出國報告(出國類別:國際研討會)

出席「亞洲土木、材料和環境科學會議 (ACCMES 2018)」心得報告

服務機關:國防大學理工學院化學及材料工程學系 姓名職稱:文職教授 汪成斌 派赴國家:日本 出國期間:107年7月9日至7月14日 報告日期:107年8月3日

摘要

亞洲土木、材料和環境科學會議(ACCMES 2018)與全球工程與應用科學會議(GCEAS 2018)合併於2018年7月10-12在日本新宿燦路都廣場大飯店同一場地舉行,是學者、研 究人員和業界人員研討土木、材料、環境科學、工程及應用科學領域之跨學科的國際研究平 台,為重要的國際會議之一。除了不能獲得二個會議的論文集,二邊會議之所有論文發表場 次均可自由聆聽,是一新奇體驗。會議共舉行三天,為遠到者著想,第一天會議僅半天(13:00 至 17:00), 第二、三天則行程滿檔(09:00 至 18:00), 計有大會專題演講, 各相關主題(化學 工程、環境工程、環境科學、應用科學、電子/電機工程、材料科學及工程、土木工程、土木 科學、機械工程、電腦工程等)之邀請講座,另提供口頭和壁報論文之發表。吸引了超過300 名來自世界各地的學者,包括澳洲、挪威、德國、瑞典、土耳其、英國、委內瑞拉、阿曼、 科威特、伊朗、印度、印度尼西亞、阿爾及利亞、菲律賓、埃及、新加坡、馬來西亞、香港、 泰國、韓國、日本、中國、台灣等,此研討會投稿論文分口頭報告及壁報展示,為一中型國 際會議。在會議中聆聽各國學者之學術演講,並於茶敘交流時間彼此交換意見並討論相關問 題。本次會議提供一個相當好的知識交流及科學合作的聯網平台,各國學者齊聚一堂研討各 種先進材料領域最新之進展和技術信息,並傳達新的研究領域和國際未來發展方向及其優先 次序。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,亦可做 為本實驗室日後研究之參考。

筆者感謝科技部之經費補助本人、一位博班研究生(吳瑞琪)及二位碩班研究生(劉久 弘、甄家葳)成行,總計發表四篇壁報論文:"Production of Hydrogen from the Steam Reforming of Bioethanol over NiRh/Ce_{0.5}Zr_{0.5}O₂ Catalysts"、"Evaluation the Oxidation of Carbon Monoxide over Different Morphologies of Cobalt Oxide"、"Graphene-based Materials Applications"、

"Sensing of Volatile Gases over Manganese Dioxide with Quartz Microbalance", 達到與各國學者切磋交流的機會,真是獲益匪淺。

目次

頁碼

| 壹、 | 會議目的 | 4 |
|----|------|-------|
| 〕〕 | 會議過程 | 4 |
| 參、 | 會議心得 | 9 |
| 肆、 | 建議事項 | 9 |

壹、 會議目的

亞洲土木、材料和環境科學會議(ACCMES 2018)與全球工程與應用科學會議(GCEAS 2018)合併於2018年7月10-12在日本新宿燦路都廣場大飯店同一場地舉行,為一跨學科國際會議。本次會議提供一個相當好的知識交流平台,各國學者齊聚一堂研討各種先進工程技術領域近期之成果、新穎應用於未來科學之進展和技術信息,並傳達新的研究領域和國際未來發展方向及其優先次序。會議宗旨在於藉由學術的發展與腦力激盪,借鑒實證研究和概念的見解,達到共享交流。依專長領域進行一系列學術研究成果發表及新知討論,以便交流最新進展和技術信息,歷年來相關之學術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經驗是很不錯的體驗,將可做為日後研究題材之參考。

貳、 會議過程

本會議屬於一中型國際研討會,於2018年7月10 - 12日在日本新宿燦路都廣場大飯店舉 行,参加人員超過300員,分別來自世界各國之學術單位、民間機構、專家學者及研究人員參 與為期三天之學術論文發表討論會。大會所討論之範圍很廣,包含化學工程、環境工程、環 境科學、應用科學、電子/電機工程、材料科學及工程、土木工程、土木科學、機械工程、電 腦工程等,與會者多為各國在該領域學有專精之工程師、技術員、教授、研究生與學者。本 次台灣與會人數眾多(包含中研院、地震研究中心、中油、東華、慈濟、宜大、海大、淡江、 文化、台科大、大同、北醫、明志、城市大學、建國科大、中原、長庚、清大、交大、聯大、 逢甲、中興、靜宜、彰師大、雲科大、南台科大、南華科大、崑山、嘉大、成大、義守、中 山、高雄第一大學、高雄科大、美和科大、屏科大及國防大學等),初估參與之教授、技術 員及研究生約有百人,於研討會期間與各學者相互密切交流之下獲益良多。三天與會期間過 程十分順利,由於每天議程都有不同主題分別在不同的場地同時進行,因而無法全面顧及, 謹將本人出席參與的部分簡要介紹如下。

<u>7月10日</u>(大會第一天)

大會第一天安排了二組(化學工程/能源工程、生物工程/環境科學)研討議題。第一場聆聽了 印度尼西亞Setyaningsih學者的演講「甘油與乙酸選擇性酯化反應製備三乙酸甘油酯」,目前 全球對生物柴油需求的增加,如何將低成本甘油轉化為高附加價值之產品引起眾人研發興 趣。Triacetin是一種衍生產品,可用於提高燃油中辛烷值的甘油。在這項研究中選用經活化之 沸石進行合成三乙酸甘油酯,唯有可能形成單乙酸甘油酯和二乙酸甘油酯中間產物,因此必 須控制到最佳條件才能將三乙酸甘油酯選擇性提高。中場休息時間請教Setyaningsih學者如何 活化沸石及提升產物選擇性,建議我們可以調控酸鹼值及甘油與乙酸的摩爾比,回國後可嚐 試。第二場聆聽了另一位印度尼西亞Oktafiani學者的演講「從椰子油合成生物柴油」,椰子 油被選為生物柴油原料,特別是在印度尼西亞因它是豐富並滿足多種需求,具有高脂肪酸和 酯含量,且可大規模生產,良好的燃燒性能和生態友好。研究方向包含找到可以產生大量的 最佳質量比之生物柴油,並了解一些變量的影響,如原料之間的質量比溶劑,反應溫度和所 用催化劑的百分比等。研究成果顯示椰子油可以用作製造高純度(96%)的生物柴油和生物 柴油中含有的最高脂肪酸是月桂酸的原料。另藉由貴重儀器對系列材料及產物之結構做一詳 盡探討,評估其應用效能,獲得在座學者熱烈的迴響並提出不同觀點,Oktafiani學者均能詳 加解說。近來原油價格的變化及燃燒化石原料對環境之嚴重衝擊,發展再生能源已是全球努 力的方向及重要方針,實驗室正好可以踏入此項研究主題。

<u>7月11日</u>(大會第二天)

大會第二天安排了二場相大會專題演講,及分組(基礎應用科學、電腦工程與技術、環境工 程與科學等)的研討議題。其中一場大會專題演講邀請美國密西西比州立大學Parajuli教授主 講「Watershed Science and Engineering Assessment: Surface-Ground Water Modeling Case Studies」,以水文和流域,地表和地下水過程可能受到影響的管理實例,介紹流域科學與工 程之評估。藉由提高對流域特徵的了解,保護的妥善管理,使用水文和水質建模工具,可改 善農業生態系統的水質、水量和農業生產力。在流域系統中經常會針對點和非點污染源進行 保護措施,目的是減少非點污染源,農業流域的水,土壤和養分的流失。保護措施將專注在

流域系統,實施評估其對河流水質和水質的影響數量,使用水文和水質模型模擬輸出,和現 場觀察溪流並監控水質數據。建模方案可能包括流域、水質污染物(沉積物及養分)運輸過 程、土地利用和氣候變化影響、營養源評估、模型校準和驗證策略與統計(例如回歸分析, 相關係數,Nash-Sutcliffe效率指數,根均值方誤差)以及流域建模的未來挑戰。雖然此專題 演講與本實驗室的研究領域不同,不過,專心聽講仍是有收穫的,增長知識。在分項演講中 印象最深刻的是菲律賓Dalida教授的論文「Design and Performance of an Immobilized Photocatalytic Reactor for Water Treatment」發表,該研究是利用光催化將廢物和洪水處理提供 了可持續和創新的解決途徑。610 mL容量之光催化反應器設計是以硼矽酸鹽玻璃製成的,並 使用二氧化鈦(TiO₂, Degussa P25,混合99%乙醇噴塗到光催化反應器上)光觸媒和紫外燈光 源可有效減少水中的有機污染物(以亞甲基藍來模擬水中有機化合物進行性能測試)。使用 Box-Benkhen設計所獲得的最佳轉化率可達57.8%,最佳化之反應參數分別為pH7、亞甲基藍 初始濃度為2.69 ppm、光催化時間為20分鐘、流速則為2.83 L/min。從Dalida教授介紹的內容 來看,仍有很大的改進方向,如何提高光催化效率是最重要的一環。不同反應器的組裝、光 觸媒種類及塗佈的量、光強度均可作為改善的參數。

我們壁報展示亦安排在今天早上(09:00 - 10:30):「Production of Hydrogen from the Steam Reforming of Bioethanol over NiRh/Ce_{0.5}Zr_{0.5}O₂ Catalysts」、「Evaluation the Oxidation of Carbon Monoxide over Different Morphologies of Cobalt Oxide」、「Graphene-based Materials Applications」、「Sensing of Volatile Gases over Manganese Dioxide with Quartz Microbalance」, 達到與各國學者切磋交流的機會,真是獲益匪淺。綜整各學者提供之建議如下:合金相之鑑 定需再確認、乙醇重組產氫之機制需做修正、需提出一氧化碳氧化之機制、石墨烯基材之拉 曼光譜鑑定需詳述、VOCs感測需考慮濕氣之影響。感謝各學者之建議,擬於暑假期間將實驗 補齊,並逐一將文章撰寫完成並投稿。

<u>7月12日</u>(大會第三天)

在多次參與國際會議中未曾見過科威特的學者,今在一分項演講正好是來自科威特石油公司的Al-Baroud工程師的演講「Kuwait Environmental Remediation Program (KERP): Remediation

Strategy of Oil Contaminated Soils in North Kuwait Oil Fields 1, 在1991年海灣戰爭期間,科威 特有將近114平方公里的沙漠土地被引爆的油井嚴重破壞,油井和油田的相關基礎設施均遭到 嚴重破壞,導致約十億桶原油釋出而進入大地環境,形成中、大型的濕油湖。因此,污染的 土壤改變了沙漠土壤的性質和生態景觀,造成植物和動物的死亡;並滲透深入地下土壤層, 威脅到北科威特 (NK) 珍貴和稀少的新鮮地下水資源。為全面修復受污染的土地 (即整個科 威特油田的26萬立方米污染土壤),聯合國賠償委員會(UNCC)、科威特國家聯絡點(KNFP) 和科威特石油公司(KOC)提出科威特環境修復(KERP)的環境保護計劃進行合作,期能 清理大區域受汗染的土地。採用的技術包含生物修復、物理和化學處理方法及工程填埋設施, 這是一浩大的工程,創造美好的地球環境是地球上每一份子的責任。在另一分項演講聆聽了 中國武漢地球科學大學Yang教授講述「Facile Enhancement in Stability of PtRu Electrocatalyst by Cerium Oxide Coating in Direct Methanol Fuel Cell Applicatio 1, 鉑-釕(PtRu) 電催化劑傳 統上用於直接甲醇燃料電池(DMFCs)作為陽極電催化劑,其中Ru可促進CO的氧化,避免 鄰近Pt的中毒,唯Ru在酸性介質中可溶解,導致Pt-Ru電催化劑的耐久性變差。為減緩Ru在酸 性介質中的溶解並增強CO抗中毒作用,可在PtRu奈米粒子的表面上塗佈二氧化鈰(CeO₂)薄 層,經4200次電位循環測試評估,電催化劑之電化學表面積(ECSA)僅17%損失;未塗佈 CeO2薄層電催化劑之ECSA則損失55%。同時與未塗佈CeO2薄層電催化劑相比,塗佈CeO2薄 層電催化劑因CeO2層可防止CO吸附在Pt奈米顆粒表面上,且高氧含量的CeO2可促進CO轉化 成CO₂,對甲醇電催化氧化反應(MOR)活性高出2.8倍。另CeO₂層可穩定存在於酸性介質中, 保護Ru不易溶於酸性介質。我們實驗室正準備踏入此項研究,相關內容是很重要的考資料, 因Yang教授報告完即離開,錯過交談的機會,回國後將閱讀Yang教授發表的系列文章,再構 思研究方向。

氫能燃料電池為日本重要之Future Secondary Energy,2014年日本經濟產業省制定「氫能、燃料電池戰略藍圖,第一階段自即日起至2025年,主要為安裝微熱電燃料電池系統、燃料電池 車及大型熱電燃料電池系統;第二階段於2020~2030年建構氫氣供電系統及氫氣量產產業13 鏈;第三階段自2040年起,建構無二氧化碳排放之氫能供應系統。另日本燃料電池車已於2014

年底推出,惟目前加氫站數量不多,以福岡市為例僅有三座(一座位於九州大學內),日本 東京將於二年後(2020年)舉辦奧運會,屆時東京預估將建造完成200座加氫站提供燃料電池 車輛使用。搜尋到離會場最近之加氫站位於東京車站附近,遂利用空檔走訪,如下所示照片, 左圖為現場二座充氫氣的硬體裝置,右圖則為液態氫氣的儲存廠房。氫燃料電池是以高壓氫 為能量來源,故加氫站需要有高壓儲存裝備,而裝載於車上時同樣也需要能承受高壓之容器, 因此加氫站的建造成本自然高出「加油站」許多。日本政府傾全力發展氫經濟, 並對硬體建 設大力支援。從氫氣車、加氫站到家用燃料電池電熱共生系統,無一不是砸重金補貼、扶植, 除節能減碳與分散能源考量外,更寄望藉領先世界的燃料電池技術,帶動國家產業升級與轉 型,策略性地思考氣經濟的全面發展。當我們在現場巡視時,正好有輛Mirai氣氣燃料汽車進 站充氫氣,本想拍照卻因安全顧慮而被工作人員制止。Mirai之「油箱蓋」位置為H2充填口, 亦可直接充電(使用日本CHAdeMO直流系統),補充氫燃料約三分鐘,充滿即可行駛650km, 在長距離行駛方面較占優勢能,並能作為急難時的緊急供電站(在車尾設置有一直流電接孔, 可透過電流轉換器,將直流電轉換成交流電供家庭使用)。FC電堆總成及FC增壓轉換器置於 車體中央位置以均衡配重;原廠為求較佳行駛里程表現,犧牲後座空間設計成4人座位,將空 間擺放儲氫瓶與相關線路;「引擎室」內配置動力控制元件(包括電動馬達),負責管理動 力的輸出及回生。





參、 會議心得

本研討會為一跨學科國際會議,主題涵蓋化學工程、環境工程、環境科學、應用科學、 電子/電機工程、材料科學及工程、土木工程、土木科學、機械工程、電腦工程等的工程師、 技術員、教授、研究生與學者,就專長領域進行一系列學術研究成果發表及新知討論。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200餘篇。大會 所討論之範圍很廣,包含土木、材料、環境科學、能源、工程及應用科學領域等,且相關論 述主題亦十分具參考價值。

本人及三位碩班研究生參與會議並有四篇壁報論文發表,透過各國學者不同領域的經 驗,於問答問各取所需,達到知識精進功效,並積極與各國學者交換演講意見達到學術交流 目的。本次會議提供一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

亞洲土木、材料和環境科學會議(ACCMES 2018)與全球工程與應用科學會議(GCEAS 2018)合併於2018年7月10-12在日本新宿燦路都廣場大飯店同一場地舉行,為一跨學科國際會議。探討範圍包含土木、材料、環境科學、能源、工程及應用科學領域等,值得相關研究人員與學者參與。這次研討會台灣與會人數眾多,初估參與之教授、技術員及研究生約 有百人。出席國際學術會議情況是大學辦學績效評估中非常重要的指標參考依據,各校應積 極鼓勵研究生及老師踴躍出席國際學術會議,以展現研究成果之決策應該持續推動。本人參 加這次會議,發現除主辦國,菲律賓、印度、科威特、韓國等國家之出席人數亦多,鄰近國 家重視全方位科學研究與發展之務實態度值得借鏡。個人認為科技部應提供更多的經費補 助,鼓勵研究生參與,以鼓勵並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,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,本次研討會攜回會議論文冊乙本。

作者發表之論文(一)

Production of Hydrogen from the Steam Reforming of Bioethanol over NiRh/Ce_{0.5}Zr_{0.5}O₂ Catalysts







Evaluation the Oxidation of Carbon Monoxide over Different Morphologies of Cobalt Oxide





Sensing of Volatile Gases over Manganese Dioxide with Quartz Microbalance





KEREKEREKERE BEREKEREKEREKEREKEREKEREKEREKEREKERE

Certificate of Presentation

Asian Conference on Civil, Material and Environmental Sciences July 10-12, 2018 Tokyo, Japan

Chung Cheng Institute of Technology National Defense University Jia-Wei Zhen

Has attended the conference and presented a paper entitled

Sensing of Volatile Gases over Manganese Dioxide with Quartz Microbalance

Chief Executive Committee

97 10 月后 97

Certificate of Presentation

Asian Conference on Civil, Material and Environmental Sciences July 10-12, 2018 Tokyo, Japan

Chung Cheng Institute of Technology National Defense University Chiu-Hung Liu

Has attended the conference and presented a paper entitled

Graphene-Based Materials Applications

Chief Executive Committee



Graphene-based Materials Applications



Evaluation the Oxidation of Carbon Monoxide over Different Morphologies of Cobalt Oxide

<u>Ruei-Ci Wu</u>¹, Chih-Wei Tang², Chih-Chia Wang¹ and Chen-Bin Wang¹*

¹Department of Chemical and Materials Engineering, Chung Cheng Institute of Technology, National Defense University, Taoyuan, 33509, Taiwan, ROC ²Department of General Education, Army Academy ROC, Chungli, Taoyuan, 32092, Taiwan, ROC

E-mail address: richard82801@gmail.com

Abstract

Cobalt nitrate (0.5M) and three precipitants (0.1M) were used, namely urea (CO(NH₂)₂, U), hexamethylenetetramine (HMTA, H) and sodium hydroxide (NaOH, N). Samples were prepared by hydrothermal method, which were Co₃O₄ (U), Co₃O₄ (H) and Co₃O₄ (N). In addition, the prepared sample was placed in a calcining furnace and kept at 300 °C for 2 h to obtain Co₃O₄(U)-300, Co₃O₄(H)-300 and Co₃O₄(N)-300, respectively. The activity test was performed in a laboratory-made mobile micro-reaction system. The catalytic performance of CO oxidation was evaluated in a laboratory continuous flow microreactor. Co₃O₄(U)-300 forms a rod-like rod-like shape from rods; the morphology of Co₃O₄(H)-300 changes from rosette to begonia; Co₃O₄(N)-300 turns from ant to beehive. After activity and long-term tests, the catalytic activity of T₅₀ (CO conversion rate reaches 50 %) is: Co₃O₄(U)-300 > Co₃O₄(H)-300 > Co₃O₄(N)-300. For the best sample, the nanorod Co₃O₄(U)-300 showed preferential catalytic performance for CO oxidation of T₅₀ at 88 °C. Two stability tests were carried out: a long-term test at 125 °C with a conversion of 95 %. The other one carried out five cycles and found almost no inactivation.

Keywords: Carbon monoxide; Cobalt oxide; Morphology; Hydrothermal

1. Introduction

The most common human contact is the air, but the industrial revolution continues to cause damage to his wife, and cause air pollution, usually "air pollution indicators (Pollutant Standard Index, PSI)" represents the quality of the air. PSI is for the air of five common pollutants (carbon monoxide, sulfur dioxide, suspended particulates, ozone and nitrogen dioxide). And carbon monoxide is a colorless, odorless, odorless gas, is not a complete by-product of combustion. Carbon monoxide and hemoglobin affinity 220 times larger than oxygen, so the presence of carbon monoxide in the air, the priority and hemoglobin will be combined to produce carbon monoxide hemoglobin (CO-Hb), the loss of hemoglobin oxygen transport capacity, as a suffocating gas. The easiest way to eliminate carbon monoxide is to react with oxygen in the air to produce carbon dioxide. From the thermodynamic point of view, the oxidation of CO is a spontaneous reaction

 $CO + 1/2 O_2 \rightarrow CO_2$ $\Delta G_{298 K} = -257 \text{ kJ/mol}$

CO in the air burning up to 652 $^{\circ}$ C, indicating that the activation of the reaction is higher, if the direct way to convert it into CO₂ is not economic benefits, if you choose the appropriate catalyst, reduce the activation energy and conversion The temperature, the elimination of carbon monoxide is the most effective is the main goal.

(Pt, Pd, Rh, Ru, Au, Ag) and base metals (Cu, Co, Fe, In, Ga) are supported on carriers (zeolite, alumina, silica and activated carbon) by different catalysts for catalytic CO oxidation. Due to the high cost of catalyst for noble metals (Pt, Pd, Rh, Ru, Au, Ag) and low selectivity at high temperatures, national researchers have been looking for alternative catalysts to find cobalt trioxide from transition metal oxides (Co_3O_4) structure with mobile oxygen, on the catalytic CO oxidation with high activity, another possible reason for the oxygen vaporization heat is low, said Co_3O_4 Co-O bond can be weak, easy from the lattice oxygen (Reactive oxygen) [1-3].

It is known from the above that the cobalt catalyst has a high activity for catalyzing the CO oxidation reaction. In this paper, the concentration of CO in the fire is about 3000 - 4000 ppm. In this study, the concentration of CO in the feeds is 2 - 4 times higher than that in the fire. The concentration of CO in the mixed gas was controlled for the deployment of 5000 ppm and 15000 ppm, respectively. The cobalt catalyst was prepared by hydrothermal method and cobalt catalyst was prepared by different precipitants. Evaluate the performance of the catalytic CO oxidation reaction, and determine the effect of the structure on activity [4].

2. Experimental

In this experiment, precursors of catalyst cobalt were prepared by hydrothermal and different precipitants (Urea,U), hexamethylene tetramine (HMTA,H) and sodium hydroxide (NaOH,N) [as-prepared -T, Co_3O_4 (U)-T, Co_3O_4 (H)-T, Co_3O_4 (N)-T) catalyst, the name and preparation process of the catalyst are respectively Described below.

2.1 Preparation of different cobalt oxide

 $(Co(NO_3)_2 \cdot 6H_2O)$ and urea (U) were dissolved in an appropriate amount of deionized water and mixed at 100 °C with ultrasonic aid, and the mixture was stirred continuously. After 2 h, the cells were placed in a serum bottle and the serum was then placed in an oven at 110 °C for 12 h and then allowed to stand for 6 h to room temperature. And then washed with a large amount of deionized water to pH = 7 to 8, filtered and dried at 60 °C and ground into a powder, which is a precursor of catalyst cobalt as-prepared (U); precipitant HMTA is prepared as-prepared (H); and precipitant NaOH was prepared as-prepared (N). And then, respectively, in the air flow from the high temperature furnace calcined to Y °C holding temperature for 2 h, namely the preparation of

black Co_3O_4 oxide, named Co_3O_4 -X-CY, X = U, H, N; Y = 3, 5 and 7 (3, 5, 7 calcined at 300, 500, 700 °C).

3. Results and discussion

3.1 Identification of the properties of the catalyst

XRD, TEM/SEM, TGA and H_2 -TPR were used to identify the properties of the catalyst, the morphology, the size of the catalyst, the size of the catalyst, Reduction properties, surface area and pore size distribution.

Objective In order to control the morphology, we added different precipitants, namely urea, hexamethylenetetramine and sodium hydroxide. The comparison JCPDS database is a mixture of two different types. Because the morphology is different (color structure particle size), we compare the three samples.

XRD patterns of cobalt catalyst precursors prepared by different precipitation agents by hydrothermal method. The JCPDS (Joint Committee on Powder Diffraction Standar) database is used to estimate the lattice and TEM/SEM profiles of the diffraction line position and the peak intensity. As-prepared (U) Conform to JCPDS 48-0083, $Co(OH)_x(CO_3)_{0.5}$ ·0.11H₂O and JCPDS 29-1416, $Co_2(OH)_2CO_3$. (NH₄)_{1.89}Co_{7.88}(CO₃)₆(OH)₆·4H₂O is JCPDS 52-0552 is flower-like structure and (NH4)_{1.89}Co_{7.88}(CO₃)₆(OH)₆·4.27H₂O and as-prepared (N) is α -Co(OH)₂ and β -Co (OH)₂, For JCPDS 46-0605 and 74-1057 as shown in Figure 3.1 [5-7].

Objective In order to control the morphology, we added different precipitants, namely urea, hexamethylenetetramine and sodium hydroxide. The comparison JCPDS database is a mixture of two different types. Because the morphology is different (color structure particle size), we compare the three samples. And these structures are observed from the SEM/TEM diagram. As shown in Figure 3.2 and Figure 3.3 [8-13], it can be found that the precipitant urea is a rod-like structure, while the HMTA precipitant forms a flower-like structure. Finally, NaOH precipitates a honeycomb structure. Through TEM observation, it can be clearly seen that $Co_3O_4(U)$ -300 indeed aggregates and accumulates to form long strips, while flower patterns are formed by lamellae, and honeycombs are formed by particle aggregation. $Co_3O_4(H)$ -300 and $Co_3O_4(N)$ -300 are more likely to accumulate and may therefore be one of the causes of poor activity [14].

After 300 $^{\circ}$ C calcination will form Co₃O₄, but showing a different appearance, the precipitant is urea is a long rod-like structure, after calcination into particles into a rod-like; HMTA is the form of flower-like structure, calcined as a flower-like, but by small particles gathered into a sheet, in the formation of flower-like appearance; and NaOH as a precipitant, after calcination or honeycomb structure. It can be seen from Fig. 3.4 that the bar-like reduction temperature is smaller than that of honeycomb. Judge from the curve shows that the two reduction peaks were Co_3O_4 reduction. The two reduction peaks are shown in the two-step reduction process: the first step is to restore Co_3O_4 to CoO (Equation 3.1) and the second step to CoO reduction to Co metal (Equation 3.2) [15-18].

 $\operatorname{Co}_{3}\operatorname{O}_{4} + \operatorname{H}_{2} \to 3\operatorname{CoO} + \operatorname{H}_{2}\operatorname{O}$ (3.1)

 $CoO + H_2 \rightarrow Co + H_2O$

(3.2)

Figure 3.5 based on the TGA results, it can be concluded that Co_3O_4 is formed when the firing temperature is 300 °C by thermal analysis, and deoxidation and CoO formation occurs when heating is continued to 860 °C. It can be clearly seen that the three kinds of samples are divided into two steps to reduce, indicating that two different crystal forms are extracted, which is consistent with the XRD results. Among them, the Co_3O_4 (N) structure is less likely to be destroyed, and the remaining 80% remains; and the hexamethylenetetramine remains only 67%, the least.

3.2 Catalyst activity evaluation

The activity of CO oxidation was evaluated by the self-made flow microreactor system. The reaction temperature range was 25 °C - 200 °C, the gas feed was controlled (1.5% CO/4.4% O₂/1840 ppm H₂O). Comparison different morphology of cobalt catalysts (Co₃O₄ (U)-300, Co₃O₄ (H)-300 and Co₃O₄ (N)-300) showed in Figure 3.6. The results showed that the CO- Comparison with T₅₀ (conversion of 50 % of the temperature) as a benchmark, the results T₅₀ rod < flower < honeycomb. In order to know the difference between the calcination temperature and the activity, calcination at 300 °C, 500 °C and 700 °C for comparison, as shown in Figure 3.7 can be higher calcination temperature, will make the catalyst particles become larger and worse activity [19-21]. And then in order to enhance the activity, and the catalyst activation, the first catalyst through the oxygen, at different temperatures (25, 50, 100 and 150 °C) oxidation for two hours, as shown in Figure 3.8, found to be activated Co₃O₄ (U) -300 Catalyst, but the activity is the best.

3.3 Stability test

The best sample $\text{Co}_3\text{O}_4(\text{U})$ -300 nanorods showed preferential catalytic performance for CO oxidation at 88 °C. Two kinds of stability tests were conducted. One set a long time of 50 h and maintained at 125 °C, the activity still maintained a 95 % conversion rate, while the other was tested after a catalytic activity and then cooled down to room temperature before the activity test. In this cycle, five cycles were performed, and it turned out that almost no deactivation occurred [22]. Afterwards, the XRD and TPR were performed for the samples after long and five cycles, as shown

in Figure 3.11 and Figure 3.12. Therefore, there was no significant difference in the absence of particles. Instead, the structure of intact Co_3O_4 was still observed.

Conclusion

Three nanostructured cobalt oxides, nanorods, flower-like nanosheets and granular nanoparticles are prepared by different precipitants with hydrothermal method. The correlations between catalytic activity and nanostructure are obtained and show as follows:

1. The affects of morphology on the catalytic behavior of Co_3O_4 show that the nanorods $[Co_3O_4(U)-300]$ are more active in catalysis than the flower-like nanosheets $[Co_3O_4(H)-300]$ and granular nanoparticles $[Co_3O_4(N)-300]$, the T_{50} order is 88 °C, 119 °C, and 126 °C, respectively. 2. From a comparison of catalysis with particle size and reductive property, 15.2 nm and 332 °C

for $\text{Co}_3\text{O}_4(\text{U})$ -300, 12.2 nm and 335 °C for $\text{Co}_3\text{O}_4(\text{H})$ -300, 12.8 nm and 340 °C for $\text{Co}_3\text{O}_4(\text{N})$ -300, indicating that the reductive property is the key factor in CO oxidation rather than the particle size under low temperature pretreatment.

3. The T₅₀ decreased significantly with increasing the calcined temperature, i.e., $Co_3O_4(U)$ -300 (88 °C) < $Co_3O_4(U)$ -500 (117 °C) < $Co_3O_4(U)$ -700 (163 °C). After 50 h reaction at 125 °C, the $Co_3O_4(U)$ -300 catalyst indicates almost no deactivation in catalytic activity over 96 % conversion.

Acknowledgement

We are pleased to acknowledge the financial support for this study from the Ministry of Science and Technology of the Republic of China under contract number of MOST 106-2113-M-606-001-.

References

- M. J. Zhou, L. L. Cai, M. Bajdich, M. Garc ´a-Melchor, H. Li, J. J. He, J. Wilcox, W. D. Wu, A. Vojvodic, X. L. Zheng, "Enhancing catalytic CO oxidation over Co₃O₄ nanowires by substituting Co²⁺ with Cu²⁺", *ACS Catal.*, Volume 5, pp 4485-4491, 2015.
- [2] T. L. Lai, Y. L. Lai, C. C. Lee, Y. Y. Shu, C. B. Wang, "Microwave-assisted rapid fabrication of Co₃O₄ nanorods and application to the degradation of phenol", *Catalysis Today*, Volume 131, Issues 1-4, pp 105-110, 2008.
- [3] Ghosh K, Balog E R M, Sista P, Williams D J, Kelly D, Martinez J S and Rocha, "Temperature-dependent morphology of hybrid nanoflowers from elastin-like polypeptides", *Apl Materials*, Volume 2, pp 021101, 2014.
- [4] R. Xu, H. C. Zeng, "Dimensional control of cobalt-hydroxide-carbonate nanorods and their thermal conversion to one-dimensional arrays of Co₃O₄ nanoparticles", *J. Phys. Chem. B*,

Volume 107, pp 12643-12649, 2003.

- [5] Y. Wang, H. J. Zhang, J. Wei, C. C. Wong, J. Lina and A. Borgnaa. "Crystal-match guided formation of single-crystal tricobalt tetraoxygen nanomesh as superior anode for electrochemical energy storage", *Energy & Environmental Science*, Volume 4, pp 1845-1854, 2011.
- [6] H. Cui, Y. Zhao, W. Ren, M. Wang, Y. Liu. "Large scale selective synthesis of a-Co(OH)₂ and b-Co(OH)₂ nanosheets through a fluoride ions mediated phase transformation process", *Alloys* and Compounds, Volume 562, pp 33-37, 2013.
- [7] J. Jansson, A.E.C. Palmqvist, E. Fridell, M. Skoglundh, L. Ö sterlund, P. Thormählen, V. Lange r. "On the catalytic activity of Co₃O₄ in low-temperature CO oxidation", *J. Catal.*, Volume 211, pp387-397, 2002.
- [8] M.M. Natile and A. Glisenti. "Study of surface reactivity of cobalt oxides: Interaction with methanol", *Chem. Mater*, Volume 14, pp3090-3099, 2002.
- [9] L. Hu, Q. Peng, Y. Li, "Selective synthesis of Co₃O₄ nanocrystal with different shape and crystal plane effect on catalytic property for methane combustion", *J. Am. Chem. Soc*, Volume 130, pp 16136-16137, 2008.
- [10] H.M. Choi, S.J. Lee, S.H. Moon, T.N. Phan, S.G. Jeon, C.H. Ko, "Comparison between unsupported mesoporous Co₃O₄ and supported Co₃O₄ on mesoporous silica as catalysts for N₂O decomposition", *Catal. Commun.*, Volume 82, pp 50-54, 2016.
- [11] B.Y. Bai, H. Arandiyan, J.H. Li, "Comparison of the performance for oxidation of formaldehyde on nano-Co₃O₄, 2D-Co₃O₄, and 3D-Co₃O₄ catalysts", *Appl. Catal. B-Environ.*, Volume 142, pp 677-683, 2013.
- [12] Y. Zhang, J.J. Zhou, G.S. Wu, D.S. Mao, G.Z. Lu, "Influence of the surface species over Co₃O₄ on the formaldehyde catalytic oxidation performance", *Chem J Chinese U*, Volume 35, pp 2598-2604, 2014.
- [13] X. Xie, Y. Li, Z.Q. Liu, M. Haruta, W. Shen, "Low-temperature oxidation of CO catalysed by Co₃O₄ nanorods", *Nature*, Volume 458, pp 746-749, 2009.
- [14] L. Hu, K. Sun, Q. Peng, B. Xu, Y. Li, "Surface active sites on Co₃O₄ nanobelt and nanocube model catalysts for CO oxidation", *Nano Res*, Volume 3, pp 363-368, 2010.
- [15] L. Zeng, K. Li, F. Huang, X. Zhu, H. Li, "Effects of Co₃O₄ nanocatalyst morphology on CO oxidation: Synthesis process map and catalytic activity", *Chinese J Catal*, Volume 37, pp 908-922, 2016.
- [16] Z. Zhang, H. Geng, L. Zheng, B. Du, "Characterization and catalytic activity for the NO decomposition and reduction by CO of nanosized Co₃O₄", *Journal of Alloys and Compounds*,

Volume 392, pp317-321, 2005.

- [17] R. Xu, H.C. Zeng, "Self-generation of tiered surfactant superstructures for one-pot synthesis of Co₃O₄ nanocubes and their close- and non-close-packed organizations", *Langmuir*, Volume 20, 9780-9790, 2004.
- [18] H. Xu, J.X. Wu, Y. Chen, W.J. Jing, B.Q. Zhang, "Synthesis and catalytic performance of Co₃O₄ particles with octahedral crystal shape", *Ionics*, Volume 21, pp1495-1500, 2015.
- [19] Z. Fan, Z. Zhang, W. Fang, X. Yao, G. Zou, W. Shangguan, "Low-temperature catalytic oxidation of formaldehyde over Co₃O₄ catalysts prepared using various precipitants", *Chinese J Catal*, Volume 37, pp947-954,2016.
- [20] Y. Zhao, X. Xu, Y. Zhao, H. Zhou, J. Li and Jin H "Synthesis and their physicochemical behaviors of flower-like Co₃O₄ microspheres", *Journal of Alloys and Compounds*, Volume 654, pp523-528, 2016.
- [21] C. S. Lee, Z. Dai, S. Y. Jeong, C. H. Kwak, B. Y. Kim, D. H. Kim, H. W. Jang, J. S. Park and J. H. Lee, "Monolayer Co₃O₄ inverse opals as multifunctional sensors for volatile organic compounds", *Chemistry*, Volume 22, pp7102-7107, 2016.
- [22] J. M. Xu and J. P. Cheng, "The advances of Co₃O₄ as gas sensing materials: A review", *Journal of Alloys and Compounds*, Volume 686, pp753-68, 2016.

Table Captions

1. Different morphologies of Co₃O₄ and catalytic activity of CO oxidation.

Figure Captions

- 1. XRD profiles of Co₃O₄ samples with different morphologies.
- 2. SEM images of Co₃O₄ samples with different morphologies.
- 3. TEM images of Co₃O₄ samples with different morphologies.
- 4. H₂-TPR profiles of different cobalt catalyst.
- 5. TGA profiles of different cobalt catalysts.
- 6. CO conversion curves: Different precipitants.
- 7. CO conversion curves: Different calcined temperature.
- 8. CO conversion curves: Different activated processes.
- 9. Durability test over $Co_3O_4(U)$ -300 catalyst.
- 10. Activities for five cycles CO oxidation over $Co_3O_4(U)$ -300 catalyst.
- 11. XRD profiles after stability test.
- 12. TPR profiles after stability test.



Figure 3.1 XRD profiles of Co₃O₄ samples with different morphologies.



Figure 3.2 SEM images of Co₃O₄ samples with different morphologies.



Figure 3.3 TEM images of Co₃O₄ samples with different morphologies.



Figure 3.4 H₂-TPR profiles of different cobalt catalyst.



Figure 3.5 TGA profiles of different cobalt catalysts.



Figure 3.6 CO conversion curves: Different precipitants.



Figure 3.7 CO conversion curves: Different calcined temperature.



Figure 3.8 CO conversion curves: Different activated processes.



Figure 3.9 Durability test over $Co_3O_4(U)$ -300 catalyst.



Figure 3.10 Activities for five cycles CO oxidation over $Co_3O_4(U)$ -300 catalyst.



Figure 3.11 XRD profiles after stability test.



Figure 3.12 TPR profiles after stability test.

| Catalyst | Color | Morphology* | d (nm)** Fresh Used | | S.A. (m^2/g) | CO oxidation $T_{50}(^{\circ}C)$ |
|--|-------|-------------|------------------------|------|----------------|-------------------------------------|
| Co ₃ O ₄ (U)-300 | Pink | Rod-like | 15.2 | 16.2 | 79 | 88 |
| Co ₃ O ₄ (H)-300 | Green | Flower-like | 12.2 | 18.4 | 69 | 119 |
| Co ₃ O ₄ (N)-300 | Brown | Honeycomb | 12.8 | 13.4 | 89 | 126 |
| | | | | | | |

Table 1 Different morphologies of Co_3O_4 and catalytic activity of CO oxidation

*Images of SEM. **Calculated from the XRD.

Production of Hydrogen from the Steam Reforming of Bioethanol over NiRh/Ce_{0.5}Zr_{0.5}O₂ Catalysts

Ruei-Ci Wu, Chin-Liang Lai, Chih-Chia Wang and Chen-Bin Wang*

Department of Chemical and Materials Engineering, Chung Cheng Institute of Technology, National Defense University, Tahsi, Taoyuan 33509, Taiwan, ROC

Abstract

Both precipitants (Na₂CO₃ and KOH) were chosen to prepare the Ce_{0.5}Zr_{0.5}O₂ support by co-precipitation method. Further, the NiRh/Ce_{0.5}Zr_{0.5}O₂ bimetallic catalysts (5 wt% Ni and 1 wt% Rh) were prepared by sequent incipient wetness impregnation and co-impregnation for hydrogen production on the steam reforming of bioethanol (SRBE). The preliminary results indicated that the catalytic performance and hydrogen selectivity increase with weak base of precipitant and co-impregnation method. This is attributed to the Ni-rich alloy oxide, $A^{Ni}O_x$, located on the surface that can enhance the catalytic activity and depress the carbon deposition. The NiRh/CeZr(N)-I catalyst shows the preferential performance with less selectivity of CH₄ (< 4%) and CO (< 1%) at the low temperature (450 °C) and can depress the carbon deposition (< 0.3%) among series catalysts. The NiRh/CeZr(N)-I catalyst can significantly reduce carbonaceous species to enhance stability and the durability test at 400 °C exceeds 400 h.

Keywords: Steam reforming of bioethanol; Biofuel; Hydrogen fuel, Coke.

1. Introduction

Hydrogen is a potential and attractive source of energy since its combustion to provide energy only water product. The major advantages are system efficiency and environmental benefits in conjunction with fuel cells [1]. Several catalytic processes for hydrogen production from ethanol have been investigated, including steam reforming (SR), partial oxidation, and auto-thermal reforming [2]. Steam reforming of ethanol for the production of hydrogen is very attractive among the various processes, because ethanol is abundantly available from bio-fuel that easy to store and is nontoxic. Another advantage of using ethanol is that the CO_2 produced during steam reforming of ethanol is equal to the CO_2 required for biomass growth and thus provides a closed cycle for CO_2 consumption.

Supports also play important roles in SRE, as supports help in the dispersion of metal catalyst and may enhance metal catalyst activity via metal-support interactions. Supports may promote migration of OH group toward the metal catalyst in the presence of water at high temperature [3]. CeO₂-ZrO₂ solid solution with high oxygen mobility is widely applied in exhaust gas purification, the reforming of hydrocarbon, and water gas shift (WGS) reaction, and the capacity of CeO₂-ZrO₂ involving oxygen diffusion and surface adsorption strongly depends on the texture and structure, which is affected greatly by the preparation method [4]. Jilei et al. [5] investigated NiO/Ce_{0.5}Zr_{0.5}O₂ catalyst had highly active and selective for hydrogen production from steam reforming of ethanol. Especially, the prepared catalysts were very active at low temperature and exhibited good stability for both carbon resistance and anti-sintering. So, the Ce_{0.5}Zr_{0.5}O₂ support is a promising candidate for SRE and its catalytic performance will be influenced by the preparation method markedly. Nickel-based catalysts are widely used in commercial reforming process and recognized as appropriate catalyst in SRE for their low cost, relatively high activity towards C–C bond cleavage and hydrogenation/dehydrogenation reactions [6, 7] in Addition to this,Rh catalysts also have been favored for ethanol steam reforming because they show the greatest activity toward C–C bond cleavage [8, 9]. Furthermore,Kugai et al [10] had shown that ethanol is adsorbed on Rh and Ni surface as ethoxide species, which formed an oxametallacycle intermediate and favored C–C bond rupture.

2. Experimental

2.1 Preparation of supports and catalysts

The ceria-zirconia composite oxide with 1:1 molar ratio was prepared by co-precipitation (CP) method. Initially, a stoichiometric aqueous solution of cerium nitrate [Ce(NO₃)₃·6H₂O, 99.5%, Acros] and zirconium oxychloride [ZrOCl₂.8H₂O, 99%, Showa] was added slowly with two kinds of aqueous solution of 2 M Na₂CO₃ or KOH at 80 °C for 2 h, respectively. The obtained suspension was filtered and washed with DI water. Finally, it was dried at 110 °C overnight and further calcined at 400 °C in air for 3 h which assigned as CeZr(N) and CeZr(K).

The NiRh/Ce_{0.5}Zr_{0.5}O₂ catalysts were prepared by sequent IWI and co-impregnation methods, respectively. In the IWI method, an aqueous solution of Ni(NO₃)₂·6H₂O (5wt%) was loaded on the support. The obtained samples were dried at 110 °C for overnight and calcined at 400 °C in air for 3 h which assigned as Ni/CeZr(N) and Ni/CeZr(K). Then, an aqueous solution of RhCl₃·6H₂O (1wt%) was further loaded and calcined at 400 °C in air for 3 h. The obtained catalysts were named as NiRh/CeZr(N) and NiRh/CeZr(K). The co-impregnation of Ni(NO₃)₂·6H₂O (5wt%) and RhCl₃·6H₂O (1wt%) obtained catalysts assigned as NiRh/CeZr(N)-I and NiRh/CeZr(K)-I.

2.2 Characterization of catalysts

XRD measurement was performed using a BRUKER, D2 PHASER diffractometer with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.5405$ Å) at 40 kV and 30 mA. The reduction behavior of the NiRh/CeZr catalysts was studied by temperature-programmed reduction (TPR). About 50 mg of the sample was

heated in a flow of 10% H_2/N_2 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. Thermogravimetry analysis (TGA) was performed using a TGA Q50 in air (20 ml·min⁻¹) at heating rate of 10 °C·min⁻¹. The BET surface area of the samples was measured using a Micromeritics ASAP 2010 analyzer by nitrogen adsorption at the boiling temperature of liquid nitrogen.

2.3 Evaluation of catalysts

The catalytic activities of the NiRh/CeZr catalysts towards the SRE reaction were performed in a fixed-bed flow reactor. 100 mg catalyst 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 400 °C for 3 h. The activity was tested stepwise by increasing the temperature from 200 to 500 °C. The analysis of the reactants and products was carried out online by gas chromatography with columns of Porapak Q and Molecular Sieve 5A to separate.

3. Results and discussions

Fig. 1 shows the XRD patterns of NiRh/CeZr catalysts. Diffraction peaks of 29.2, 34.0, 48.8 and 58.0° were ascribed to the primitive structure of $Ce_{0.5}Zr_{0.5}O_2$ (JCPDS 38-1436) for all catalysts. In addition, the crystallite size of support can be calculated with the (101) plane and is in the range of 4.1 - 4.6 nm, which confirms that nano-crystallite size can be achieved by a co-precipitation method. Comparison the (200) and (211) planes of NiRh/CeZr(N)-I with NiRh/CeZr(K)-I, the peak shifts slightly toward low angle. This indicates that the doped zirconia incorporates into the ceria lattice by using the Na₂CO₃ precipitant for the NiRh/CeZr(N)-I sample. The signal of NiO, Rh₂O₃ and/or alloy oxide does not observe in all samples. This indicates that the doped Ni and Rh incorporate into the ceria lattice. The intensity of diffraction patterns of $Ce_{0.5}Zr_{0.5}O_2$ decreases with Ni and Rh loading. This can be confirmed by the decrease in support lattice parameter, due to the incorporation of Ni²⁺ with small ionic radius (0.072 nm) into the support lattice [11] indicates that the doped Ni, Rh and/or NiRh-alloy can be well-dispersed.



Figure 1 XRD patterns of (a) NiRh/CeZr(N)-I (b) NiRh/CeZr(K)-I (c) NiRh/CeZr(N) (d) NiRh/CeZr(K)

Fig. 2 shows the TPR profiles of Ce_{0.5}Zr_{0.5}O₂ supports and NiRh/CeZr catalysts. The CeZr(N) support exhibits three peaks (414, 510 and 727 °C) and only one broad peak (569 °C) for the CeZr(K) support. This indicates that the precipitant can influence the formation of composite oxide. Besides the Ce_{0.5}Zr_{0.5}O₂ composite oxide, separated CeO₂ exists by using the Na₂CO₃ precipitant. The first peak (414 °C) attributes to the removal of surface capping oxygen of CeO₂, and the third peak (727 °C) is related to the reduction of subsurface CeO₂ [12]. The broad peak at 500 - 600 °C was attributed to the reduction of the Ce_{0.5}Zr_{0.5}O₂ composite oxide. All NiRh/CeZr catalysts exhibit two main hydrogen consumption peaks around 107 – 131 °C (T_{r1}) and 283 – 315 °C (T_{r2}), respectively. The low temperature peak (T_{r1}) is corresponding to the reduction of rhodium oxide [10], the second peak (T_{r2}) is attributed to the reduction of nickel oxide [10, 13]. Comparison of the prepapration method, the T_{r1} and T_{r2} peaks for the co-impregnation method are slightly shifted to the higher and lower temperature, respectively, than the IWI method. The melting point of Ni and Rh are 1455 °C and 1964 °C, respectively, the segregation of nickel is apparent than the rhodium in co-impregnation method that forms the Ni-rich alloy oxide (A^{Ni}O_x) located at the surface layer of the NiRh alloy. Conversely, the Rh-rich alloy oxide (A^{Rh}O_x) forms by using the sequent IWI method.

Effect of temperature on catalytic activity of the NiRh/CeZr catalysts was examined. Table 1 shows the T_{95} (the temperature for the conversion of ethanol reached 95%) and catalytic performance of the different prepared method catalysts at 450 °C. Above all, the Ni/CeZr catalysts although had more low conversion temperature and less byproducts such as CO and CH₄, but in the reaction was observed after more coke formation is easy to make the catalysts to cause deactivation of the catalysts. Therefore, by adding Rh metal to improve coke situations, and can be found prepared by co-impregnation method which the catalysts had the conversion at the lower temperature and high H₂ production.



Figure 2 TPR profiles of (a) CeZr(N) (b) CeZr(K) (c) NiRh/CeZr(N)-I (d) NiRh/CeZr(K)-I (e) NiRh/CeZr(N) (f) NiRh/CeZr(K)

| Catalvete | $T_{95}(^{\circ}C)$ — | Produc | Coke* | | |
|----------------|-----------------------|--------|-----------------|-----|-----|
| | | H_2 | CH_4 | CO | (%) |
| Ni/CeZr(N) | 250 | 71 | 10 | 1.9 | 1.9 |
| Ni/CeZr(K) | 275 | 74 | 3.4 | 1.4 | 2.4 |
| NiRh/CeZr(N) | 250 | 59 | 7.1 | 0.2 | 0.4 |
| NiRh/CeZr(K) | 300 | 71 | 3.4 | 0.1 | 0.5 |
| NiRh/CeZr(N)-I | 250 | 73 | 3.3 | 0.9 | 0.4 |
| NiRh/CeZr(K)-I | 250 | 71 | 8 | 0.9 | 0.4 |

Table 1 Effect of catalysts on conversion and products distribution from SRE at 450 °C.

*Measured by TGA.

The catalytic performance of NiRh/CeZr catalysts in the steam reforming of ethanol under different precipitants is demonstrated in Figs. 3 and 4. Fig. 3 summarizes the effect of precipitants on the conversion of ethanol over NiRh/CeZr catalysts. Preliminary results showed that the ethanol can be converted completely at 300 °C for all catalysts. Apparently, the weak base of precipitant in the preparation can promote the activity which NiRh/CeZr(N)-I catalyst activity as best (250 °C). Fig. 4 compares the CH₄ and CO selectivity of NiRh/CeZr catalysts. The results indicate that the temperature of WGS is lowest for NiRh/CeZr(N)-I among the four catalysts (< 250 °C). Fig. 5 shows the ethanol conversion and the distribution of products for the NiRh/CeZr(N)-I catalyst. According to the products distribution, the dehydrogenation of ethanol to form acetaldehyde then intermediate followed decomposition into methane and CO with the reaction temperature which is the main reaction of SRE initially. As the temperature exceeds 250 °C, with increasing temperature, selectivity of CH₄ decreases due to its reformation with H₂O, which becomes thermodynamically

favorable at higher temperature. In the same, the CO can be transferred rapidly into CO_2 and H_2 by the WGS reaction. When temperature increases, methane and water are consumed resulting in increase in the selectivity of H_2 and CO_2 . The H_2 , CO and CH_4 products distribution at 425 °C were 71%, 1.3% and 7.4%, respectively over the NiRh/CeZr(N)-I catalyst. Furthermore, this catalyst possesses the capacity of re-dispersion that can avoid the sintering and depress carbon deposition.



Figure 3 Effects of ethanol conversion toward the SRE reaction over NiRh/CeZr catalysts.



Figure 4 Products distribution on the SRE reaction over NiRh/CeZr catalysts: (A) CH₄ (B) CO.



Figure 5 Ethanol conversion and products distribution for NiRh/CeZr(N)-I catalyst toward SRE reaction.

4. Conclusions

We have investigated the different precipitants to prepare $Ce_{0.5}Zr_{0.5}O_2$ support that can influence the catalytic activity on the SRE reaction over the NiRh/CeZr catalysts. The conversion and hydrogen selectivity increase with weak base of precipitant and co-impregnation method. The NiRh/CeZr(N)-I catalyst shows the best catalytic performance with the less selectivity of CH₄ and CO that can be transferred rapidly into CO₂ at the low temperature. This is attributed to the Ni-rich alloy oxide, $A^{Ni}O_x$, located at the surface layer of the NiRh alloy that can enhance the catalytic activity.

5. Acknowledgement

We are pleased to acknowledge the financial support for this study by the National Science Council of the Republic of China under contract number of MOST 106-2113-M-606-001-.

6. References

[1] Winter C.J., 2009, "Hydrogen energy - abundant, efficient, clean: A debate over the energy system of change.", *International Journal of Hydrogen Energy*, Vol. 34, No. 14, pp. s1-s52.

[2] Kiratzis N., Holtappels P., Hatchwell C.E., Mogensen M., J.T.S., 2001, "Preparation and characterization of copper/yttria titania zirconia cermets for use as possible solid oxide fuel cell anodes.", *Fuel Cells*, Vol. 1, No. 3-4, pp. 211-218.

[3] Mohamed A.E., Dalia R.A.E., Radwa A.E. and Lamia. S.M., 2012, "Ni supported high surface area CeO₂–ZrO₂ catalysts for hydrogen production from ethanol steam reforming.", *RSC Advances*, Vol. 2, No. 21, pp. 8145-8156.

[4] Wu X., Liang Q., Wu X., Weng D., 2007, "Role of surface adsorption in fast oxygen/release of CeO₂-ZrO₂ mixed oxides.", *Journal of Rare Earths*, Vol. 25, No. 4, pp. 416.

[5] Jilei YE, Yang W., Yuan L., 2008, "NiO-Ce_{0.5}Zr_{0.5}O₂ catalysts prepared by citric acid method for steam reforming of ethanol." *Journal of Rare Earths*, Vol. 26, No. 4, pp. 831-835.

[6] Mathure PV., Ganguly S., Patwardhan AV., Saha RK., 2007, "Steam reforming of ethanol using a commercial nickel-based catalyst.", *Industrial & Engineering Chemistry Research*, Vol. 46, No. 25, pp. 8471-8479.

[7] Muroyama H., Nakase R., Matsui T., Eguchi K., 2010, "Ethanol steam reforming over Ni-based spinel oxide.", *International Journal of Hydrogen Energy*, Vol. 35, No. 4, pp. 1575-1581.

[8] Liguras D.K., Kondarides D.I. and Verykios X.E., 2003, "Production of hydrogen for fuel cells by steam reforming of ethanol over supported noble metal catalysts." *Applied Catalysis B: Environmental*, Vol. 43, No. 4, pp. 345-354.

[9] Breen J.P., Burch R. and Coleman H.M., 2002, "Metal-catalysed steam reforming of ethanol in the production of hydrogen for fuel cell applications." *Applied Catalysis B: Environmental*, Vol. 39, No.1, pp. 65-74.

[10] Kugai J., Velu S., Song C.S., 2005, "Low-temperature reforming of ethanol over CeO₂-supported Ni-Rh bimetallic catalysts for hydrogen production.", *Catalysis Letters*, Vol. 101, No.3-4, pp. 255-264.

[11] Shan W., Luo M., Ying P., Shen W., Li C., 2003, "Reduction property and catalytic activity of Ce_{1-x}Ni_xO₂ mixed oxide catalysts for CH₄ oxidation.", <u>Applied Catalysis A: General</u>, Vol. 246, No.1, pp. 1-9.

[12] Trovarelli A., Zamar F., Llorca J., Leitenburg C., Dolcetti G., Kiss JT., 1997, "Nanophase fluorite-structured CeO₂ – ZrO₂ catalysts prepared by high energy mechanical milling.", *Journal of Catalysis*, Vol. 169, No.2, pp. 490-502.

[13] Biswas P., Kunzru D., 2007, "Steam reforming of ethanol for production of hydrogen over Ni/CeO₂ – ZrO₂ catalyst: Effect of support and metal loading.", *International Journal of Hydrogen Energy*, Vol. 32, No.8, pp. 969-980.