

出國報告（出國類別：國際研討會）

出席 2011 年台日雙邊研討會-「奈米材料應用於再生能源和化學品」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

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摘要

2011 台日雙邊會議是由台灣及日本交流協會共同贊助之會議，由二國相互輪流主辦，前身爲中日觸媒研討會，前後已舉辦了 12 屆，本次由日本主辦，會議地點爲日本仙台。日方延續過去秉持之精神，負責這次會議之籌備工作，於 2011 年 11 月 20-24 在日本仙台 Taikanso Hotel 舉行。本次會議之主題爲奈米材料應用於再生能源和化學品，計有台灣 12 位代表及日方 10 位代表於會議中提出論文報告，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，提供參與學者們一個溝通互相觀摩學習的機會，雖爲小規模之會議，會議籌備頗爲週延詳盡，使大會顯得熱鬧非凡，賓主盡歡。其中台灣地區則有包括台灣大學、台灣科技大學、中央大學、國防大學、清華大學、東海大學、中正大學、高雄應用大學、中央研究院、東華大學及碧氫公司等許多單位參與，共計 12 員。在會議中聆聽學者之學術演講，其中 Shawn D Lin 針對 CuNi 觸媒進行乙醇蒸氣重組反應製氫之研究，從熱力學觀點及實驗數據推導乙醇蒸氣重組反應機制，領域與我們較相近，對我們的啓發及受益最大。本次會議提供個相當好的學術交流平台，藉由此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，將可做爲本實驗室日後研究之參考。

筆者此次感謝獲國科會經費補助成行，其發表題目爲“Reforming of Ethanol to Produce Hydrogen over Zirconia Supported PtRu Catalysts”，達到與專家學者切磋交流的機會，真是獲益匪淺。

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壹、會議目的

本屆台日雙邊研討會-「奈米材料應用於再生能源和化學品」為第 13 屆，是由日方東工大 Professor Tatsumi 主辦，為二國在催化領域之重要學術會議，其會議宗旨在於結合二國有關化學工程和應用、催化應用、石化工業研究領域之學者專家，就專長領域進行系列學術研究成果發表及新知討論，歷年來所主辦之研討會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)本會議屬於小型的台日雙邊研討會，參加人員計有台灣12位代表及日方10位代表於會議中提出論文報告。上屆是由我方台灣科技大學主辦(2007)，除論文口頭報告(邀請演講)，亦包含壁報論文，參與聆聽交流人數較多(近百員)。本屆於2011年11月20-24在日本仙台Taikanso Hotel舉行，因限於經費，僅23位學者全程參與，難能可貴的是當初催生第一屆會議的雙方代表：Tanabe (85高齡)及雷敏宏教授(75高齡)均出席此次會議，此研究精神足作為後進學者之表率。大會所發表的論文範圍很廣，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，與會者多為該領域學有專精之教授與學者，於研討會期間與各學者相互密切交流之下獲益良多。

(二)會議行程之安排為二天口頭報告(09:00 - 18:00)、一天旅遊活動、半天參訪東北大學(會議行程詳如下表)。為能使發表論文的學者有機會與其他學者們面對面討論，每場之研討時間均欲罷不能而超出排定之時段，以便能詳細解說討論與互換研究心得，效果非常好。在聆聽及交流過程中可體會各與會學者對研究之投入是非常的專注，研究成果均是心血的結晶。第三天的參訪活動特地實際了解仙台遭受地震受損及修護的情形，可感受大自然的無情摧殘，及人定勝天的精神，日方能在短時間內將大部分的機能修護、建設完成，使恢復正常機能並順利運轉。另日方對文化古蹟的保存

及維護，均值得我們學習。

2011 TW-JP Joint Symposium of Nanomaterials for Renewable Energy and Chemicals

Date/Time	November 20 (Sunday)	November 21 (Monday)	November 22 (Tuesday)	November 23 (Wednesday)	November 24 (Thursday)
07:30--09:00	Lv. Taipei or Cities in Japan	Breakfast	Breakfast	Breakfast	Breakfast
09:00--09:40		Lecture 1	Lecture 12	Study Tour of Earthquake Damage (Box Lunch) & Excursion	Lv. Matsushima
09:40--10:20		Lecture 2	Lecture 13		Tohoku University Laboratories Tour
10:20--10:40		Coffee Break	Coffee Break		
10:40--11:20		Lecture 3	Lecture 14		
11:20--12:00		Lecture 4	Lecture 15		
12:00--12:40		Lecture 5	Lecture 16		Lv. Sendai
12:40--13:30		Lunch	Lunch		
13:30--14:10	Ar. Sendai	Lecture 6	Lecture 17		
14:10--14:50		Lecture 7	Lecture 18		
14:50--15:30		Lecture 8	Lecture 19		
15:30--16:00	Ar. Matsushima	Coffee Break	Coffee Break		
16:00--16:40		Lecture 9	Lecture 20		
16:40--17:20		Lecture 10	Lecture 21		
17:20--18:00	Opening Ceremony	Lecture 11	Lecture 22		
18:00--19:00	Break	Break	Break		
19:00--21:00	Reception	Dinner	Banquet	Dinner	

Lecture 1: Kazunari Domen, The University of Tokyo, “Potential for large scale application of solar fuel”

Lecture 2: Jeffrey C. S. Wu, National Taiwan University, “A membrane photoreactor for photocatalytic water splitting and CO₂ reduction”

Lecture 3: Akihiko Kudo, Tokyo University of Science, “Solar water splitting for green innovation”

Lecture 4: Hsin-yu Lin, National Dong-Hwa University, “Microwave assisted hydrothermal synthesis of M doped TiO_{2-x}N_x (M=Cu, Nb, Ni) for hydrogen production by photocatalytic water splitting”

Lecture 5: Tsunehiro Tanaka, Kyoto University, “Photo-assisted oxidative removal of gaseous ammonia”

- Lecture 6:** Jen-Ray Chang, National Chung Cheng University, "Vanadia catalysts for catalytic oxidation of 1,2-dichlorobenzene: implication of vanadia structure"
- Lecture 7:** Yu-Wen Chen, National Central University, "Synthesis of flower-like NiO and ZnO by a template-free method and their catalytic activities"
- Lecture 8:** Keiichi Tomishige, Tohoku University, "Conversion of biomass to value-added chemicals for sustainable society"
- Lecture 9:** Kuo-Tseng Li, Tunghai University, "Esterification of lactic acid over Ti-based catalysts"
- Lecture 10:** Atsushi Fukuoka, Hokkaido University, "Biomass conversion to renewable chemicals by heterogeneous catalysis"
- Lecture 11:** Chung Yuan Mou, National Taiwan University, "Strong metal-support interaction (SMSI) in gold nanocatalyst"
- Lecture 12:** Min-Hon Rei, Green Hydrotech Inc., "Preparation of copper catalyst on the porous stainless steel support - A highly thermo-conductive catalyst for endothermic reaction"
- Lecture 13:** Miho Yamauchi, Hokkaido University, "Challenge to materialization of carbon neutral energy cycle"
- Lecture 14:** Shawn D. Lin, National Taiwan University of Science and Technology, "CuNi bimetal catalysts for ethanol steam reforming"
- Lecture 15:** Yasutake Teraoka, Kyushu University, "Oxygen separation with perovskites as potential low-carbon technology"
- Lecture 16:** Chen-Bin Wang, National Defense University, "Study on the reforming of ethanol over PtRu/ZrO₂ catalyst"
- Lecture 17:** Koichi Eguchi, Kyoto University, "Microstructures and materials of electrodes for solid oxide fuel cells"
- Lecture 18:** Shang-Bin Liu, Institute of Atomic and Molecular Sciences, Academia Sinica, "A novel acidity scale for solid and liquid acids by P-31 NMR chemical shifts of phosphine oxides"
- Lecture 19:** Atsushi Muramatsu, Tohoku University, "Nanoparticulate-catalyst synthesis for creation of alternative energy by liquid-phase synthesis method"
- Lecture 20:** Chia-Min Yang, National Tsing-Hua University, "Nanocomposite catalysts based on bimodal mesoporous silica SBA-15: Case studies on Au/TiO₂@SBA-15 and PtRu/CMK-3"
- Lecture 21:** Tseng-Chang Tsai, National University of Kaohsiung, "Preparations and catalytic applications of mesoporous zeolites"
- Lecture 22:** Takashi Tatsumi, Tokyo Institute of Technology, "Synthesis of light olefins from non-petrochemical resources"

參、會議心得

本研討會規模雖小，卻也結合了七個領域的內容：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，會議是由日方東工大Professor Tatsumi主辦，為二國在催化領域之重要學術會議。參加人員為二國之專家學者，共計發表論文22篇(均為口頭報告)。大會所討論之範圍很廣，包含綠色能源、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。本次會議提供一個相當好的知識交流平台，藉由此學術交流進而瞭解未來研究發展方向及趨勢，真是獲益匪淺。

肆、建議事項

因限於經費，台日雙邊會議參與人數較少，值得將研討會規模擴大，廣邀相關領域之研究人員與學者參與。除藉此與專家學者交換研究心得外，亦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。本次研討會攜回會議論文資料與東北大學多元物質科學研究所之簡介。

作者發表之論文

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



Reforming of Ethanol to Produce Hydrogen over PtRu/ZrO₂ Catalyst

Jia-Lin Bi¹, Chi-Han Wang¹, Shih-Yi Yang¹, Chin-Ling Lee¹,

Chuin-Tih Yeh^{2,3} and Chen-Bin Wang^{1*}

¹Department of Chemical and Materials Engineering, Chung Cheng Institute of Technology, National Defense University, Tahsi, Taoyuan, 33509, Taiwan, R.O.C.

²Department of Chemical Engineering and Materials Science, Yuan Ze University
Chungli, Taoyuan, Taiwan, R.O.C.

³Fuel Cell Center, Yuan Ze University Chungli, Taoyuan, Taiwan, R.O.C.

Abstract

The aim of this study is focused on the design of ethanol reforming catalysts to produce hydrogen at low-temperature with higher ethanol conversion (X_{EtOH}), hydrogen yield (Y_{H_2}) and lower CO distribution. Highly dispersed PtRu/ZrO₂ catalyst was prepared by impregnation method. Evaluation of catalytic activities and products distribution toward ethanol reforming reactions were tested in a fixed bed reactor. Three processes of ethanol reforming were compared: steam reforming of ethanol (SRE), partial oxidation of ethanol (POE) and oxidative steam reforming of ethanol (OSRE). According to the distribution of products can be concluded that the optimal reaction temperatures (T_R) for POE, SRE and OSRE were 310 – 350 °C, 380 – 460 °C and 300 – 360 °C, respectively. Although the T_R of POE was lower, the hydrogen yield (Y_{H_2}) was lower (2.65 under 330 °C) and the CO distribution was higher (16% under 330 °C) than other reforming reactions. The highest Y_{H_2} (5.7 under 460 °C) and lower CO distribution (4% under 460 °C) was obtained through the SRE, while, the reaction required higher temperature to achieve.

Keywords: Reforming of ethanol, Zirconia, Hydrogen production.

*To whom the correspondence should be addressed.

E-mail address: chenbinwang@gmail.com and chenbin@ccit.edu.tw

Background

Hydrogen is a multi-function material that used widely as a feedstock in the petrol (hydrotreatment and hydrocracking process), chemical (ammonia and methanol synthesis), food processing (oil and fat hydrogenation), steel and electronics manufacture [1]. But hydrogen is not produced as an energy carrier or as a fuel for electric power generator by the present industry. Using hydrogen as an energy carrier can support sustainable global economic growth as well as reduce air pollution and greenhouse effect. However, there are several technical handicaps that have to be conquered to produce and transfer the great amounts of hydrogen that will be required in a hydrogen economy. Hydrogen can be produced from ethanol through different reforming processes, i.e., steam reforming of ethanol (SRE), partial oxidation of ethanol (POE) and oxidative steam reforming of ethanol (OSRE). The OSRE operation is the combined steam-reforming and partial-oxidation operation. Moreover, lowering the energy demand for the reforming operation, the operation has the main advantage of reducing the coke-formation rate. Based on thermodynamic analysis of hydrogen production from ethanol by catalytic processes, the OSRE process has many advantages in terms of heat management and reforming efficiency. Besides choosing a single active component (noble or non-noble metals) as the reforming catalyst, multi-component catalysts have been reported in various catalytic reactions. In particular, the catalytic ability of PtRu catalyst for hydrogen production in reforming reaction, a PtRu/ZrO₂ was an excellent catalyst for low temperature OSRE.

Effect of support on the OSRE reaction

Bimetallic PtRu catalysts were prepared by method of impregnation by using H₂PtCl₆ and RuCl₃ as precursors. Six supports (reducible oxides: ZrO₂, CeO₂, Co₃O₄ and irreducible oxides: ZnO, Al₂O₃, NiO) are chosen to prepare bimetallic catalysts. The

optimized molar ratios of $O_2/EtOH$ and $H_2O/EtOH$ feeds are 0.44 and 4.9, respectively. Under this reforming condition, the six bimetallic PtRu catalysts can completely convert the ethanol at low temperatures for reducible oxides (CeO_2 , $ZrO_2 \approx 280\text{ }^\circ C$, $Co_3O_4 > 300\text{ }^\circ C$) supported catalysts with only C_1 species (CH_4 , CO and CO_2). While, the ethanol at higher temperatures for irreducible oxides ($Al_2O_3 > 350\text{ }^\circ C$, $NiO > 400\text{ }^\circ C$, $ZnO > 450\text{ }^\circ C$) supported catalysts with C_1 species and a trace amount of C_2H_4 and CH_3CHO formation. Although the catalytic performance of PtRu/ Co_3O_4 catalyst is excellent, longer reaction periods produce a progressive deactivation of the activity by the carbon deposition. The hydrogen yield (Y_{H_2}) is high for PtRu/ NiO catalyst, while the reaction temperature (T_R) approaches high temperature that initiates the decomposition of ethanol to increase the S_{CO} as the T_R above $500\text{ }^\circ C$. Both PtRu/ Al_2O_3 and PtRu/ ZnO catalysts possess lower Y_{H_2} and higher S_{CO} . Among these catalysts, both PtRu/ ZrO_2 and PtRu/ CeO_2 are excellent OSRE catalysts to produce hydrogen at low temperature. The maximum Y_{H_2} is 4.4 and the CO distribution is 3.3 mol % under $340\text{ }^\circ C$ for PtRu/ ZrO_2 catalyst; the Y_{H_2} is 3.5 and the CO distribution is 3.0 mol % for PtRu/ CeO_2 catalyst, respectively.

Reforming of ethanol to produce hydrogen over PtRu/ ZrO_2 catalyst

The aim of this study is focused on the design of ethanol reforming catalysts to produce hydrogen at low-temperature with higher ethanol conversion (X_{EtOH}), Y_{H_2} and lower CO distribution. Three processes of ethanol reforming were compared: SRE, POE and OSRE. The SRE reaction requires higher temperature to achieve complete conversion of ethanol than both POE and OSRE reactions. According to the distribution of products can be concluded that the optimal reaction temperatures for POE, SRE and OSRE were $310 - 350\text{ }^\circ C$, $380 - 460\text{ }^\circ C$ and $300 - 360\text{ }^\circ C$, respectively. The distribution of CO is minor for both SRE and OSRE reactions ($< 4\%$ for both reactions). This demonstrates that the water gas shift (WGS) reaction is an important side-reaction in the reforming of

ethanol to produce H_2 and CO_2 . Although the T_R of POE was lower, the hydrogen yield (Y_{H_2}) was lower (2.65 under 330 °C) and the CO distribution was higher (16% under 330 °C) than other reforming reactions. The highest Y_{H_2} (5.7 under 460 °C) and lower CO distribution (4% under 460 °C) was obtained through the SRE, while, the reaction required higher temperature to achieve.

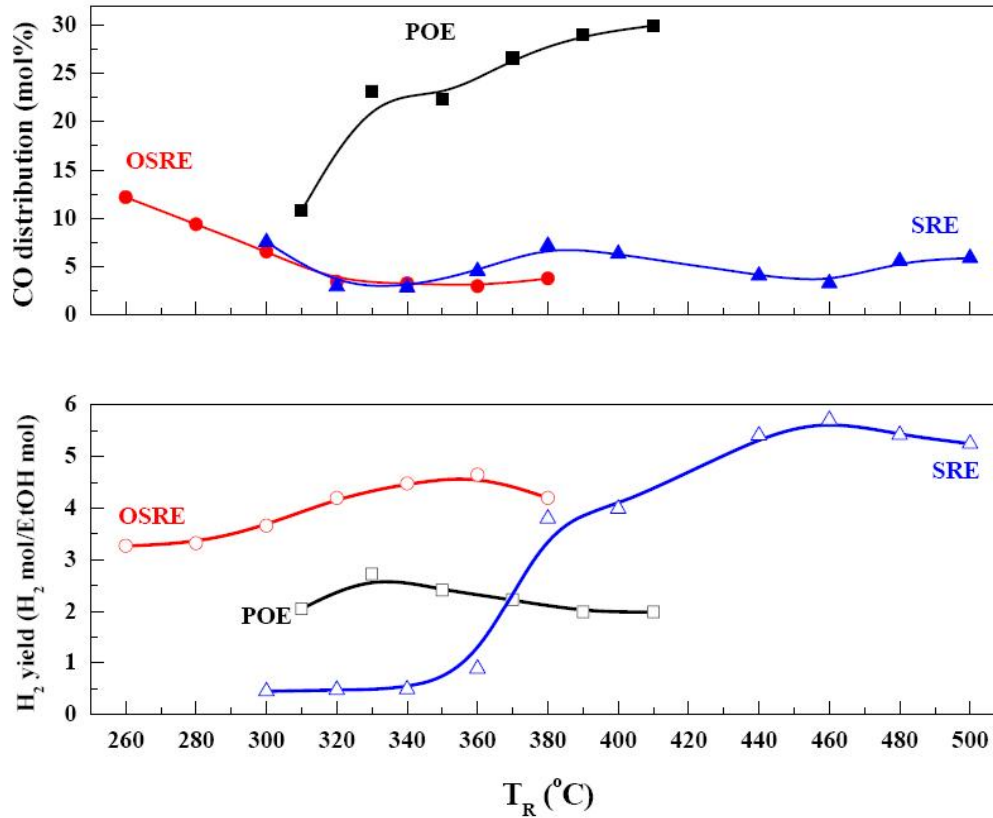


Figure Y_{H_2} and CO distribution for ethanol reforming reaction under various temperatures

Acknowledgements

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