

Research Article

Reforming of Ethanol to Produce Hydrogen over PtRuMg/ZrO₂ Catalyst

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A modified PtRu/ZrO₂ catalyst with Mg is evaluated for the oxidative steam reforming of ethanol (OSRE) and the steam reforming of ethanol (SRE). In order to understand the variation in the reaction mechanism on OSRE and SRE, further analysis of both fresh and used catalyst is concentrated on for TEM, TG, Raman, and TPR characterization. The results show that the OSRE reaction requires a higher temperature ($T_R \sim 390^\circ\text{C}$) to achieve 100% ethanol conversion than the SRE reaction ($T_R \sim 2500^\circ\text{C}$). The distribution of CO is minor for both reactions (< 5% for OSRE, < 1% for SRE). This demonstrates that the water gas shift (WGS) reaction is an important side-reaction in the reforming of ethanol to produce H₂ and CO₂. A comparison of the temperature of WGS (T_{WGS}) shows it is lower for the SRE reaction ($T_{\text{WGS}} \sim 250^\circ\text{C}$ for SRE, $\sim 340^\circ\text{C}$ for OSRE).

1. Introduction

The prospect of global energy shortages as well as increasingly stringent emission regulations has stimulated interest in renewable energies. Production of hydrogen from renewable sources derived from agricultural or other waste streams offers the possibility of lower or even no net greenhouse gas emissions [1, 2]. Among the candidates for hydrogen production, ethanol produced by the fermentation of biomass offers many advantages, such as low toxicity, high biodegradability, and easy transport [3–5]; thus, the reforming of ethanol is seen as a promising method for hydrogen production from renewable resource [6, 7]. Hydrogen can be produced from ethanol through different reforming processes, for example, steam reforming of ethanol (SRE), partial oxidation of ethanol (POE), and oxidative steam reforming of ethanol (OSRE). Moreover, a high yield of hydrogen can be obtained from the SRE reaction [4–14].

The nature of the metal and its support strongly affect both stability and products distribution [5, 15]. In view of the ZrO₂-supported system, noble metal catalysts such as Pt and Ru are well known for their high catalytic activities, which have been extensively investigated. The size-selective capability of Pt/ZrO₂ catalysts on the catalytic decomposition of alcohol for the production of hydrogen was reported by Cuenya's group [7, 16]. However, this catalyst deactivated at high temperatures due to carbon deposition. De Lima et al. [17] reported that the side-products of acetaldehyde and ethane were favored on Pt/ZrO₂ in the SRE. Relatively low reaction temperatures around 100 to 200°C in the POE and OSRE over a Pt/ZrO₂ and PtRu/ZrO₂ catalysts were reported by our previous studies [18–21], and 300°C was reported by Mattos and Noronha [22] in the POE reaction. The main problem found when using these catalysts is deactivation by sintering and carbon deposition. The use of basic oxides as supports and the addition of metal species (Li, Na, K, and Cu, etc.) have

been found to improve catalytic performance and overcome the disadvantages [9, 23–25]. Recently, Carrero et al. [26] reported the effect of alkaline earth metals over Cu-Ni/SiO₂ catalysts where a high hydrogen selectivity was obtained with Mg, while the incorporation of Ca reduced coke formation.

Therefore, the main objective of this paper is to study PtRuMg/ZrO₂ catalyst for the SRE and OSRE reactions to produce hydrogen at a temperature lower than 300°C with higher ethanol conversion (X_{EtOH}), hydrogen yield (Y_{H_2}), and lower CO distribution. The expectation is that the catalytic activity and stability against the coke deposition of the PtRuMg/ZrO₂ catalyst on the reforming of ethanol could be enhanced. The characterization of fresh and used catalysts was analyzed by TEM, TG, Raman, and TPR characterization.

2. Experimental

2.1. Catalyst Preparation. A sol-gel method was used for the preparation of the ZrO₂ support using Zr[O(CH₂)₃CH₃]₄ (Strem) as the precursor. The PtRuMg/ZrO₂ catalyst was prepared by the method of sequent incipient wetness impregnation using H₂PtCl₆ and RuCl₃ as precursors (1.5 wt% for each component) first to disperse on the ZrO₂. After drying at 110°C and calcination at 400°C for 4 h, 1.0 wt% of Mg(NO₃)₂·6H₂O was incipient sequentially. After drying at 110°C, the prepared sample was crashed to 60 ~ 80 mesh and stored as fresh catalyst (labeled as PtRuMg/ZrO₂).

2.2. Catalyst Characterization. Transmission electron micrographs (TEMs) were taken on a PHILIPS (CM-200) microscope at an accelerated voltage of 200 kV. Thermal gravimetric 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 1000°C under air flowing with a rate of 100 mL·min⁻¹. The measurements of the Raman spectroscopy were recorded using a Nicolet Almega XR Dispersive Raman spectrometer. The spectra were collected between 500 and 2000 cm⁻¹, using the beam of a diode laser (780 nm), with the sample exposed to the air under ambient conditions. Reduction behavior was studied by temperature-programmed reduction (TPR). A sample of about 50 mg was introduced a flow of 10% H₂/N₂ gas mixture at a flow rate of 10 mL·min⁻¹. During TPR, the temperature was increased at 7°C·min⁻¹ from room temperature to 900°C.

2.3. Catalytic Activity Measurement. Catalytic activities of the prepared sample towards the SRE and OSRE reactions were tested in a fixed-bed flow reactor at atmospheric pressure. Catalyst in the amount of 100 mg was placed in a 4 mm i.d. quartz tubular reactor and held by glass-wool plugs. Before the reaction, the catalyst was activated by reduction with hydrogen at 300°C for 3 h. 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) for the SRE reaction; while the GHSV was maintained at 56,000 h⁻¹, the O₂/EtOH molar ratio was

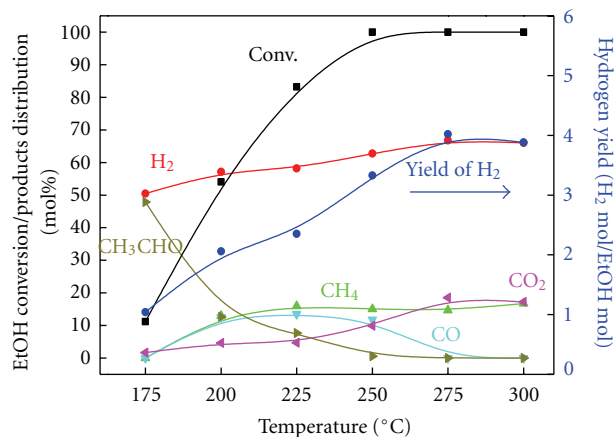


FIGURE 1: Catalytic performance in the SRE reaction over PtRuMg/ZrO₂ catalyst.

0.26, and the H₂O/EtOH molar ratio was 4.86 for the OSRE reaction. A 5 h time-on-stream tests were maintained at each measured temperature. The analysis of the reactants and all reaction products was carried out online by gas chromatography, with columns of Porapak Q and Molecular Sieve 5A for separation. The evaluation of the catalytic activity depended on the conversion, products distribution, and the yield of hydrogen:

$$X_{\text{EtOH}} = \frac{(n_{\text{EtOH-in}} - n_{\text{EtOH-out}})}{n_{\text{EtOH-in}}} \times 100\%,$$

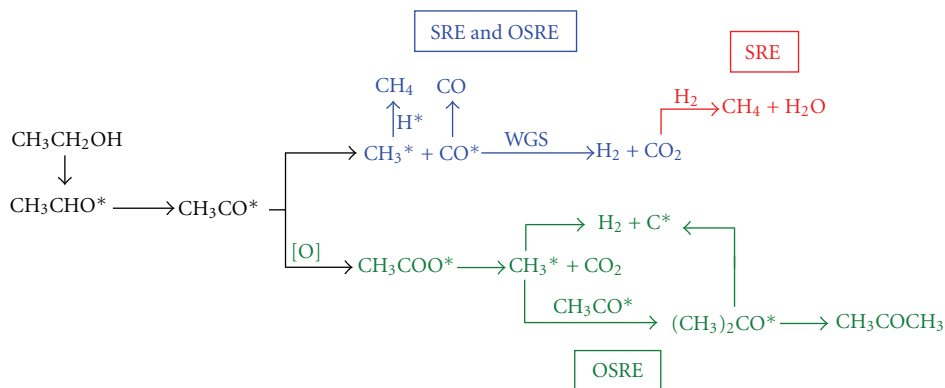
$$Y_{\text{H}_2} = \frac{n_{\text{H}_2\text{-out}}}{n_{\text{EtOH-in}}}, \quad (1)$$

$$S_i = \frac{nP_i}{n \sum P_i} \times 100\%,$$

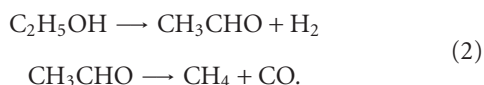
where X_{EtOH} is the conversion of ethanol, Y_{H_2} is the yield of hydrogen, S_i is the distribution of different products, P_i is the different products, and n is the amounts of moles.

3. Results and Discussion

3.1. Catalytic Evaluation. Figure 1 illustrates the X_{EtOH} , products distribution (water excluded), and Y_{H_2} from SRE with an H₂O/EtOH molar ratio of 13 over the PtRuMg/ZrO₂ catalyst between 175 and 300°C. About 1 h to reach the steady state and the recorded date was 5 h time-on-stream tests at each reaction temperature. The concentration of hydrogen increased progressively with increases in temperature (T_R). The detailed proposed pathway was shown in the Scheme 1. Below 200°C, the main product besides hydrogen was acetaldehyde, thus indicating that it behaved as a dehydrogenation of ethanol, and then acetaldehyde decomposition into methane and CO with increasing temperature. This indicated that both platinum and ruthenium had a stronger

SCHEME 1: Reaction routes of SRE and OSRE over PtRuMg/ZrO₂ catalyst.

capacity for breaking the C–C bond in the reforming of ethanol



At higher temperatures ($T_R > 225^\circ\text{C}$), concentrations of CO₂ up to 18% accompanied the decreasing of CO to 0.2%. At the same time, the concentration of methane through the decomposition of acetaldehyde was significant. This indicated that the water-gas shift (WGS) reaction occurred at a lower temperature than that of the cobalt oxide [12] and the PtRu/ZrO₂ catalyst [20]. This showed that the addition of magnesium improved the reforming activities and enhanced the WGS reaction at lower temperatures



When the T_R increased to 280°C, the amount of CH₄ side-product increased slightly to approach 16% and decreased the yield of hydrogen since the reversed water-gas shift reaction (RWGS) occurred. The maximum Y_{H_2} approached 4.0 around 275°C for the SRE reaction

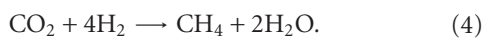
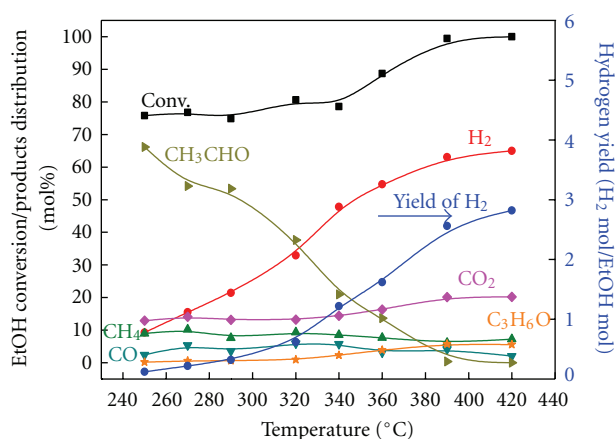


Figure 2 displays the X_{EtOH} , products distribution (water excluded), and Y_{H_2} from OSRE with an EtOH/H₂O/O₂ at a molar ratio of 1 : 4.86 : 0.26 over a PtRuMg/ZrO₂ catalyst between 250 and 420°C. As compared with the SRE reaction, there were significant differences in the different reactions. The SRE reaction preceded complete conversion of the ethanol at 250°C, while there was only 75% conversion at this temperature and full ethanol conversion exceeded 390°C for the OSRE reaction. The temperature for the decomposition of acetaldehyde (D_T) showed that the easy cracking promoted the formation of hydrogen. The D_T on the SRE reaction approached 200°C, and above 250°C for the OSRE reaction. The acetaldehyde disappeared at 275°C for the SRE reaction, and at 420°C for the OSRE reaction. A comparison of the temperature of WGS (T_{WGS}) showed that it was lower for the SRE reaction ($T_{\text{WGS}} \sim 250^\circ\text{C}$ for SRE, $\sim 340^\circ\text{C}$ for OSRE). The distribution of CO was

FIGURE 2: Catalytic performances in the OSRE reaction over PtRuMg/ZrO₂ catalyst.

minor for both reactions (<5% for OSRE, <0.5% for SRE). Besides the main products of H₂ and CO₂, the decreasing of acetaldehyde accompanied with the trace amounts of acetone was produced through the condensation of acetaldehyde (shown in the Scheme 1) at $T_R > 340^\circ\text{C}$. At a further temperature increase, the acetone was still detected. This clearly influenced the yield of hydrogen and also, possibly, the coke deposition. The maximum Y_{H_2} only approached 2.8 around 420°C for the OSRE reaction.

3.2. Characterization of Used Catalyst. The design of a stable and applicable catalyst is one of the most important issues in the production of hydrogen from ethanol. The significant deactivation reported for hydrogen production from ethanol reforming is usually attributed to carbon formation and sintering of active metals, which is strongly influenced by the nature of the support, catalyst, and reaction conditions (especially temperature and H₂O/EtOH/O₂ ratio) [9, 27–29]. In order to obtain more information about the behavior of the used catalyst, TEM, TG, Raman, and TPR characterizations were pursued for the samples after the SRE and OSRE catalytic tests.

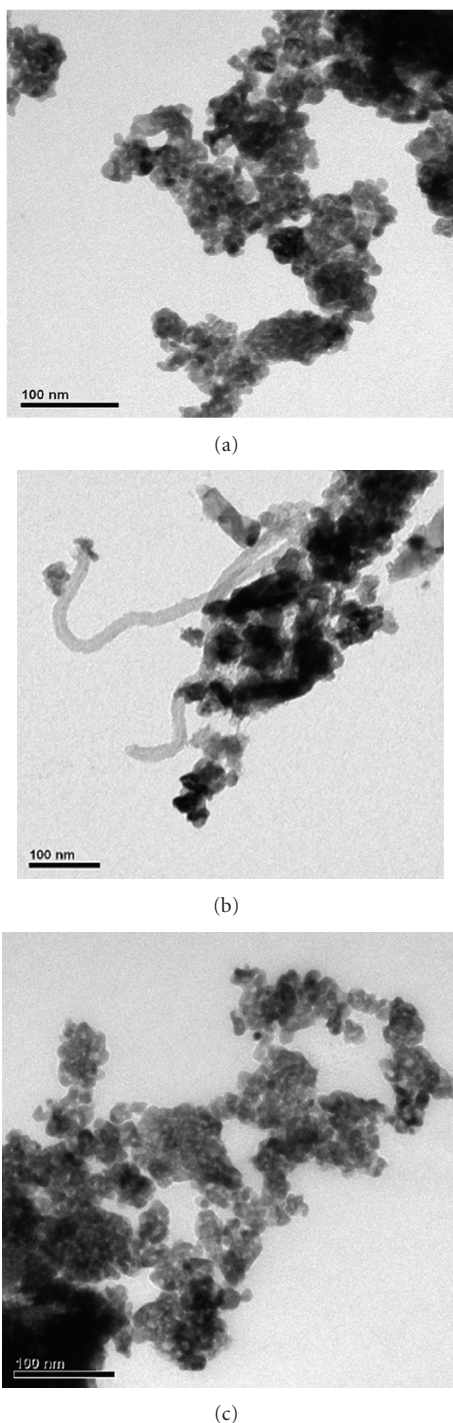


FIGURE 3: TEM images of fresh and used catalysts: (a) fresh, (b) after OSRE reaction, and (c) after SRE reaction.

Figure 3 shows the TEM micrographs of both fresh and used catalysts. A comparison with the fresh sample (see Figure 3(a)) showed an apparent deposition of coke on the used catalyst after the OSRE reaction (see Figure 3(b)). There was no obvious coke formation observed after the SRE reaction (see Figure 3(c)). The specific weight loss of combustion of

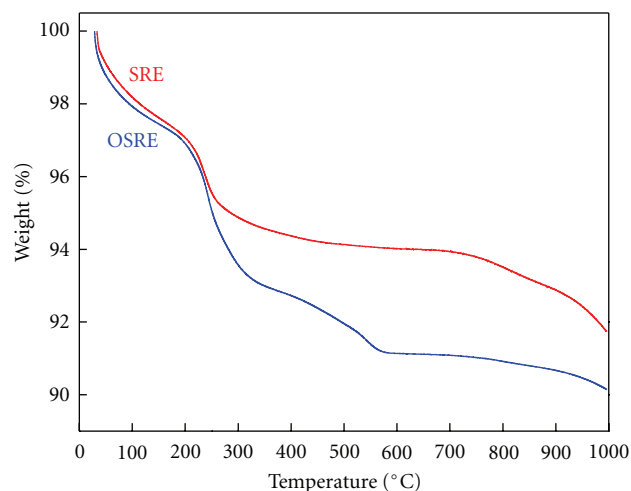
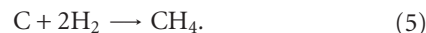


FIGURE 4: TG curves of used catalyst after SRE and OSRE reaction.

adsorbed C_1 species (200~300°C) and coke (400~600°C) on the catalyst surface was obtained from the TG results (see Figure 4). Since the addition of magnesium modified the catalyst becomes slightly base which may be adsorbed C_1 species after the reforming reaction. It was apparent that only after the OSRE reaction was the combustion of coke observed. Furthermore, the Raman spectra (see Figure 5) of the used catalyst after the SRE reaction differed from the OSRE reaction. There were two bands centered at 1320 (D-band) and 1590 (G-band) cm^{-1} , characteristic of poorly ordered carbon deposition [30], observed after the OSRE reaction but not after the SRE reaction. This result indicated that the coke formed through the OSRE reaction. Also, the evidence of coke formation can be demonstrated by the TPR analysis. Figure 6 shows the TPR profiles of the used catalyst after the SRE and OSRE reactions. Two reduction regions can be distinguished: one region for the adsorbed C_1 species (around 298°C) and the other region for coke (around 584°C), with the broad signal coming from the methanation of deposited carbon [8]



From the characterization of the used catalyst, we observed a more pronounced coke formation in the OSRE reaction and confirmed that the designed PtRuMg/ZrO₂ catalyst was a suitable application on the SRE reaction.

4. Conclusions

A novel and high performance PtRuMg/ZrO₂ catalyst had been designed and applied on the SRE and OSRE reaction to produce hydrogen at low temperature. The results showed that the distribution of CO was minor for both reactions (<5% for OSRE, <1% for SRE). The OSRE reaction required a higher temperature ($T_R \sim 390^\circ\text{C}$) to achieve 100% ethanol conversion than the SRE reaction ($T_R \sim 250^\circ\text{C}$). Also the temperature of WGS accompanying the OSRE reaction was higher ($T_{WGS} \sim 340^\circ\text{C}$) than that of the SRE reaction

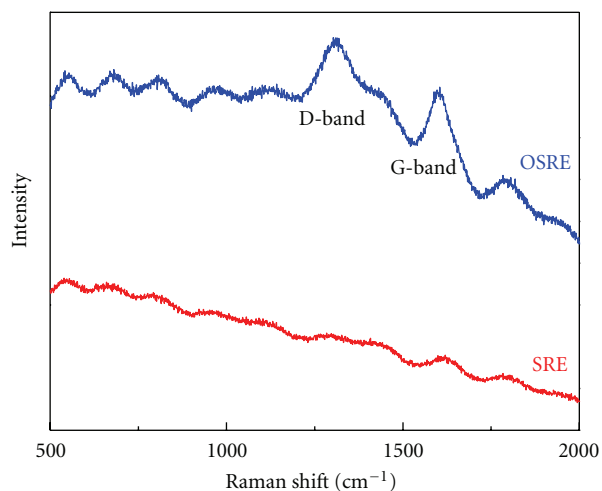


FIGURE 5: Raman spectra of used catalyst after SRE and OSRE reaction.

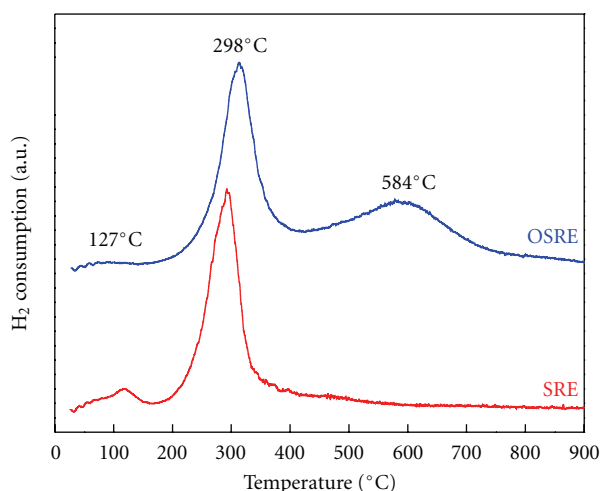


FIGURE 6: TPR profiles of used catalyst after SRE and OSRE reaction.

($T_{WGS} \sim 250^\circ\text{C}$). A more pronounced coke formation was observed in the OSRE reaction. In considering the catalytic stability against the coke deposition, application of PtRuMg/ZrO₂ catalyst on the SRE reaction is suitable.

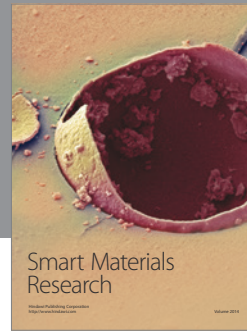
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