

出國報告（出國類別：開會）

PtRuMg/ZrO₂觸媒上乙醇重組製氫之 研究

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摘要

第六屆東京催化(TOCAT6)及第五屆亞太區觸媒(APCAT5)研討會合併舉行，由日本催化學會延續過去秉持之精神，負責這次會議之籌備工作，於2010年7月18-23在日本札幌會議中心舉行。據大會統計，共計發表之論文約1000篇。本次會議為緊密聯繫業界與學界之間之橋樑，並鼓勵年輕學者投入催化領之研究，特將主題分為三大區塊：General, Industrial and Youth sessions，內容涵蓋基礎催化、綠色化學、能源及環境催化、均相及異相催化、生物奈米科技及潔淨科技、石油煉製及精緻化學品、燃料電池之創新科技等，提供全世界相關領域學者們一個溝通互相觀摩學習最好的機會，會議籌備頗為週延詳盡，有規模的組織與現代化，使大會不但顯得蓬勃人氣旺盛，熱鬧非凡，同時也給對跨組內容感興趣參與者很多方便。其中台灣地區則有包括台灣大學、清華大學、長庚大學、元智大學、中央研究院、國防大學等許多單位參與，師、生共計24員。在會議中聆聽各國學者之學術演講，其中Pirez學者針對 $CeNi_xO_y$ 觸媒進行乙醇重組反應製氫之研究與我們的領域相近，對我們的啟發及受益最大。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，其發表題目為“Reforming of Ethanol to Produce Hydrogen over PtRuMg/ZrO₂ Catalyst”，達到與各國學者切磋交流的機會，真是獲益匪淺。

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壹、會議目的

第六屆東京催化(TOCAT6)及第五屆亞太區觸媒(APCAT5)合併之會議，是由日本催化學會(Catalysis Society of Japan)主辦，為該國重要之國際學術會議，其會議宗旨在於結合世界各國有關化學工程和應用、環境科學和開發、催化應用、石化工業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工業界、專家學者及研究人員參與為期六天之學術論文發表及討論會。第六屆東京催化(TOCAT6)及第五屆亞太區觸媒(APCAT5)合併之會議，是由日本催化學會(Catalysis Society of Japan)主辦，於2010年7月18日至7月23日在日本札幌國際會議中心舉行。大會所討論之範圍很廣，包含基礎催化、綠色化學、能源及環境催化、均相及異相催化、生物奈米科技及潔淨科技、石油煉製及精緻化學品、燃料電池之創新科技等，與會者多為各國在該領域學有專精之工程師、技術研發人員、教授與學者，於研討會期間與各國學者相互密切交流之下獲益良多。

(二)會議行程之安排為白天都是口頭報告的部分，晚上則是海報展示部分。為能使發表壁報論文的學者或研究生有機會與其他學者們面對面討論他們的研究工作，大會安排一個時段作為"壁報論文討論時間"，而發表論文學者站在壁報旁邊，詳細解說討論與互換研究心得，效果非常好。

(三)本口頭報告的部分每天安排於不同研討會議地點同時舉行不同領域之議題發表，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，其研究領域如后。

1. New concepts and advanced materials for catalysis
2. Catalysis for green/sustainable chemistry

3. Catalysis in energy conversion and environmental protection
4. Petroleum refining and petrochemicals
5. Reactor designed on the engineering
6. Biocatalysis and photocatalysis
7. Application of fuel cell
8. Developed and/or commercialized industrial catalysts and processes

(四)本次會議為亞洲區相當大的會議，參與國家有台灣、日本、韓國、澳洲、伊朗、泰國、新加坡、英國、美國、挪威、美國、德國、菲律賓、馬來西亞等，中國政府方面也是相當重視，參與人數超過 50 員。會議請來相當多的催化領域的學者開幕致詞，也邀請來許多國際知名的期刊主編，針對目前發展方面來做一個整體的剖析，即將面臨的挑戰以及基礎研究最應該重視的部份。此次會議筆者及學生也以海報發表五篇論文「Reforming of Ethanol to Produce Hydrogen over PtRuMg/ZrO₂ Catalyst」、「Influence of Crystalline of Zirconia on the CoO_x-ZrO₂ Composite Oxide for the Steam Reforming of Ethanol」、「Ultrasonic-Assisted Fabrication of LaNiO_x Composite Oxide Nanotubes and Application to the Steam Reforming of Ethanol」、「Effect of Surface Area of Zinc Oxide on the Steam Reforming of Ethanol over Pt/ZnO Catalysts」及「Oxidative Steam Reforming of Ethanol over PtRu(Na, Mg)/ZrO₂ Catalysts」，在發表過程中有多位學者對我們的研究感到相當有興趣，並發進行雙方問答交流，使筆者及筆者的學生得到相當多的啟發及經驗的交流。

參、會議心得

本研討會結合了七個領域的國際會議：基礎催化、綠色化學、能源及環境催化、均相及異相催化、生物奈米科技及潔淨科技、石油煉製及精緻化學品、燃料電池之創新科技，會議是由日本催化學會(Catalysis Society of Japan)主辦，為該國重要之國際學術會議。參加人員為世界各國之專家學者，據大會統計，共計發表之論文約1000篇(包含口頭報告及海報展示)。大會所討論之範圍很廣，包含環境與經濟問題、綠色能源、潔淨技術、燃料電池之創新科技及燃料電池之應用等。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，值得相關領域之研究人員與學者參與。除藉此與各國與會之專家學者交換研究心得外，也可吸取很多寶貴經驗與靈感。在此筆者有感於研究技術日新月異，應多與各國之研究學者專家交流，才能以獲裨益。願以此次的與會心得與大家分享共勉之。

本次研討會除攜回會議論文資料與會議議程表，並搜集展示場展示內容之相關資料。

筆者發表之論文

「Reforming of Ethanol to Produce Hydrogen over PtRuMg/ZrO₂ Catalyst」

Reforming of Ethanol to Produce Hydrogen over PtRuMg/ZrO₂ Catalyst

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Abstract

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 are concentrated on for TEM, TG, Raman and TPR characterization. The results show that the OSRE reaction requires a higher temperature ($T_R \sim 390$ °C) to achieve 100% ethanol conversion than the SRE reaction ($T_R \sim 250$ °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 ($T_{WGS} \sim 250$ °C for SRE, ~ 340 °C for OSRE).

Keywords: Steam reforming of ethanol (SRE), Oxidative steam reforming of ethanol (OSRE), Hydrogen production

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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]. Moreover, a high yield of hydrogen can be obtained from the steam reforming of ethanol (SRE) [4-14].

The nature of the metal and its support strongly affect both stability and products distribution [5, 15]. In general, transition metals have shown a good level of activity and selectivity for the SRE reaction. The main problem found when using these catalysts is deactivation by sintering and carbon deposition [16-18]. 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, 16, 19, 20].

This study focused on the design of an ethanol reforming catalyst to produce hydrogen at a temperature lower than 300 °C with higher ethanol conversion (C_{EtOH}), hydrogen yield (Y_{H_2}) and lower CO distribution. The expectation was 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 catalysts.

2.2 Catalyst characterization

Transmission electron micrographs (TEM) 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 ($\text{H}_2\text{O}:\text{EtOH} = 80:20$ by volume) for the SRE reaction; while the GHSV was maintained at $56,000 \text{ h}^{-1}$, the O_2/EtOH molar ratio was 0.26 and the $\text{H}_2\text{O}/\text{EtOH}$ molar ratio was 4.86 for the OSRE reaction. 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 of ethanol (C_{EtOH}), the distribution of products (mol %) and the yield of hydrogen (Y_{H_2}).

3. Results and discussion

3.1 Catalytic evaluation

Figure 1 illustrates the C_{EtOH} , products distribution (water excluded) and Y_{H_2} from SRE with a $\text{H}_2\text{O}/\text{EtOH}$ molar ratio of 13 over the PtRuMg/ ZrO_2 catalyst between 175 and 300 °C. The concentration of hydrogen increased progressively with increases in temperature (T_{R}). 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 capacity for breaking the C–C bond in the reforming of ethanol.



At higher temperatures ($T_{\text{R}} > 250 \text{ °C}$), concentrations of CO_2 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/ ZrO_2 catalyst [21]. 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 250 °C, the amount of CH_4 side-product approached 16% and decreased the yield of hydrogen. The maximum Y_{H_2} approached 4.0 around 275 °C for the SRE reaction.

Figure 2 displays the C_{EtOH} , products distribution (water excluded) and Y_{H_2} from OSRE with a $\text{EtOH}/\text{H}_2\text{O}/\text{O}_2$ at a molar ratio of 1:4.86:0.26 over a $\text{PtRuMg}/\text{ZrO}_2$ catalyst between 250 and 420 °C. As compared with the SRE reaction, there were significant differences in the catalyst activity due to the different reactions. The SRE reaction had better activity which preceded complete conversion of the ethanol at 250 °C, while there was only 75% conversion at this temperature and then only full ethanol conversion above 390 °C for the OSRE reaction. A comparison of 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 ($T_{\text{WGS}} \sim 250$ °C for SRE, ~ 340 °C for OSRE). The distribution of CO was minor for both reactions ($< 5\%$ for OSRE, $< 0.5\%$ for SRE). Besides the main products of H_2 and CO_2 , with the decreasing of acetaldehyde, trace amounts of acetone were produced through the condensation of acetaldehyde at $T_R > 340$ °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, 22-24]. 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 shows the TEM micrographs of both fresh and used catalysts. A comparison with the fresh sample [see Fig. 3(A)] showed an apparent deposition of coke on the used catalyst after the OSRE reaction [see Fig. 3(B)]. There was no obvious coke formation observed after the SRE reaction [see Fig. 3(C)]. The specific weight loss of combustion of adsorbed C₁ species (200 ~ 300 °C) and coke (400 ~ 600 °C) on the catalyst surface was obtained from the TG results (see Fig. 4). Since the addition of magnesium modified the catalyst becomes slightly base which may be adsorbed C₁ 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 Fig. 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 [25], observed after the OSRE reaction but not after the SRE reaction. This result indicated that the coke formed through the OSRE reaction. Evidence of coke formation was also demonstrated by TPR. 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 C₁ 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 preferable for the SRE reaction.

4. Conclusions

A novel catalyst, PtRuMg/ZrO₂, used in the reforming of ethanol was designed and evaluated on its OSRE and SRE reactions. The results showed that the addition of magnesium improved the reforming activities and enhanced the WGS reaction at a lower temperature in both reforming reactions to produce H₂ and CO₂. The distribution of CO was minor for both reactions (< 5% for OSRE, < 1% for SRE). The OSRE reaction required a higher temperature ($T_R \sim 390$ °C) to achieve 100% ethanol conversion than the SRE reaction ($T_R \sim 250$ °C). Also, the temperature of WGS accompanying the OSRE reaction was higher ($T_{WGS} \sim 340$ °C) than that of the SRE reaction ($T_{WGS} \sim 250$ °C). A more pronounced coke formation was observed in the OSRE reaction and, through this study, it was confirmed that the PtRuMg₁/ZrO₂ catalyst is preferable for the SRE reaction.

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Figure Captions

1. Catalytic performance in the SRE reaction over PtRuMg/ZrO₂ catalyst.
2. Catalytic performances in the OSRE reaction over PtRuMg/ZrO₂ catalyst.
3. TEM images of fresh and used catalysts: (A) fresh (B) after OSRE reaction (C) after SRE reaction.
4. TG curves of used catalyst after SRE and OSRE reaction.
5. Raman spectra of used catalyst after SRE and OSRE reaction.
6. TPR profiles of used catalyst after SRE and OSRE reaction.

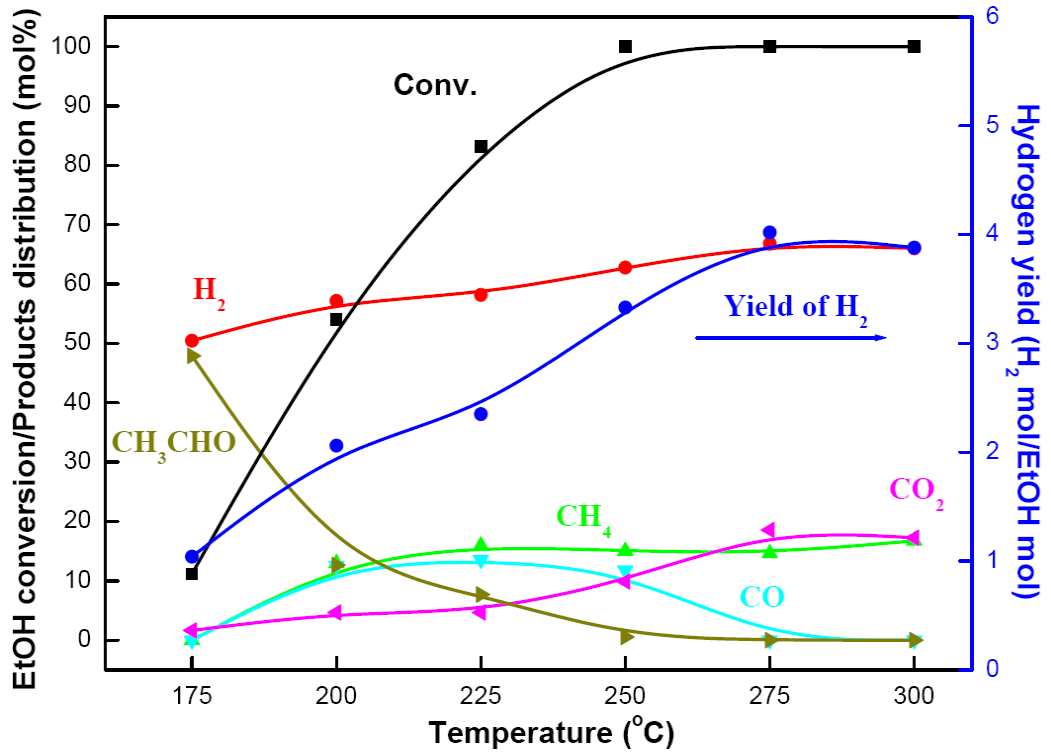


Fig. 1

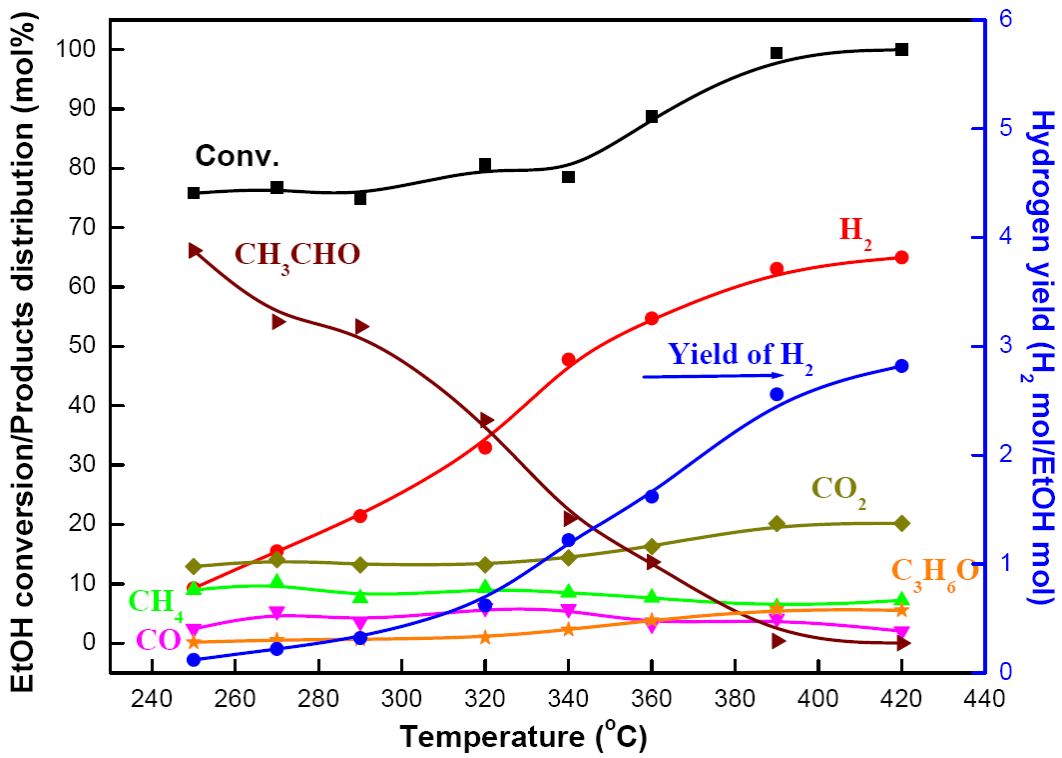


Fig. 2

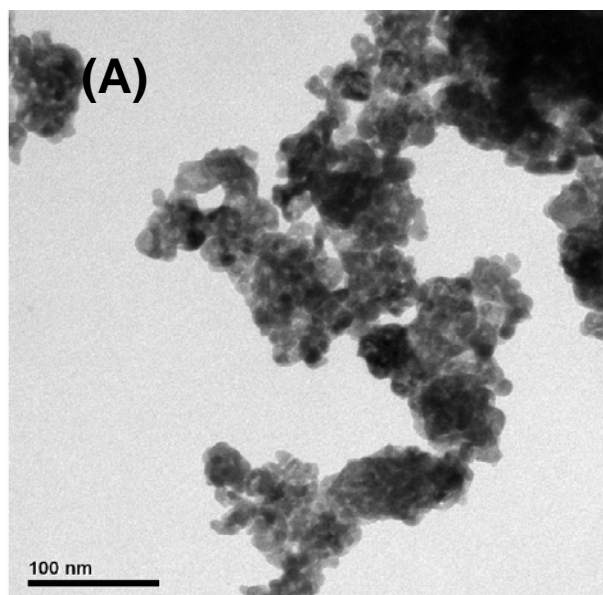


Fig. 3(A)

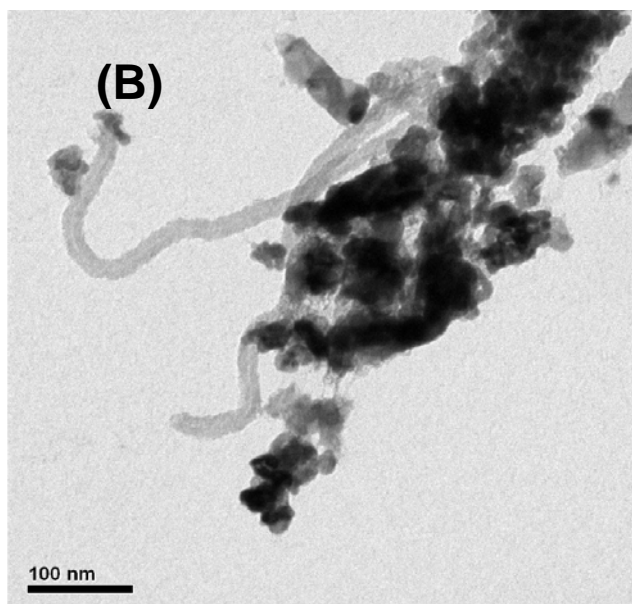


Fig. 3(B)

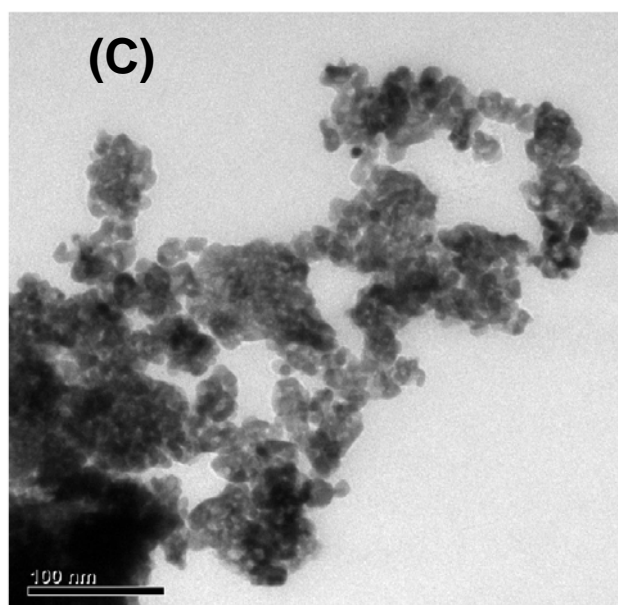


Fig. 3(C)

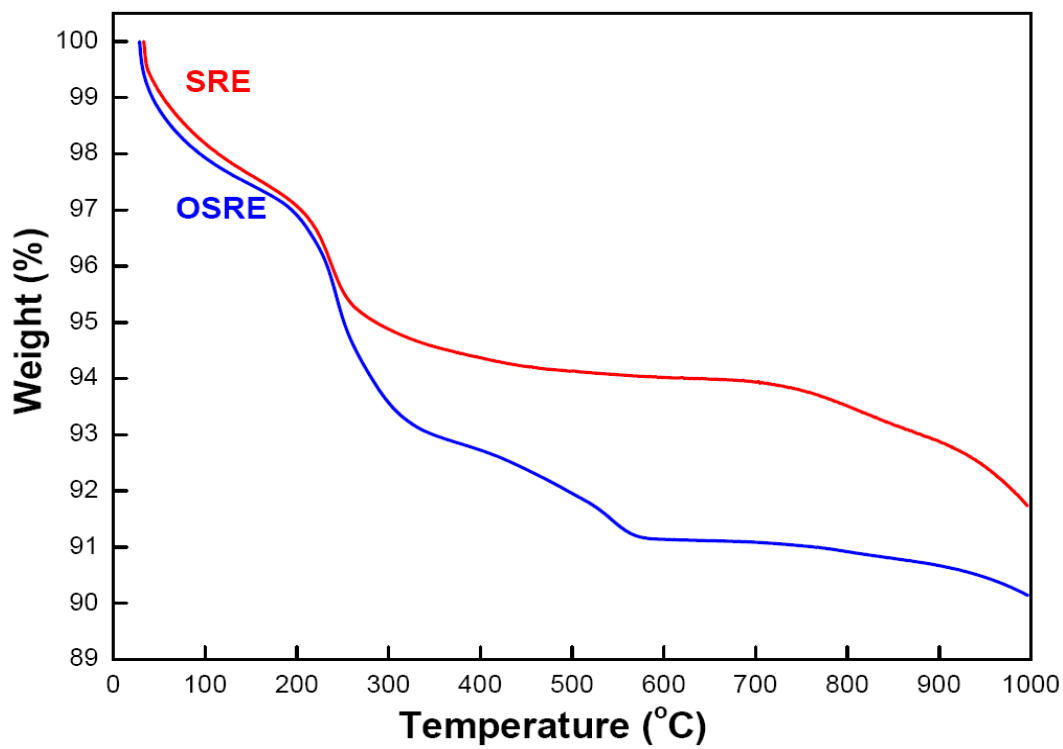


Fig. 4

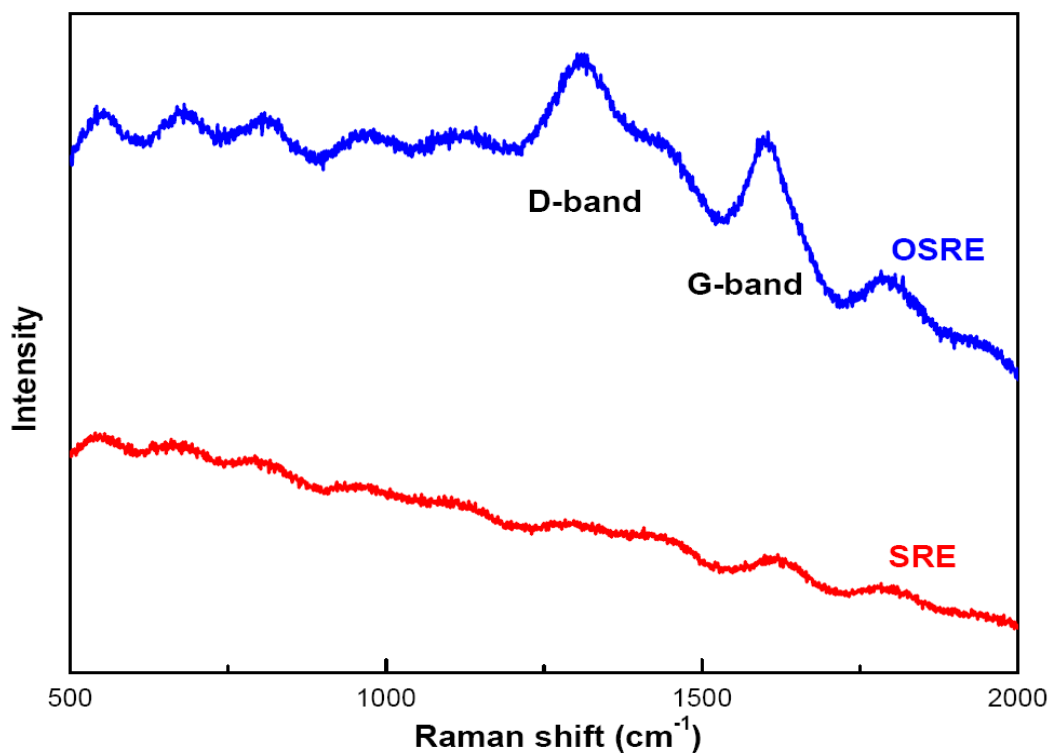


Fig. 5

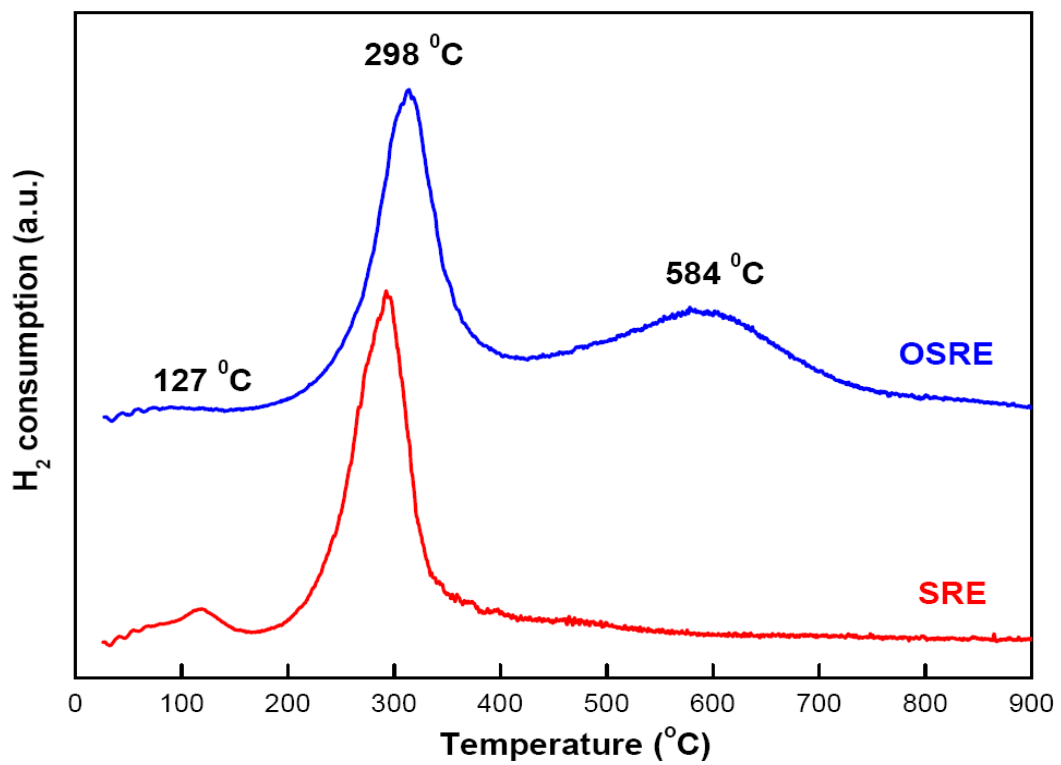


Fig. 6