POE) was examined in a fixed-bed reactor in a temperature range between 373 and 473 K. The results indicated that significant ethanol conversion ($C_{EtOH} > 50\%$) was found at the low reaction temperature with a feed ratio of O_2/EtOH ratio >0.75. Oxygen molecules introduced in reactant were completely consumed in POE reactions performed. H_2, H_2O, CO and CO_2 were the major products detected. The selectivity of hydrogen (S_{H_2}) and CO (S_{CO}) varied significantly with reaction conditions. High selectivity of hydrogen ($S_{H_2} > 95\%$) and low selectivity of CO ($S_{CO} \sim 0\%$) were found from a mild oxidation at T_R = 373 K over Pt/ZrO_2. However, these two selectivities were drastically deteriorated through oxidation at high T_R, high O_2/EtOH ratio or over Pt/Al_2O_3 catalyst.

Keywords: Ethanol; Partial oxidation; H_2 production; Supported platinum catalyst

1. Introduction

Hydrogen is a clean fuel that may generate electricity through fuel-cell systems. However, the application of hydrogen fuel cell (HFC) is hindered by the delivery of hydrogen fuel. The delivery problem can be eliminated by alternative fuels from which hydrogen can be produced onsite where it can be used in fuel cells for power generation. Among various liquid fuels, ethanol distinguishes itself as a potential fuel as it is renewable. It is non-toxic and may be fermented from biomass [1].

Hydrogen may be produced directly from ethanol by different processes such as steam reforming (SRE, Eq. (1)) [2–6], partial oxidation (POE, Eq. (2)) [7–9] or oxidative steam reforming (OSRE, a combination of SRE and POE) [10–17].

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2,\quad \Delta H^\circ_{298} = +347.4\,\mathrm{kJ/mol} \qquad (1)$$

$$C_2H_5OH + 3/2O_2 \rightarrow 3H_2 + 2CO_2,\quad \Delta H^\circ_{298} = -557.2\,\mathrm{kJ/mol} \qquad (2)$$

The SRE is an endothermic reaction which needs a high reaction temperature of $T_R > 873$ K. The POE route is exothermic and may be processed at lower T_R.

POE reaction has been explored and reported recently by Lu et al. using Cu, Fe and Ni based catalysts [7–9]. Mattos and Noronha [18,19] studied the effect of the support on the performance of Pt-based catalysts in partial oxidation of ethanol at 573 K. They find that the Pt/Al_2O_3 catalyst produced acetic acid as a major product. On the other hand, Schmidt et al. [20] have reported a high selectivity towards H_2 over Rh/CeO_2 around 973 K. However, the process produces significant amount of CO.

The CO is a poison to Pt-based catalysts used in electrodes of hydrogen fuel cells, especially for proton exchange membrane fuel cells (PEMFC). The contamination of CO in hydrogen-rich gas obtained from reforming of hydrocarbon has to be reduced to a low level (below 50 ppm) before feeding into the PEMFC. Selective catalytic CO oxidation is a promising method to reduce the CO contamination. Platinum is one of the catalysts

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that can preferentially oxidize CO [21–23] in the presence of hydrogen. In order to increase the S_{H_2} and decrease the S_{CO} of POE, platinum catalyst is chosen to explore in this study. Reducible oxide (ZrO_2) and non-reducible oxide (Al_2O_3) are used to disperse platinum into fine particles to study the effect of support material on the performance of Pt catalysts. The influences of experimental parameters, such as O_2/EtOH molar ratio and reaction temperature are also investigated in this study.

2. Experimental

2.1. Catalyst preparation and characterization

Pt/Al_2O_3 catalyst was prepared by incipient wetness impregnation of γ-alumina (Merck) with an aqueous solution of H_2PtCl_6 (Merck). A sol–gel method was used for the preparation of Pt/ZrO_2 catalyst using $Zr[O(CH_2)_3CH_3]_4$ (Strem) and H_2PtCl_6 as precursors. They were completely dissolved in ethanol and the solution was gelatized with deionized water. After drying at 383 K and calcination at 673 K, the samples were stored as fresh catalysts. Platinum loadings in the fresh catalysts were determined by the atomic-emission technique using an inductively coupled plasma-mass spectrometer (ICP-MS) from Perkin-Elmer.

Hydrogen adsorption isotherms were determined by a volumetric technique at 298 K. Monolayer coverage uptakes (N_{H_2}) were obtained for each catalyst by extrapolating hydrogen uptakes in the pressure range between 0 and 75 Torr to zero pressure. The dispersion (D, percentage of atoms exposed to surface) of platinum was calculated from N_{H_2} by assuming that each surface platinum atom chemisorbed 1.1 hydrogen atoms [24,25]. BET surface area (S_{BET}) was estimated by nitrogen adsorption experiments at the liquid N_2 temperature in the same volumetric system. Obtained dispersion and surface area of supported platinum catalysts were summarized in Table 1.

Transmission electron microscopy (TEM) and powder X-ray diffraction (XRD patterns) were used to calculate the size of supported platinum particles. These experiments were performed in JEOL JEM-2010 system and a Siemens D5000 diffractometer. The patterns were run with a Ni-filtered Cu Kα$_1$ radiation (40 kV, 30 mA, λ = 1.5405 Å).

Table 1
Characterization of supported platinum catalysts

Catalyst	Hydrogen chemisorption		d_{Pt} (nm)[b]	S_{BET} ($m^2\ g^{-1}$)
	D (N_H/N_{Pt})	d_{Pt} (nm)[a]		
1.9% Pt/ZrO_2	0.71	1.5	1.5	134
1.2% Pt/Al_2O_3	0.30	3.7	3.4	130

[a] Average diameter of platinum crystallite calculated from $d = 1.1/D$ [24].
[b] Average diameter of platinum crystallite calculated from TEM images.

2.2. Activity tests

The catalytic activity of prepared samples towards POE was carried out in a fixed bed reactor as shown in Fig. 1. About 100 mg of the catalyst was placed in a 4 mm ID quartz tubular reactor and held by glass-wool plugs. Before reaction, each catalyst was pre-activated in flowing hydrogen at 673 K for 1 h. Temperatures of POE reaction (T_R) were controlled by a heating tape and measured by a coaxial thermocouple (1.2 mm ID) at the center of the reactor bed. A 100 ml min^{-1} stream of reactant gas [12% O_2 (controlled by mass-flow controller) and 8% ethanol (feeding by a liquid pump and preheated to about 423 K) in 80% Ar] was catalyzed with 100 mg of catalyst for each run. Reaction products were separated with columns of Porapak Q (for the separation of CO_2, C_2H_4, H_2O, CH_3CHO, C_2H_5OH, CH_3OCH_3, etc.) and Molecular sieve 5A (for the separation of H_2, O_2, CH_4, CO, etc.) and analyzed with two sets of TCD-GC. The reactor temperature was raised stepwise from a room temperature to 473 K.

Major components in the reaction product were H_2, H_2O, CO, CO_2 and un-converted ethanol. Traces (<1% according to number of carbon atoms) of CH_3CHO has been detected as by-product. The ethanol conversion (C_{EtOH}), the selectivity of hydrogen (S_{H_2}) and carbon monoxide (S_{CO}) in the POE reactions were calculated in this study according to following equations:

$$C_{EtOH}\ (\%) = \frac{n_{EtOH\text{-in}} - n_{EtOH\text{-out}}}{n_{EtOH\text{-in}}} \times 100 \qquad (3)$$

$$S_{H_2}\ (\%) = \frac{n_{H_2\text{-out}}}{n_{H_2\text{-out}} + n_{H_2O\text{-out}}} \times 100 \qquad (4)$$

$$S_{CO}\ (\%) = \frac{n_{CO\text{-out}}}{n_{CO\text{-out}} + n_{CO_2\text{-out}}} \times 100 \qquad (5)$$

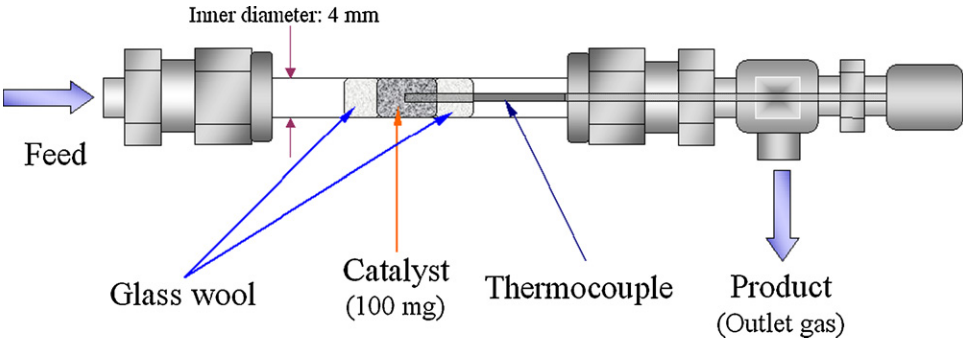

Fig. 1. Schematic diagram of the reactor employed on POE reaction.

3. Results and discussion

The partial oxidation of ethanol has been investigated at 373–473 K for both Pt catalysts, i.e., 1.2% Pt/Al_2O_3 and 1.9% Pt/ZrO_2. Within the temperature ranges, oxygen was completely consumed. Noticeable components in the reaction product are H_2, H_2O, CO and CO_2 and un-converted ethanol.

3.1. Effect of O_2/EtOH molar ratio at T_R = 373 K

Fig. 2 compares the effect of O_2/EtOH molar ratio on activity of POE and selectivity of different products over both 1.2% Pt/Al_2O_3 and 1.9% Pt/ZrO_2 catalysts at a reaction temperature of $T_R = 373$ K. Fig. 2(A) indicates that both platinum catalysts are active toward POE at this low T_R. A C_{EtOH} of 50% with a high S_{H_2} (>90%) was found at O_2/EtOH = 0.75 (Fig. 2(B)). Evidently, both Pt catalysts were active for breaking C–C bond [26] at 373 K. Oxygen was found completely consumed in O_2/EtOH molar ratios between 0.75 and 1.13. Instead of an expected C_{EtOH}, S_{H_2} was found drastically decreased with increasing O_2/EtOH from 0.75 to 1.13. The decrease in S_{H_2} may be attributed to burning of hydrogen according to the following reaction:

$$H_2 + 1/2O_2 \rightarrow H_2O \qquad (6)$$

The support of Pt catalysts also affects the S_{CO} in POE (Fig. 2(C)). Negligible CO contamination is detected over 1.9% Pt/ZrO_2 catalyst throughout the O_2/EtOH region studied. Over 1.2% Pt/Al_2O_3 catalyst, however, the CO contamination becomes evident ($S_{CO} \sim 60\%$) and decreases slightly with the O_2/EtOH ratio. Ruckenstein and Wang [27,28] compared the rhodium supported on reducible oxides and non-reducible oxides for the partial oxidation of methane. They report that Rh supported on reducible oxides exhibits lower S_{CO} due to the ability of reducible oxides to participate in the oxidation reaction. Also, Matsumoto et al. [29] and Breen et al. [3] report that zirconia-supported Pt catalysts are much more active than the corresponding alumina-supported Pt catalysts in the production of hydrogen by steam reforming of ethanol. We suggest that the oxygen storage and releasing capacity of ZrO_2 can migrate the lattice oxygen to the Pt surface and can contribute to the selective CO oxidation [30,31]. On the other hand, the adsorbed oxygen on the Pt surface of Al_2O_3 support is less active for the selective oxidation of CO.

Numerous studies on POE reaction [7–9,18–20] have been reported in the literature (see Table 2). A reaction temperature $T_R > 473$ K was reported. In this study we found that properly prepared Pt catalysts may be active for POE at $T_R = 373$ K. This mild POE at this low temperature also exhibits a high selectivity of hydrogen with $S_{H_2} > 90\%$. In fact, high selectivity of hydrogen ($S_{H_2} > 95\%$) and low selectivity of CO ($S_{CO} \sim 0\%$) are found from a mild oxidation at $T_R = 373$ K and O_2/EtOH = 0.75 over Pt/ZrO_2 catalyst.

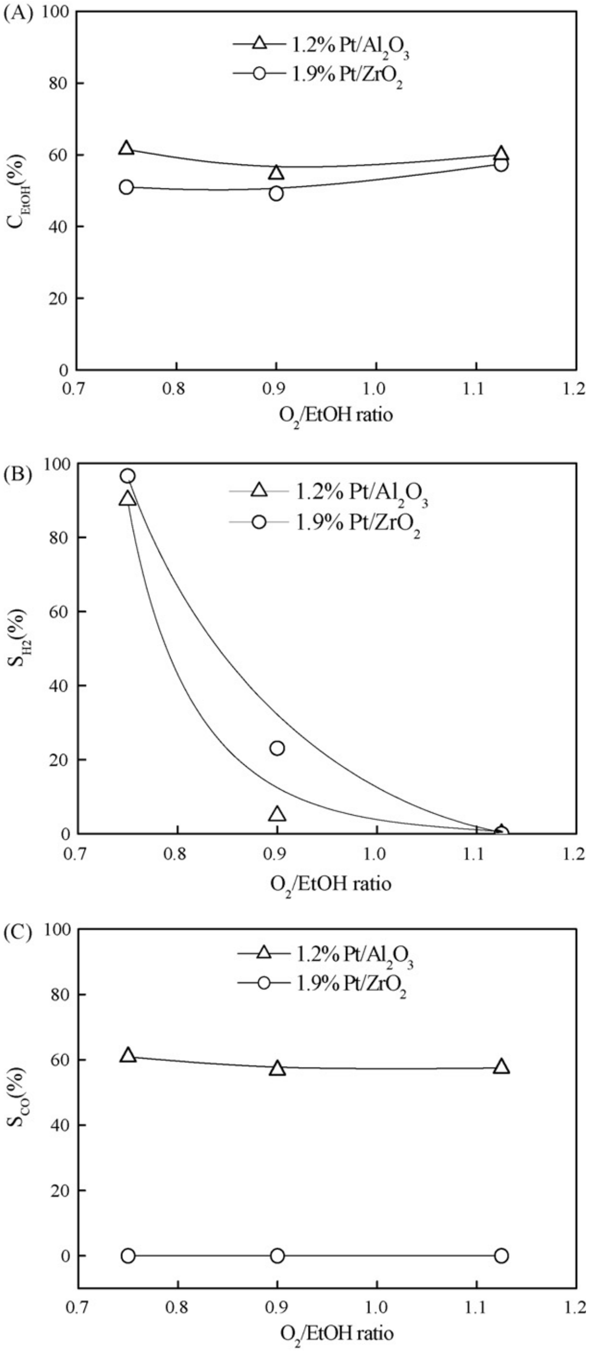

Fig. 2. Effect of O_2/EtOH molar ratio on POE over both 1.2% Pt/Al_2O_3 and 1.9% Pt/ZrO_2 catalysts at $T_R = 373$ K: (A) C_{EtOH}; (B) S_{H_2}; (C) S_{CO}.

3.2. Effect of temperature

Fig. 3 presents temperature profiles of ethanol conversion and products selectivity under O_2/EtOH ratio of 0.75 for both 1.2% Pt/Al_2O_3 and 1.9% Pt/ZrO_2 catalysts. The C_{EtOH} was 60% and 51% over 1.2% Pt/Al_2O_3 and 1.9% Pt/ZrO_2, respectively, at a temperature of 373 K. The C_{EtOH} increases slightly with increasing the reaction temperature (Fig. 3(A)). Comparably, 1.2% Pt/Al_2O_3 catalyst has a higher increasing rate than 1.9% Pt/ZrO_2 catalyst around $T = 400$ K.

Table 2
Comparison of POE performance reported in previous literatures

Catalyst	Activity				Reference
	T_R (K)	C_{EtOH} (%)	S_{H_2} (%)	S_{CO} (%)	
Cu/Zn/Ni	473–523	97–99	57	10	[7]
$Ni_{50}Fe_{50}$	573	87–90	44–46	20	[8]
$Ni_{48}Fe_{48}La_4$	823	96	74	–	[9]
Pt/Al_2O_3	573	80	(~80% acetic acid obtained)	18	
Pt/CeO_2	573	70	(Y_{H_2} ~ 0.8)[a]	80	[19]
Rh/CeO_2	973	>95	~80	~40	[20]
Pt/ZrO_2	373	51	97	NA	This work

[a] Hydrogen yield (H_2 mol/consumed EtOH mol).

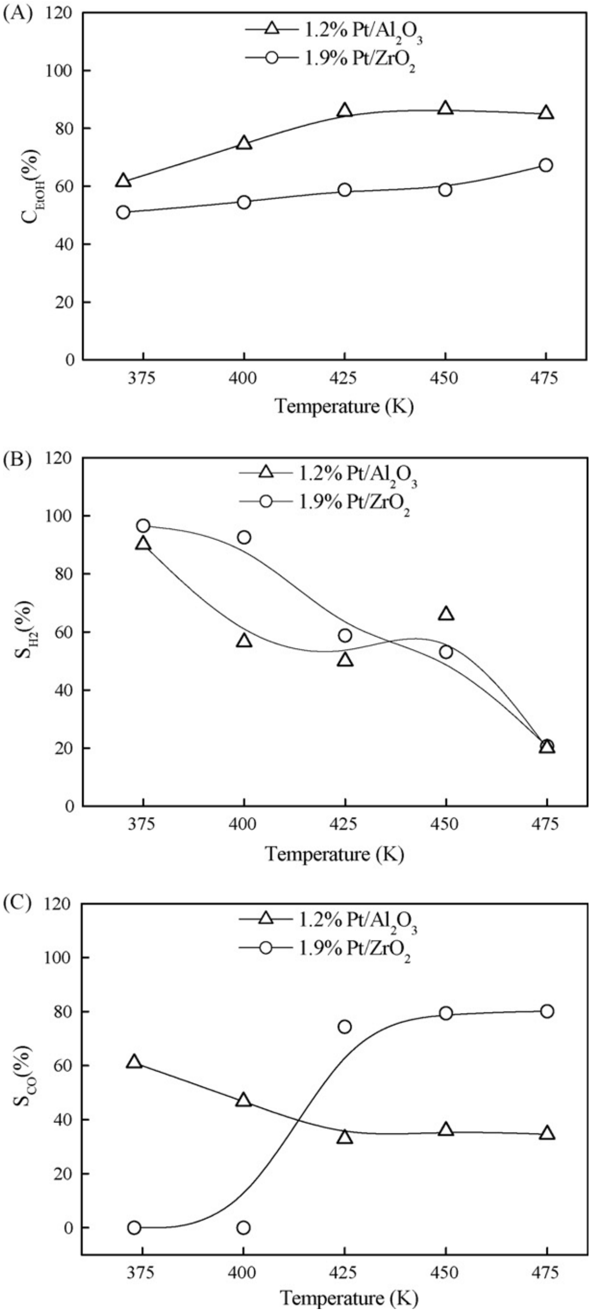

Fig. 3. Effect of reaction temperature on POE over both 1.2% Pt/Al_2O_3 and 1.9% Pt/ZrO_2 catalysts at O_2/EtOH = 0.75: (A) C_{EtOH}; (B) S_{H_2}; (C) S_{CO}.

However, S_{H_2} drastically deteriorated at high T_R conditions over both Pt catalysts studied. Experimental S_{H_2} dropped from 97% to 20% with increasing T_R from 373 to 473 K (Fig. 3 (B)). The variation may be attributed to an increase of the rate of reaction with T_R. Concomitantly, S_{CO} was generally high (>50%) with increasing T_R over 400 K.

3.3. Characterization of catalysts

XRD pattern of 1.2% Pt/Al_2O_3 and 1.9% Pt/ZrO_2 catalysts are shown in Fig. 4. No significant diffraction signal of Pt(1 1 1) is found from both catalysts. Probably, the size of platinum particles dispersed on these catalysts was below the detection limit (>5 nm) of XRD. In this study the size of platinum particles on these catalysts were characterized with TEM technique and hydrogen chemisorption. Fig. 5 displays TEM images of the particle size distribution of 1.2% Pt/Al_2O_3 and 1.9% Pt/ZrO_2 catalysts. Platinum particles are found uniformly dispersed on the surface of supports. The attached histograms were size distribution of 100 particles in several parts of TEM in each photograph. Mean platinum diameter of $d_{Pt} = 1.5$ and 3.4 nm was calculated for 1.9% Pt/ZrO_2 and 1.2% Pt/Al_2O_3 catalysts, respectively. The sol–gel method (for 1.9% Pt/ZrO_2) led a highly dispersed catalyst than the impregnation method (for 1.2% Pt/Al_2O_3). To our satisfactory, size of platinum particles calculated [24] from the irreversible part of H_2

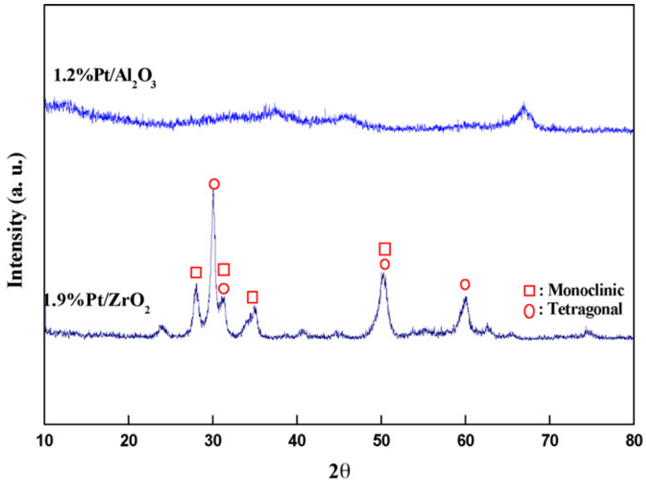

Fig. 4. XRD patterns of both 1.2% Pt/Al_2O_3 and 1.9% Pt/ZrO_2 catalysts.

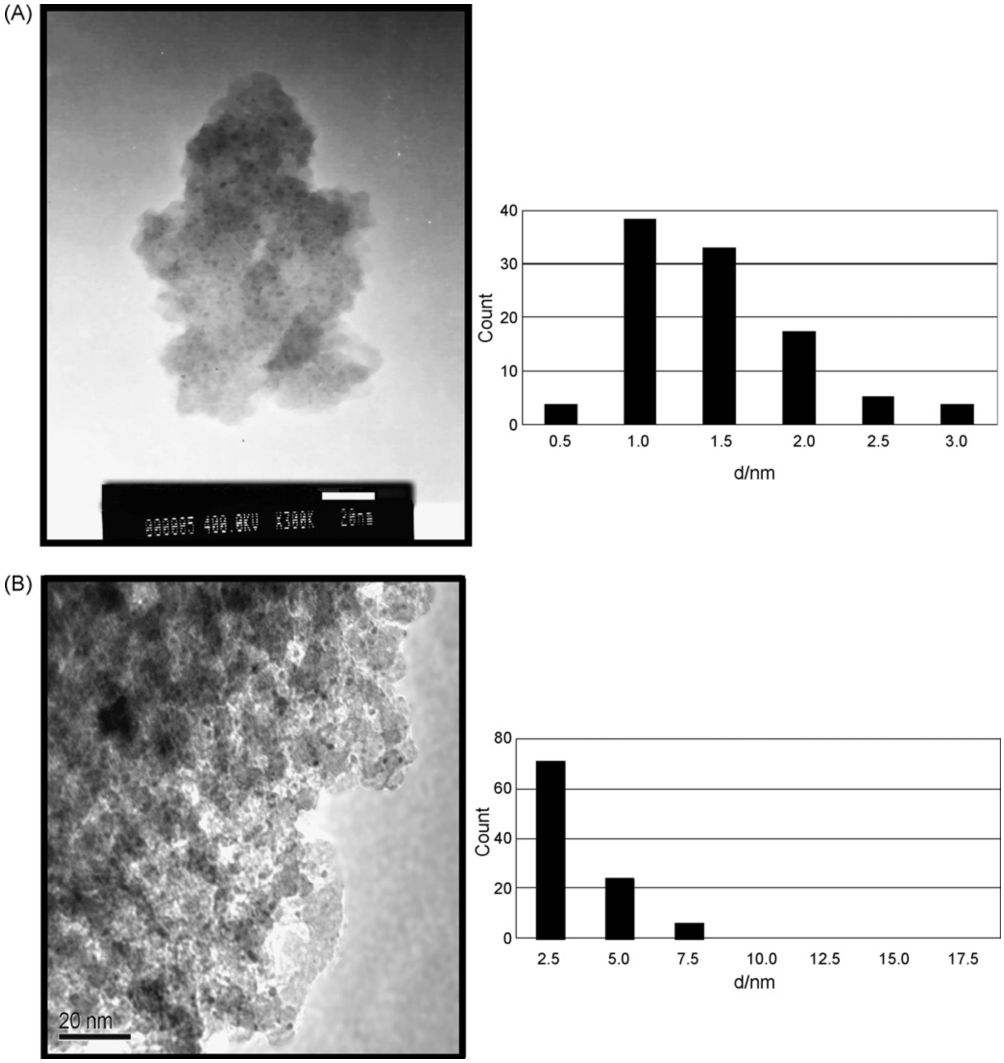

Fig. 5. TEM images and histograms of the particle size distribution of supported platinum catalysts: (A) 1.9% Pt/ZrO_2; (B) 1.2% Pt/Al_2O_3.

chemisorption measurements is in good agreement with d_{Pt} from the TEM analysis (see the third column of Table 1).

3.4. Comparison of supported platinum catalysts

In this study, we choose different supports to prepare supported platinum catalysts. According to above POE catalytic performance, we find that all catalysts are able to convert half of ethanol at low temperature ($T_R \sim 373$ K) and O_2/EtOH = 0.75. However, the selectivity of S_{H_2} and S_{CO} varies with O_2/EtOH, reaction temperatures and the kind of support used. The Pt/Al_2O_3 catalyst has a high S_{H_2} (>90%) but its S_{CO} is also high. To our interest, Pt/ZrO_2 catalyst has good selectivity towards the desired products (H_2 and CO_2). The variation of S_{CO} over Pt/ZrO_2 and Pt/Al_2O_3 at 373 K can be interpreted by two kinds of oxygen intermediate. The reducible ZrO_2 of Pt/ZrO_2 catalyst can provide the lattice oxygen (O_L) that has a high activity for oxidation of CO to CO_2:

$$O_L + CO_{ad} \rightarrow CO_2 \qquad (7)$$

The lattice oxygen is absent in Pt catalyst supported on the non-reducible Al_2O_3. In this case, oxygen molecules have to be adsorbed on the Pt surface as O_{ad}. The O_{ad} is less effective than O_L for reaction (7). Consequently, a high S_{CO} was resulted from desorption of partially oxidized CO:

$$CO_{ad} \rightarrow CO \qquad (8)$$

4. Conclusion

The performance of supported platinum catalysts for the partial oxidation of ethanol depends on T_R of reaction and the catalyst used. Hydrogen can be selectively ($S_{H_2} > 95\%$) produced with negligible S_{CO} from a mild oxidation of ethanol over Pt/ZrO_2 catalyst at O_2/EtOH = 0.75 and a low temperature of $T_R < 400$ K. However, S_{H_2} and S_{CO} were significantly deteriorated in mild oxidation conditions of high O_2/EtOH ratio and/or high T_R. It is our suggestion that POE under mild condition may be developed as an efficient process to produce hydrogen from ethanol (Fig. 6).

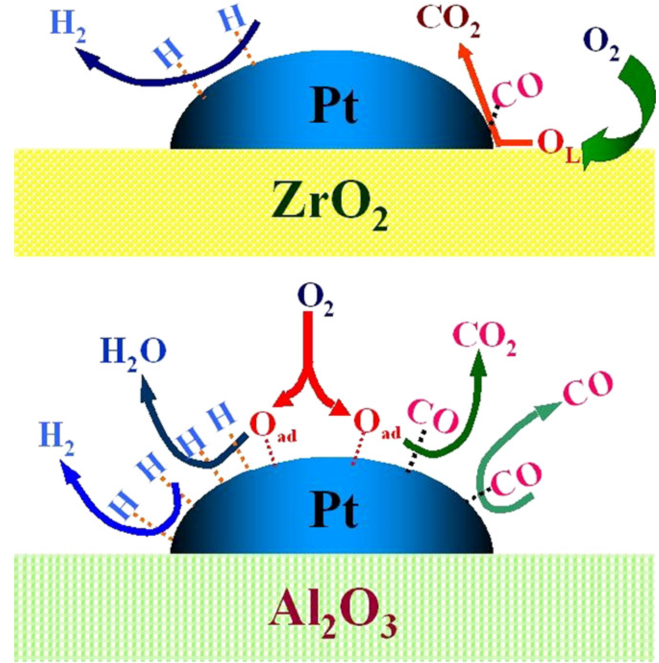

Fig. 6. The reaction models for POE over both 1.9% Pt/ZrO_2 and 1.2% Pt/Al_2O_3 catalysts.

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