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摘要

19WHEC2012 會議是由加拿大氫能與燃料電池學會主辦，大會地點為多倫多喜來登中心，為燃料電池及氫能產業界最重要的國際會議之一。參加人員來自世界各地，包括加拿大、美國、韓國、德國、日本、中國、台灣、丹麥、希臘、法國和英國等多國之專家學者，此研討會投稿論文分口頭報告及壁報展示，共計 400 餘篇。在會議中聆聽各國學者之學術演講，其中以希臘學者 Verykios 針對低溫乙醇重組產氫反應之研究對我們的研究受益最大。大會所討論之範圍很廣，包含能源、燃料電池之創新科技及燃料電池之應用、教育及市場分析等。世界各國學者齊聚一堂討論不同領域的研究成果與應用。本次會議提供個相當好的知識交流平台，藉由此學術交流進而瞭解國際未來研究發展方向及趨勢，真是獲益匪淺。此外，藉由參與大會各國專家學者之交換研究心得及吸取他人寶貴之研究經驗，將可做為本實驗室日後研究之參考。

筆者此次感謝獲國科會研究計畫之補助成行，發表題目共計三篇：“Oxidative Steam Reforming of Ethanol over Nickel Oxides”，“Effect of Pretreatment Temperature of Microwave-assisted LaNiO_3 Perovskite catalyst on Steam Reforming of Ethanol for Hydrogen Production”，“Doping of Praseodymium to Modify $\text{Ce}_{0.5}\text{Co}_{0.5}\text{O}_2$ Catalyst to Use on the Steam Reforming of Ethanol”，達到與各國學者切磋交流的機會，並試乘了價值昂貴的氫能燃料電池汽車，真是獲益匪淺。

目次

	頁碼
壹、 會議目的.....	4
貳、 會議過程.....	4-5
參、 會議心得.....	6
肆、 建議事項.....	6

壹、會議目的

19WHEC2012 世界氫能會議(the 19th World Hydrogen Energy Conference)是由加拿大氫能與燃料電池學會主辦，為二年舉辦一次之國際學術會議，下一屆將由韓國主辦(20WHEC2014)。其會議宗旨在於結合世界各國有關氫能與燃料電池技術研究領域之學者專家，就專長領域進行一系列學術研究成果發表及新知討論，該學會歷年來所主辦之學術研究年會、研討會及專題討論會，皆對該學術領域有深遠的影響及貢獻。因此，藉由此學術交流進而瞭解國際未來研究發展方向及趨勢，並與各國專家學者交換研究心得及吸取他人寶貴之研究經驗，將可做為日後研究之參考。

貳、會議過程

(一)本會議屬於國際型研討會，參加人員為來自世界各國之民間機構、專家學者及研究人員參與為期五天之學術論文發表及討論會。19WHEC2012世界氫能會議是由加拿大氫能與燃料電池學會主辦，於2012年6月3日至6月7日在多倫多喜來登中心舉行。此為氫能與燃料電池領域非常重要的研討會之一，與會者多為各國在該領域學有專精之教授與學者，本次台灣參與之人員多達二十人(台大、國防大學、中央、成大、崑山、工研院等)以上。於此與各國學者相互交流之下獲益良多。

(二)本次研討會每天安排不同研討會議地點同時舉行不同議題發表，與會者可在會議期間自行選擇有興趣的場次參與研討過程，其研究領域與大會流程如后。

June 3, 2012: 1. Young scientist program

2. Hydrogen storage session

June 4, 2012: 1. Hydrogen production systems: Overview

2. Hydrogen from renewable electricity

3. SOFC and PEMFC applications

4. Automotive outlook and fueling protocols

5. Hydrogen distribution technologies

6. Biological hydrogen: Dark fermentation

June 5, 2012: 1. PEM electrolysis

2. Reforming gasification, fossil energy carriers
3. Metal hydrides
4. Demonstration projects and market introduction
5. High temperature electrolysis
6. Water management

June 6, 2012: 1. Thermochemical cycles and nuclear hydrogen

2. Chemical hydrides
3. High temperature PEMFC
4. Policy, perspectives and roadmaps
5. Off-grid power and smart grids
6. Porous transport layer

June 7, 2012: 1. Test methods for H₂ and FC

2. Education and public awareness
3. Complex hydrides
4. Direct fuel cells
5. Market trends and financing

參、會議心得

本研討會以氫能與燃料電池技術研究領域為主軸，會議是由加拿大氫能與燃料電池學會主辦，為該領域中相當重要之研討會。參加人員為世界各國之專家學者，此研討會投稿論文分口頭報告及壁報展示，共計400餘篇。大會所討論之範圍很廣，包含能源、燃料電池之創新科技及燃料電池之應用、教育及市場分析等。部份足以為我國所參考之依據，另相關論述主題亦十分具參考價值。

於研討會中，透過各國學者不同領域的經驗，於問答間各取所需，達到智識精進功效，並積極與各國學者交換演講意見達到學術交流目的。經過此次研討會歷練，使本人對未來之研究更具信心，將持續於此領域探討研析，並且對於後續之研究將會

秉持精益求精的精神戮力完成。本次會議提供個相當好的知識交流平台，藉由此學術交流進而瞭解國際未來研究發展方向及趨勢，真是獲益匪淺。

肆、建議事項

本研討會歷年與會人員及論文發表數目眾多，探討範圍亦相當廣泛，值得相關研究人員與學者參與。建議未來增加國內專家學者參與機會，藉以吸收國際新知並分享研究成果。很可惜，我的二位學生及一位台大共同指導的一位學生這次都未獲得國科會的補助，希望未來能在補助的員額及經費予以提高，鼓勵學生積極參與國際會議，相信對國內各方面研究及學術工作的提昇，必定有所助益。願以此次的與會心得與大家分享共勉之，本次研討會攜回會議論文集資料。



作者發表之論文

**Doping of Praseodymium to Modify $Ce_{0.5}Co_{0.5}O_2$ Catalyst
to Use on the Steam Reforming of Ethanol**

**Doping of Praseodymium to Modify Ce_{0.5}Co_{0.5}O₂ Catalyst
to Use on the Steam Reforming of Ethanol**

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Abstract

Doping of Pr (5 and 10% loading) on Ce_{0.5}Co_{0.5}O₂ catalyst (assigned as Pr₅-Ce-Co and Pr₁₀-Ce-Co), used for steam reforming of ethanol (SRE), was prepared by incipient wetness impregnation method. The topic focused on the effect of the reduction pretreatment under 250 and 400 °C (assigned as H250 and H400). All samples were characterized by XRD, TPR and TEM. Catalytic performance of SRE was tested from 250 to 500 °C in a fixed-bed reactor. In the preliminary test, we found that the activity can be enhanced on increasing the content of Pr. Also, the reduction pretreatment can influence the distribution of products, i.e. the byproduct of acetone is higher than 30 % under H250, while, the CO byproduct is lower than 2 % under H400. According to the results, we suggested that the Pr₁₀-Ce-Co-H400 sample is a preferential SRE catalyst. The products varied with the increasing of reaction temperature, i.e. the acetaldehyde is oxidized to acetate and then, decomposes into CO₂ and methyl group. Further, the steam reforming of methyl and water gas shift reaction accompany as the temperature exceeds 375 °C. The hydrogen distribution approached 73% at 475 °C.

Keywords: Steam reforming of ethanol; Hydrogen production; Ce_{0.5}Co_{0.5}O₂.

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1. Introduction

The current shortage of global energy and stringent emission regulations has stimulated interest in renewable energies. Fuel cells have been investigated as possible devices for conversion of chemical energy into electrical energy via the hydrogen and oxygen fuels. It provides clean and highly efficient electric power for both mobile and stationary applications [1]. Using of hydrogen as an energy carrier can sustain economic growth as well as reduce pollution and greenhouse gas emissions. From the renewable point, the use of ethanol is preferred because it can obtain from biomass that offers high hydrogen content, non-toxicity, safe storage and easy handling [2]. Production of hydrogen from the steam reforming of ethanol (SRE) reaction could favor the use of hydrogen as an alternative fuel, improving the difficulties of on-board hydrogen storage and distribution. Moreover, a high yield of hydrogen can be obtained from the SRE reaction [3–5]:



In spite of reportedly high activity and selectivity, Co-based catalysts are not immune to the problem of deactivation [3, 6-11]. However, cobalt is low-cost and can be instead of the noble metals to study on the SRE reaction. Noble metal-supported catalysts have exhibited catalytic ability in SRE reaction. Ceria (CeO_2), in particular, has been widely used in SRE reaction, results in a high reducibility and an oxygen storage-release capacity. So, the gasification of the deposited carbon can be easily removed, preventing the deactivation of catalysts on steam condition [12]. The ceria-supported catalyst also promotes the water gas shift (WGS) reaction which leads to a low CO production and a high H_2 yield [13]. Moreover, ceria improves the dispersion of active phase and formation of solid solution [14]. Ceria-supported Pt, Ir and Co catalysts have been shown a significant activity over the SRE reaction [12, 15-20].

The doping of Pr into the ceria lattice can enhance the redox property of the oxide

support by creating more surface oxygen vacancies [21]. Pr-doping remarkably promoted the oxygen storage capacity (OSC) of ceria by facilitating the mobility of the surface oxygen species [22, 23]. Praseodymium and cerium have many similar characteristics; the addition of Pr can depress the deactivation by the deposited carbon and decreases the CO production [24]. In this work, we aimed to prepare the Pr-Ce-Co catalysts by incipient wetness impregnation method to compare the effect of Pr on the SRE reaction.

2. Experimental

2.1. Catalyst preparation

The cobalt-cerium composite oxide, with 1:1 molar ratio was prepared by co-precipitation-oxidation (CPO) method. Initially, a stoichiometric aqueous solution of cobalt nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Showa] and cerium nitrate [$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Showa] was mixed and stirred while a 6.4 M NaOH solution was added dropwisely to obtain precipitation. Then, a H_2O_2 solution was added drop-by-drop to oxidize the precipitant. The obtained suspension was filtered and washed seven times with DI water. Finally, it was dried at 110 °C overnight. Meanwhile, the as-prepared sample was further calcined at 500 °C for 2 h (assigned as Ce-Co).

The Pr-Ce-Co catalysts were prepared by wet impregnation method. Different Pr amounts (5 and 10% loading) from an aqueous solution of $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were prepared. The obtained samples were dried at 110 °C for overnight and finally, calcined in air at 500 °C for 3 h. The as-prepared catalysts were named as $\text{Pr}_5\text{-Ce-Co}$ and $\text{Pr}_{10}\text{-Ce-Co}$, being an indicative number of nominal Pr loading.

2.2. Characterization of catalyst

The BET surface area of the samples was measured using a Micromeritics ASAP 2012 analyzer by nitrogen adsorption at the boiling temperature of liquid nitrogen. XRD

measurement was performed using a MAC Science MXP18 diffractometer with Cu K1 radiation ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 30 mA. Physical characterization of series Pr-Ce-Co catalysts was list in the Table 1. The reduction behavior of the Pr-Ce-Co catalysts was studied by temperature programmed reduction (TPR). About 50mg of the sample was heated in a flow of 10% H₂/N₂ gas at a flow rate of 10 ml·min⁻¹. During TPR, the temperature increased at a rate of 7 °C·min⁻¹ from room temperature to 900 °C.

2.3. Evaluation of catalytic activity

The catalytic activities of the composite oxides towards the SRE reaction were performed at atmospheric pressure in a fixed-bed flow reactor. Catalyst in the amount of 100 mg was placed in a 4 mm i.d. quartz tubular reactor and held by glass-wool plugs. The feed of the reactants comprised a gaseous mixture of ethanol (EtOH), H₂O and Ar. The composition of the reactant mixture (H₂O/EtOH/Ar = 37/3/60 vol.%) was controlled by an Ar stream flow (22 ml min⁻¹) through the saturator (maintained at 130°C) containing EtOH and H₂O. The gas hourly space velocity (GHSV) was maintained at 22,000 h⁻¹ and the H₂O/EtOH molar ratio was 13. Prior to the reaction, the sample was activated by reduction with hydrogen at 250 and 400 °C for 3 h (assigned H250 and H400). The SRE activity was tested stepwise by increasing the temperature from 250 to 500 °C. The analysis of the reactants and all the reaction products was carried out online by gas chromatography with columns of Porapak Q and Molecular Sieve 5A to separate.

3. Results and discussion

Fig. 1 shows the TPR profiles of series Pr-Ce-Co catalysts. The Ce-Co sample presents three reduction peaks around 313 (T_{r1}), 375 (T_{r2}) and 487 °C (T_{r3}). According to our previous study and literature reports [12, 25], these peaks can be assigned as the reduction of: continuous reductive cobalt oxides, Co₃O₄ (T_{r1}), CoO (T_{r2}) and surface CeO₂

(T_{r3}) as shown in the following equations. The reduction peak of Ce-Co is similar with both Pr₅-Ce-Co and Pr₁₀-Ce-Co samples. The reduction temperature increases with the Pr content. The doped Pr can increase thermal stability, so we can observe the reduction signal shift to high temperature.



Fig. 2 shows the XRD patterns of series Pr-Ce-Co catalysts. The diffraction patterns (111), (200), (220) and (311) of Pr-Ce-Co samples match the JCPDS 89-8436 identifying cerium oxide, CeO₂ with cubic structure. Comparison the (111) diffraction patterns of Pr₅-Ce-Co and Pr₁₀-Ce-Co with Ce-Co sample, the peak shifts slightly toward low angle. Also, the signal of Pr and/or PrO_x does not observe in Pr₅-Ce-Co and Pr₁₀-Ce-Co samples. This indicates that the doped Pr incorporates into the ceria lattice [24, 26]. The particle size of CeO₂ in the Ce-Co, Pr₅-Ce-Co and Pr₁₀-Ce-Co catalysts calculated by the Debye-Scherrer formula according to the (111) diffraction peak of CeO₂ was 5.7, 6.2 and 6.9 nm, respectively. The intensity of diffraction patterns of Co₃O₄ decreases with Pr loading. The calculated particle size become small (from 5.81 nm to 4.39 nm) indicates that the doped Pr can increase the dispersion.

Fig. 3 shows the ethanol conversion as well as the distribution of products at different reaction temperature over the Pr₁₀-Ce-Co-H250 catalyst. Ethanol is totally converted at 375 °C. Except the main products of H₂ and CO₂, other byproduct of acetone approaches 40% at this temperature. Only minor C₂ (CH₃CHO) and C₁ (CH₄ and CO) species observes at temperature below 400 °C. Concentration of acetone increases with the temperature, then, decreases as the temperature exceeds 425 °C. At this temperature region, the concentration of H₂ and CO₂ increases rapidly and that of acetone decreases abruptly since the steam reforming of acetone is thermodynamically feasible under high temperature [27]. According to the products distribution, the dehydrogenation of ethanol

to form acetaldehyde then dehydrogenation into acetyl [Eq. (4)] and/or oxidizes to the acetate [Eq. (5)] intermediates which is the main reaction of SRE initially. As the temperature increases, C–C bond breaking occurs to form methyl group and carbon oxide (CO or CO₂) [Eq. (6), (7)]. Further formation of the acetone byproduct comes from the combination of acetyl and methyl group intermediates [Eq. (8)]. Then, steam reforming of acetone [Eq. (9)] accompanied with the increase of temperature to increase the concentration of H₂ and CO₂. In the same time, the amount of CO also increases since the unfavorable direct decomposition of ethanol [Eq. (10)] occurred that caused the slightly low of hydrogen and produced a great amount of CO.

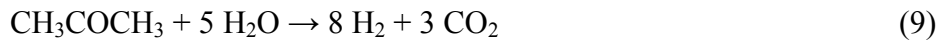


Fig. 4 compares the effect of doped Pr on the SRE conversion and products distribution over the Pr₁₀-Ce-Co-H250 sample. Since the doped Pr could enhance the thermal stability of Ce-Co sample, the temperature of complete ethanol conversion approached to high temperature [Fig. 4(a)]. The temperature for hydrogen distribution is high for the doped Pr samples. The direct decomposition of ethanol reaction accompanied for the H250 pretreatment at high temperature that increased the concentration of CO. Under this pretreatment, the hydrogen distribution only approached 65% [Fig. 4(b)]. Also, amounts of acetone byproduct [Fig. 4(c)] obtained under the same pretreatment which might be considered as the influence of residue ion under low temperature reduction. The doped Pr with Pr(NO₃)₃·6H₂O precursor was difficult reduced under 250 °C. The doped

Pr samples did not find CO at low temperature while increased 4% as temperature exceeded 400 °C.

Fig. 5 shows the ethanol conversion as well as the distribution of products at different reaction temperature over the Pr₁₀-Ce-Co-H400 catalyst. Apparently, under high temperature pretreatment (H400), no influence of residue ion derived better activity and products distribution. The main products were acetaldehyde and hydrogen at low temperature, while, main products were H₂ and CO₂. Only minor amounts of acetone (< 2%), CO (< 2%) and CH₄ (< 2%) were obtained. So, the hydrogen distribution approached 72%. Comparison the activity with the pretreatment condition, only 20% conversion arrived for H250 at 300 °C and 55% conversion for H400. In the same, totally converted at 375 °C for H250 and 350 °C for H400. According to the products distribution, the equations of (4) and (6) were the main reaction on the SRE. Since the distribution of CO and CH₄ was lower, further water gas shift reaction (WGS), consecutive dehydrogenation of methyl and oxidation of carbon might be occurred.



Fig. 6 compares the effect of doped Pr on the SRE conversion and products distribution over the Pr₁₀-Ce-Co-H400 sample. Apparently, the doped Pr samples needed higher temperature to convert ethanol [Fig. 6(a)]. Since no influence of residue ion derived the hydrogen distribution approaching 70% as the ethanol complete conversion for all samples [Fig. 6(b)]. Comparison the acetone distribution for H400 with the H250, apparent drop from 40% into lower than 10%, especially for the Pr₁₀-Ce-Co-H400 sample only attained 2% [Fig. 6(c)]. Also, only minor amounts of CO (< 2%) obtained for all samples. According to these results demonstrated that under high temperature pretreatment, no influence of residue ion derived better activity and products distribution.

4. Conclusions

The preliminary results showed that the influence of the residue ion on the sample was key point. The H400 samples had the better catalytic activity and products distribution than the H250 samples, i.e. the byproduct of acetone is higher than 30 % under H250, while, the CO byproduct is lower than 2 % under H400. The doped Pr enhanced the thermal stability and reduced the coke deposition. The Pr₁₀-Ce-Co-H400 sample shows the best catalytic performance with the less selectivity of acetone and CO.

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Figure captions

1. TPR profiles of (a) Ce-Co (b) Pr₅-Ce-Co (c) Pr₁₀-Ce-Co.
2. XRD patterns of (a) Ce-Co (b) Pr₅-Ce-Co (c) Pr₁₀-Ce-Co.
3. Catalytic performance in the SRE reaction over Pr₁₀-Ce-Co-H250 catalyst under H₂O/EtOH = 13 and GHSV = 22,000 h⁻¹.
4. Ethanol conversion and products distribution for SRE reaction over series Pr-Ce-Co-H250 catalysts: (a) ethanol conversion (b) H₂ distribution (c) C₃H₆O distribution (d) CO distribution.
5. Catalytic performance in the SRE reaction over Pr₁₀-Ce-Co-H400 catalyst under H₂O/EtOH = 13 and GHSV = 22,000 h⁻¹.
6. Ethanol conversion and products distribution for SRE reaction over series Pr-Ce-Co-H400 catalysts: (a) ethanol conversion (b) H₂ distribution (c) C₃H₆O distribution (d) CO distribution.
7. TGA analysis of series Pr-Ce-Co-H400 catalysts after the SRE reaction.

Table caption

Physical characterization of series Pr-Ce-Co catalysts.

Table 1 Physical characterization of series Pr-Ce-Co catalysts.

Sample	ICP (%)			Surface area (m ² /g)	Partical size (nm)	
	Pr	Co	Ce		Co ₃ O ₄ *	CeO ₂ **
Ce-Co				85	11.7	5.7
Pr ₅ -Ce-Co	3.54	23.1	43.5	80	9.3	6.2
Pr ₁₀ -Ce-Co	7.07	20.5	40.0	79	7.7	6.9

*Calculated from the (311) plane. **Calculated from the (111) plane.

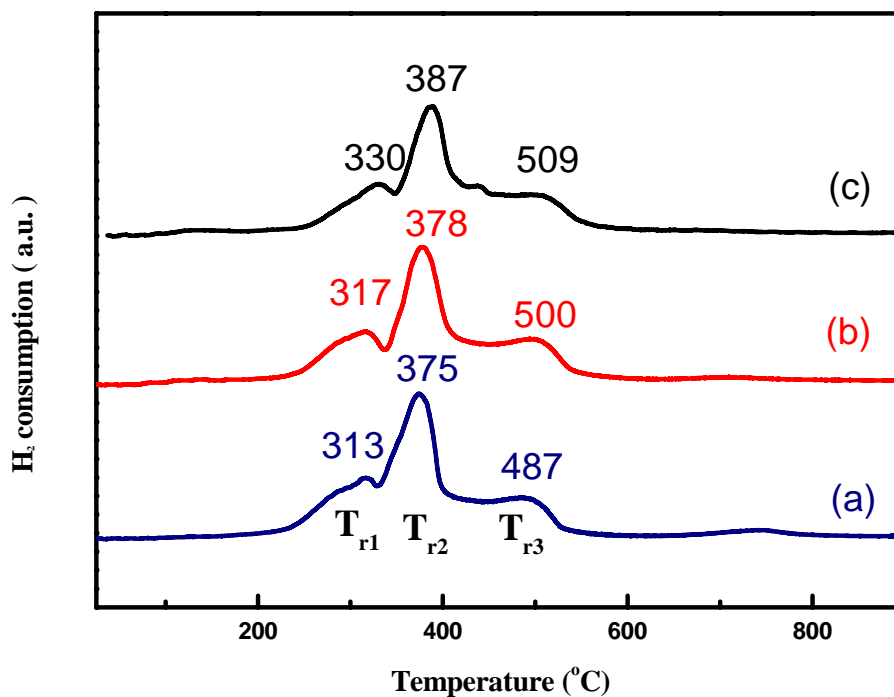


Fig1

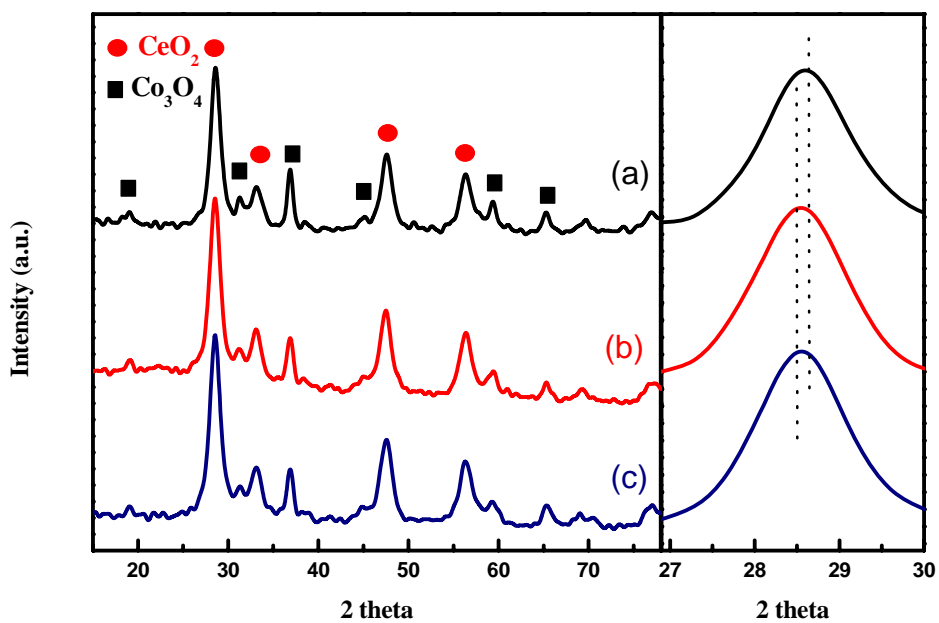


Fig2

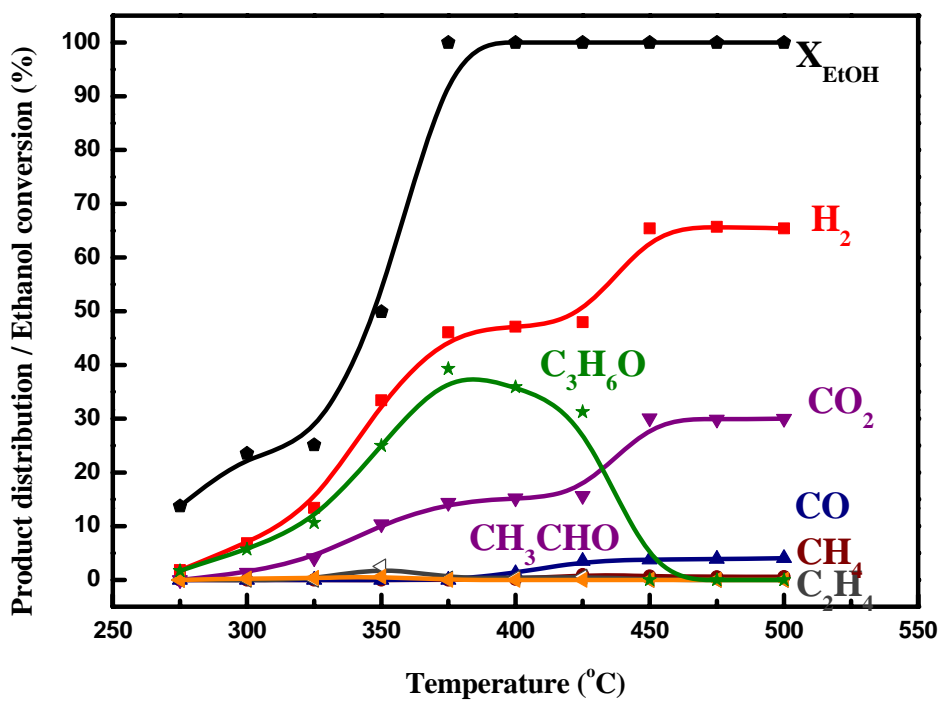


Fig3

Fig4

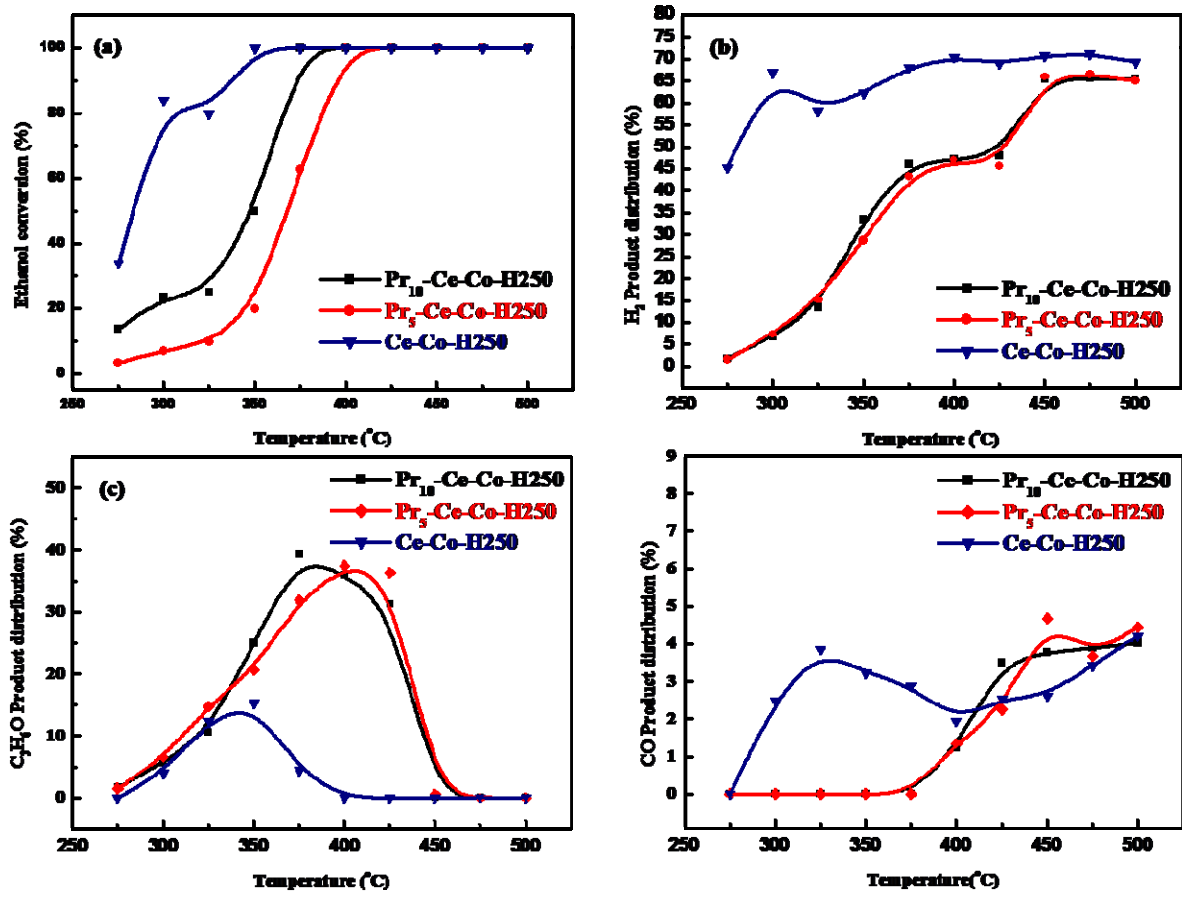


Fig5

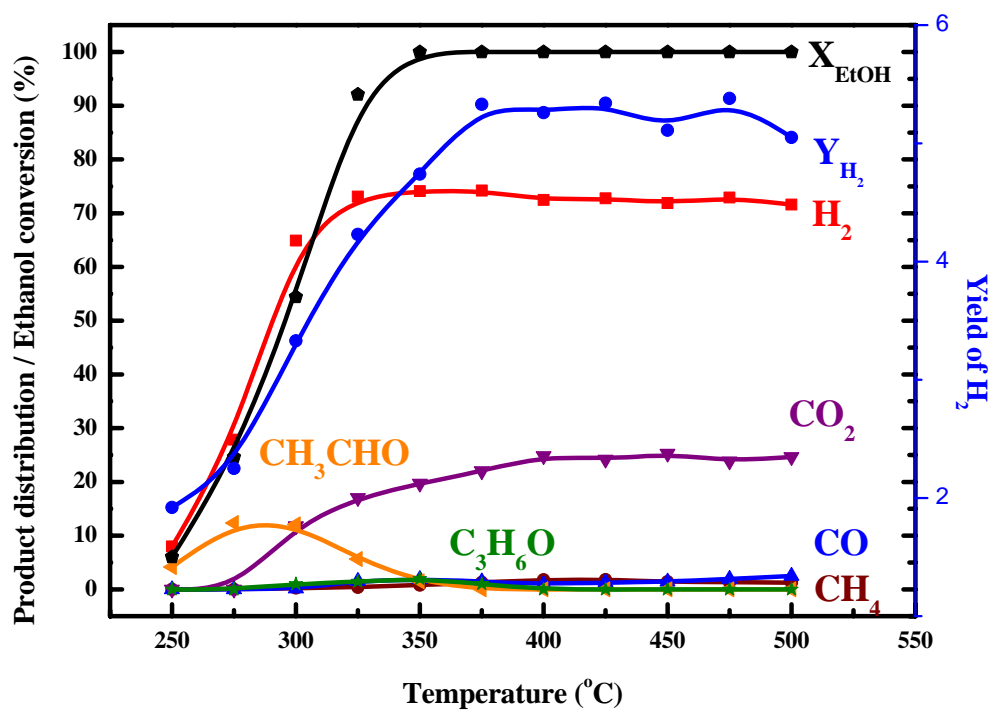


Fig6

