Surface Area Effect of Zinc Oxide for Steam Reforming of Ethanol over Supported-Platinum Catalysts*

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The effect of surface area over the ZnO-supported platinum catalysts on the catalytic performance of steam reforming of ethanol (SRE) has been studied. Various surface area of ZnO is prepared through two routes: reflux (assigned as ZnO-R), thermal decomposition under air (assigned as ZnO-A) and under N₂ (assigned as ZnO-N). Also, the commercial ZnO (assigned as ZnO-C) is chosen as reference. Four Pt/ZnO catalysts (3 wt% loading of Pt) are prepared by incipient wetness impregnation (assigned as Pt-R, Pt-A, Pt-N and Pt-C, respectively). The BET measurement shows that the ZnO-A (89 m²·g⁻¹) support possesses a higher surface area than the ZnO-R (1.3 m²·g⁻¹). The catalytic activity on the SRE reaction is evaluated in a fixed-bed reactor under 22,000 h⁻¹ GHSV and H₂O/EtOH molar ratio of 13. The results show that total ethanol conversion is observed at 225°C and 400°C over the Pt-A and Pt-R catalysts, respectively. When the temperature exceeds 350°C, acetaldehyde decomposition and acetaldehyde steam reforming are competitive on the platinum catalysts to promote H₂ production. The small particle size catalyst of Pt-A favors the decomposition of acetaldehyde to produce CH₄ and CO, and the large particle size catalyst of Pt-R favors the steam reforming of acetaldehyde to produce CH₄ and CO₂.
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Keywords: Zinc oxide; Surface area; Steam reforming of ethanol; Platinum

I. INTRODUCTION

Hydrogen is considered a potential source of clean energy, mainly because of its use as fuel in fuel-cell systems. However, to date, the production of hydrogen is still based on the reforming of fossil-derived fuels [1–3]. Several biomass sources can be supplied to produce hydrogen by the steam reforming reaction. The steam reforming of ethanol (SRE) is an endothermic reaction which produces 6 mole H₂ per mole of ethanol. However, other side reactions can also occur, such as dehydration, dehydrogenation, decomposition and condensation. These reactions result in undesirable products, such as ethylene, acetone, methane or CO, which interfere with the process. A catalyst under certain reaction conditions favors a reaction or a group of reactions among the possible network of reactions described above.

Llorca *et al.* [4] were the first to show that pure ZnO, among oxides such as alumina, magnesia, ceria and titania, was the most active, at temperatures as low as 400°C, in producing hydrogen from bio-ethanol. Also, the addition of cobalt to ZnO further upgraded the activity of the SRE reaction at low temperatures [5, 6]. ZnO and ZnO-supported catalysts have performed well in SRE reactions, possibly because ZnO has both hydrogenation/dehydrogenation activities and basic properties. Yang *et al.* [7] reported that ZnO-, La₂O₃-, MgO- and Al₂O₃-supported nickel catalysts were highly active

FIG. 1: XRD patterns of ZnO supports: (a) ZnO-C (b) ZnO-A (c) ZnO-N (d) ZnO-R.

at temperatures from 330–650°C, but that their product distributions strongly depended on the support material and the nickel loading. The effect of zinc oxide loading on the catalytic activity and product selectivity in the catalytic reforming of bio-ethanol has been reported for ZnO-supported silica catalysts [8]. In addition, in order to understand the role of acetaldehyde on product distribution during the catalytic reforming of bio-ethanol, the steam reforming of acetaldehyde over ZnO/SiO₂ catalysts also has been studied. It is likely that a better dispersion of the catalysts would be beneficial for the catalytic activity [9, 10].

Reforming reactions over ZnO-supported noble metal-based catalysts, such as Co, Cu and Ni, have shown

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a high efficiency in the production of hydrogen [7, 10–13]. Moreover, the morphology effect of ZnO-supported catalysts [14], doping extra metal in the catalytic system [15, 16] and using a new type of multi-layered reformer [17] to modify the Co/ZnO catalytic system and promote the catalytic performance were reported on recently. In the literature there have been some reports that Pt-based catalysts on different supports, including CeO₂, ZrO₂, CeZrO₂ and Al₂O₃ [18–23], exhibited good activity for hydrogen production. Recently, we investigated how ZrO₂, Al₂O₃ and ZnO-supported Pt catalysts promoted the reforming of ethanol, where the loading of Pt and support effects were studied [24–26]. In this work, four kinds of zinc oxide with different surface area were prepared and chose as the supports in designing the ZnO-supported platinum catalysts to evaluate the catalytic performance on the SRE reaction.

II. EXPERIMENTAL

A. Preparation of support and catalyst

Three kinds of prepared and commercial ZnO were used to prepare the Pt/ZnO catalysts. ZnO-R was prepared under reflux conditions, in which the equal molar ratio of Zn(NO₃)₂·6H₂O (Stream, 90%) and urea (Stream, 90%) of 0.1 mole were stirred with DI water/ethanol (80/20 mL) at room temperature for 5 min, then refluxed at 95°C for 12 h. ZnO-A and ZnO-N were obtained through the thermal decomposition of Zn(OH)₂·2ZnCO₃·*x*H₂O (Stream, 99%) in air and N₂, respectively, at 300°C for 30 min. The commercial ZnO (Sigma-Aldrich, 99%) was denoted as ZnO-C.

The Pt/ZnO catalysts were prepared by the incipient wetness impregnation method using PtCl₄ (Stream, Pt = 99.9%) as the precursor (3 wt%), and denoted as Pt-R, Pt-N, Pt-A and Pt-C, respectively. The resulting solids were then dried at 110°C overnight and calcined in air at 300°C for 2 h.

B. Characterization of support and catalyst

The reduction behavior of the ZnO supports and Pt/ZnO catalysts was studied by temperature-programmed reduction (TPR). The sample was heated in 10% H₂/N₂ (flow rate of 10 mL·min⁻¹) with a heating rate of 7°C·min⁻¹ from ambient to 800°C. The surface area (*S*_{BET}, m²·g⁻¹) of the zinc oxide was determined with nitrogen adsorption isotherms measured at -196°C. X-ray diffraction (XRD) measurements were performed using a MAC Science MXP18 diffractometer with CuKα radiation ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 30 mA. The crystallite sizes of the zinc oxide were estimated using the Scherrer equation. Transmission electron micrographs (TEM) were taken on a PHILIPS (CM-200) microscope at an accelerated voltage of 200 kV. Thermal gravimetric (TG) analysis was carried out using a Seiko SSC5000 TG system. The rate of heating was maintained at 10°C·min⁻¹. The measurement was carried from RT to 600°C under an air-flow rate of 100 mL·min⁻¹.

FIG. 2: XRD patterns of Pt/ZnO catalysts: (a) Pt-C (b) Pt-A (c) Pt-N (d) Pt-R.

C. Evaluation of catalytic activity

The catalytic activity of the Pt/ZnO catalysts towards the SRE reaction was performed in a fixed-bed quartz reactor at atmospheric pressure. The gas hourly space velocity (GHSV) was maintained at 22,000 h⁻¹ and the H₂O/EtOH molar ratio was 13 (H₂O:EtOH = 80:20 by volume). About 100 mg of the catalysts with a 60–80 mesh grain size were loaded into the reactor. Before the SRE reaction, the catalyst was activated by reduction with hydrogen at 200°C for 4 h. The analysis of the reactants and products was carried out online by gas chromatography with columns of Porapak Q and Molecular Sieve 5 A for separation purposes. The evaluation of the SRE activity of the samples depended on the conversion of ethanol (*X*_{EtOH}) and the distribution of products (mol%).

$$X_{\text{EtOH}} = n_{\text{EtOH, reacted}} / n_{\text{EtOH, fed}} \times 100[\%] \quad (1)$$

$$Y_{\text{H}_2} = n_{\text{H}_2\text{-out}} / n_{\text{EtOH, reacted}} \quad (2)$$

$$S_i = n_i / \sum n_i \times 100[\%], \quad (3)$$

where $\sum n_i$ included the H₂.

III. RESULTS AND DISCUSSIONS

A. Characterization of supports and catalysts

The crystalline phase and structure of the ZnO supports were determined by XRD and showed in Fig. 1. The average particle size of the zinc oxide crystallite (*d*_{ZnO}) was calculated using the Scherrer's equation of the corresponding peaks and collected in Table I. The diffraction signals from XRD patterns showed the hexagonal phase of ZnO (JSPDS 89-1397) that were observed on all the ZnO supports. The intensity of the diffraction patterns of ZnO-R support showed the better crystalline structure than the others, where the ZnO-R had the largest particle size of 13 nm and smallest surface area of 1.3 m²·g⁻¹. Otherwise, the ZnO-A had the smallest particle size of 4.9 nm and largest surface area of 89 m²·g⁻¹. The ZnO-N,

TABLE I: Physical properties of ZnO supports and Pt/ZnO catalysts.

Preparation method	Supports	S_{BET} (m^2/g)	Catalysts	Particle size (nm)		Metal loading ^b
				ZnO ^a	Pt ^a	
Commercial	ZnO-C	56	Pt-C	5.4	7.5	2.3
Thermal decomposition-Air	ZnO-A	89	Pt-A	4.9	6.8	2.4
Thermal-decomposition-N ₂	ZnO-N	55	Pt-N	5.7	6.3	2.4
Reflux	ZnO-R	1.3	Pt-R	13	16	2.4

^aCalculated from XRD with Scherrer's equation; ^bAnalysis from ICP-AES.

FIG. 3: TEM micrographs of Pt/ZnO catalysts: (a) Pt-C (b) Pt-A (c) Pt-N (d) Pt-R.

the similar preparation procedure with ZnO-A but under N₂ atmosphere as carrier gas, showed the larger particle size of 5.7 nm and smaller surface area of 55 $\text{m}^2\cdot\text{g}^{-1}$, where the similar data was found on commercial ZnO-C.

XRD patterns of the Pt/ZnO catalysts were quite similar to that of the zinc oxide supports (shown in Fig. 2). Only Pt-R catalyst showed the additional diffraction peaks assigning to Pt (JSPDS 4-802). According to the literatures [5, 10] reported, the ZnO can promote the dispersion of metal and avoid the sintering of metal. Apparently, the surface area of ZnO can affect the dispersion of Pt on the Pt/ZnO catalysts. Further, the particle size of Pt/ZnO catalysts might influence the catalytic performance. Observed XRD data attributed that the Pt had poor dispersion (or aggregation) on the surface of ZnO-R. Moreover, the well dispersion and smaller particle size of Pt were found on Pt-C, Pt-N and Pt-A catalysts. From the TEM images (Fig. 3), the Pt-R catalyst presented a much larger crystalline size of ZnO than the others. The crystalline property and particle size of ZnO support from TEM were also convinced with the XRD analysis.

FIG. 4: Ethanol conversion over Pt/ZnO catalysts: (a) Pt-C (b) Pt-A (c) Pt-N (d) Pt-R.

FIG. 5: Catalytic performance in the SRE reaction over Pt-A catalyst.

B. Catalytic performance on the SRE reaction

Figure 4 showed the ethanol conversion (X_{EtOH}) over the Pt/ZnO catalysts, where the temperature of X_{EtOH} arrived complete was increased in the order: Pt-A (225°C) > Pt-C (300°C) > Pt-N (350°C) > Pt-R (400°C). The catalytic performance results were summarized in Table II. The ethanol conversion and products distribution of the Pt-R and Pt-A catalysts in the SRE reaction at different reaction temperatures (T_R) were shown in Figs. 5 and 6, respectively.

TABLE II: Products distribution of Pt/ZnO catalysts.

Catalyst	TR (°C)	X _{EtOH} (%)	Products distribution (%) ^a					
			H ₂	CH ₄	CO	CO ₂	C ₂ H ₄ O	C ₃ H ₆ O
Pt-C	200	13.7	49.0	—	—	—	51.0	—
	250	60.2	49.8	2.19	0.59	—	47.4	—
	300	100	51.9	9.50	9.70	1.06	27.9	—
	350	100	58.5	12.6	12.0	1.66	15.4	—
	400	100	68.4	14.0	5.00	12.6	—	—
Pt-A	200	60.2	40.0	—	—	—	60.0	—
	250	100	39.8	2.79	0.70	—	56.7	—
	300	100	43.9	10.4	8.72	1.27	35.7	—
	350	100	44.9	18.0	19.0	—	18.1	—
	400	100	49.4	22.3	23.7	1.40	—	3.25
Pt-N	200	19.8	58.3	—	—	—	41.8	—
	250	28.2	61.6	—	—	—	38.4	—
	300	57.4	60.4	2.41	5.02	—	32.2	—
	350	100	57.1	15.6	17.0	1.36	9.00	—
	400	100	62.1	21.0	13.5	3.36	—	—
Pt-R	300	64.5	51.9	—	—	—	48.1	—
	350	99.1	59.0	—	—	—	41.0	—
	400	100	56.3	11.3	3.00	10.0	18.1	1.27
	450	100	64.2	18.3	—	14.4	—	3.16
	500	100	69.8	13.8	—	13.7	—	2.66

FIG. 6: Catalytic performance in the SRE reaction over Pt-R catalyst.

The major product of acetaldehyde at low temperature demonstrated that the preferentially erased hydrogen from ethanol by the prepared Pt/ZnO catalysts [Eq. (4)]:

The ability to erase hydrogen was enhanced with the increased surface area of the zinc oxide support, while the breakage of the C–C bond for the Pt/ZnO catalysts was worse at temperatures below 300°C. Also, we found that only minor (CH₃)₂CO formed at temperatures exceeding 350°C via the aldol condensation of ethanol, as shown in Eq. (5). Similar observations and explanations have also been suggested by other researchers [27]:

Comparison the hydrogen distribution over Pt-R and Pt-A catalysts, Pt-R catalyst was higher than Pt-A catalyst with T_R increasing. At temperatures as high as

350°C, both catalysts appeared actively to break the C–C bond and promoted H₂ production which came from the decomposition of acetaldehyde to CH₄ and CO or reformed to H₂ and CO₂. Since the CH₄ formation occurred through the possible reforming reactions [27], two competitive paths of acetaldehyde have been proposed. The decomposition of acetaldehyde [Eq. (6)] was preferred for the small particle size catalyst of Pt-A to form CH₄ and CO since the ratio of CH₄/CO approached one; while the steam reforming of acetaldehyde [Eq. (7)] was preferred for the large particle size catalyst of Pt-R to form CH₄ and CO₂. This tendency indicated that the steam reforming of acetaldehyde was thermodynamically feasible at high temperature.

A comparison of the characterizations of the catalysts indicated that the steam reforming of acetaldehyde was favorable for the catalyst with a large crystal size of zinc oxide [5, 6]. The worse dispersion of platinum on the large crystal size of ZnO-R impelled the aggregation of platinum on the surface and depressed the rate of decomposition of acetaldehyde. Contrarily, the large crystal size of the zinc oxide-supported catalyst provided an adsorption site for water [28] to promote the steam reforming of acetaldehyde. As the particle size of the platinum catalyst decreased, the activity on the decomposition of acetaldehyde would be increased and shifted to a lower temperature.

According to the evaluation of catalytic activity on the SRE reaction, we suggested that the surface area of the zinc oxide influenced the activity and selectivity of products on the Pt/ZnO catalysts. A high surface area of the zinc oxide-supported catalyst tended to push the catalyst executing the decomposition of acetaldehyde, such

FIG. 7: TG profiles of spent catalysts: (a) Pt-C (b) Pt-A (c) Pt-N (d) Pt-R.

as Pt-A, Pt-N and Pt-C catalysts. The distribution of both CH_4 and CO can not deplete with the T_R to depress the production of hydrogen, which indicated that a water gas shift (WGS) reaction was difficult occurred on the Pt-A, Pt-N and Pt-C catalysts. The minor CO distribution over Pt-R catalyst indicated that the low surface area of the ZnO-supported catalyst tended to execute the steam reforming of the acetaldehyde.

Based on the evaluation of catalytic performance over Pt/ZnO catalysts, the surface area of supported-platinum catalysts was decreased in the order: Pt-A > Pt-C $\approx$ Pt-N > Pt-R, which was confirmed with the order of X_{EtOH} . Moreover, the support with large surface area possessed the small particle size not only of support but also of active metal (see Table I). Apparently, the surface area and particle size of the support and catalyst can influence the catalytic activity.

C. Characterization of used catalysts

The stability of the active component, sintering of active species and the deposition of coke were the key rea-

sons for the catalyst deactivation in the SRE reaction. In order to obtain more information about the stability of Pt/ZnO catalysts, characterization of TG analysis was pursued for samples after the SRE catalytic tests. The TG curves for the spent catalysts showed in Fig. 7. The weight loss at the temperature range of 200-285°C was assigned for the combustion of adsorbed C_1 species (i.e. CH_x and CO_x) on the surface of catalyst. According to the competitive paths of acetaldehyde intermediate, the C_1 species could be deposited on the catalyst's surface. Furthermore, the combustion of coke approached 450-550°C, as reported in the literature; the deposition of coke was unnoticeable over the four ZnO-supported catalysts.

IV. CONCLUSIONS

The zinc oxide-supported platinum catalysts were evaluated, where the surface area of the ZnO support played an important role not only in the activity for the steam reforming of the ethanol, but also in the selectivity for the products. The Pt-A catalyst had a complete conversion of ethanol and over 40% H_2 selectivity could be obtained at a low temperature of 225°C. On the other hand, the Pt-R catalyst had a higher hydrogen distribution accompanied with a high reaction temperature. For the platinum-based catalysts, the high surface area of the zinc oxide-supported catalyst tended to execute the decomposition of acetaldehyde; otherwise, a low surface area of zinc oxide-supported catalyst promoted the steam reforming of acetaldehyde.

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