臺灣二〇〇八年國際科學展覽會

科　　　　別 ：化學

作 品 名 稱 ：均相沉澱法製備 CZA 觸媒之探討

得 獎 獎 項 ：第一名
　　　　　　　美國正選代表：美國第 59 屆國際科技展覽會

學校／作者 ：臺北市立第一女子高級中學　　蘇意涵

作者簡介

我是蘇意涵，來自北一女中，很開心這次能利用學校專題研究課的機會深入探討自己所喜歡的能源領域，更希望我的科展結果能對當前的能源問題盡一份小小的心力。

做科展的過程讓我明瞭，研究是一條漫長而艱辛的路，在課業、家人、社團與休息時間中需要很大的毅力與決心才能取得適當的平衡。每次，當我多學到了一些，總能發現更多新的問題，但學習也就是因此而美好吧。

這次能進入國際科展複審程序令我感到相當的意外，但驚喜之餘最感謝的還是實驗室的學長、兩位全力幫助我的夥伴—韻心與嘉容、很關心我的教授、總是全力支持的熊老師、國珠老師與導師，常常要到實驗室接我回家的爸媽，還有所有一路陪伴我的溫班同學們，謝謝你們！

Study of CZA Catalysts Synthesized by Homogeneous Precipitation Method

均相沉澱法製備 CZA 觸媒之探討

摘要

本研究以均相沉澱法合成多成分的銅鋅鋁觸媒系統，並嘗試克服傳統共沉澱法的不均勻性且提高比表面積，過程中我們利用改變尿素濃度、水添加量、反應溫度與時間等四種變因成功合成出具有高活性的銅鋅鋁觸媒。研究得知最佳的合成條件為尿素 3M 並添加三倍體積的水，在 95℃ 下反應 2 小時。與傳統觸媒相比，均相反應合成的銅鋅鋁觸媒除了有較小的粒徑外，其還原溫度也較低，顯示較佳的觸媒活性。而在 250℃ 甲醇重組的製氫反應條件下，均相反應合成的銅鋅鋁觸媒也有較高的甲醇轉化效率、氫氣產生率以及 CO_2 的選擇率，而添加鈰與鋯可更進一步使觸媒活性再提升。未來除可利用此合成方法合成均勻性佳的多成份材料，亦可應用此高效能觸媒進行甲醇重組反應以產生氫氣提供燃料電池使用。

Abstract

Multi-composition Cu-Zn-Al catalyst system was synthesized by homogeneous precipitation method. This method was anticipated to improve the homogeneity of metal mixing and to increase the surface area of catalyst derived by conventional co-precipitation method. In the research, we successfully synthesized Cu-Zn-Al catalyst with high activity by adjusting four experimental parameters -- urea concentration, water amount, reaction temperature and reaction time. The better catalyst can be obtained under urea concentration of 3M diluted by 3 times water, and the kinetics conditions of 95℃ and 2h. Compared with the co-precipitation method, homogeneous precipitation method derived Cu-Zn-Al catalyst performed higher methanol conversion, hydrogen production rate and CO_2 selectivity under methanol reforming reaction at 250℃. Modifying the support by addition of Ce and Zr might further improve the activity of the catalyst. In the future, not only can this method apply on synthesizing other multi-composition materials with high homogeneity, but also the high performance catalyst can be used to do methanol reforming reaction in order to supply hydrogen on fuel cell.

研究動機

　　近年來能源短缺的問題日漸嚴重，全球皆積極開發取代石化燃料的新能源。高一時化學老師曾詳細介紹目前發展的各種能源技術，如太陽能、水力、風力、火力、生質能及燃料電池等。台灣地狹人稠，在太陽能及風力發電上有天然環境的限制，火力發電產生的廢氣則會加劇溫室效應的結果。而燃料電池不受天然環境限制，達到無污染、高效率的環保要求，能在開發新能源的同時兼顧環境保護，於是我們便決定利用專題研究的機會深入探討相關的主題。

　　氫能電池是近年來快速發展的燃料電池之一，由於它是一種直接能源轉換裝置，以直接電化學方式發電，理論上可以達到極高的效率，在電力的儲存與供應亦有其優勢。在蒐集資料的過程中，我們決定選擇以 Cu-Zn-Al 觸媒(以下簡稱 CZA 觸媒)作為研究的對象。CZA 觸媒是一種在甲醇蒸汽重組與甲醇氧化型蒸汽重組產氫方法中廣泛應用的觸媒，在活性、選擇性均有極佳的表現。目前工業上製備 CZA 觸媒多使用共沉澱方法，然而共沉澱方法在製備上分散性不佳，產生嚴重的濃度梯度效應。為了改善濃度梯度對觸媒的影響，並提高觸媒的比表面積，我們決定探討以均相沉澱方法製備 CZA 觸媒，希望觸媒反應達到更高的分散性與表面積。

研究目的

　　本實驗的研究目的在改良傳統 CZA 觸媒的製備方法，以期製造效能較佳的觸媒，並以最佳的反應條件製備其他不同種類觸媒。

壹、探討均相沉澱最佳的 CZA 觸媒反應條件。

貳、探討均相沉澱法製備 CZA 觸媒時，添加 Ce, Zr 活性金屬時反應情形及最佳的反應條件。

研究設備及器材

壹、實驗器材

項目	規格	數量
烘箱	373K 上述	1
磁石攪拌器		2
pH 計	小數點下兩位	1
Temperature Controller		1
回流管裝置		1
電子天平	小數下四位	1
抽氣過濾裝置		1
超音波震盪機		1
電子溫度計		2

貳、實驗試藥

試藥	英文名稱	分子量	廠牌	純度
$Cu(NO_3)_2 \cdot 3H_2O$	Copper Nitrate	241.59	ACROS CHIMCA N.V	99%
$Zn(NO_3)_2 \cdot 6H_2O$	Zinknitrat Hexahydrat	297.46	ACROS CHIMCA N.V	98%
$Al(NO_3)_3 \cdot H_2O$	Aluminiumnitrat Nonahydrat	375.13	ACROS CHIMCA N.V	99%
$Fe(NO_3)_3 \cdot 9H_2O$	Iron Nitrate	403.99	ACROS CHIMCA N.V	99%
NH_2CONH_2	Urea	60.06	林 純藥工業	99%
$Ce(NO_3)_3 \cdot 6H_2O$	Cerium Nitrate	434.22	ACROS CHIMCA N.V	99.50%
$NaOH$	Sodium hydroxide	40	ACROS CHIMCA N.V	99%
Na_2CO_3	Sodium carbonate	105.99	ACROS CHIMCA N.V	99%
$N_2O_7Zr \cdot H_2O$	Zirconium Nitrate	231.23	ACROS CHIMCA N.V	99.50%

## 參、實驗儀器

一、 SEM (scanning electron microscope) ──掃描式電子顯微鏡。

二、 XRD(X-ray diffraction) ──X 光繞射儀。

三、 TPR(Temperature Programming Reduction) ──程溫還原分析。

四、 GC(Gas Chromatograph) ──氣相層析儀。

五、 ICP(inductively coupled plasma Optical Emission Spectrometry) 感應耦合電漿光學放射光譜儀分析

研究過程及方法

壹、 均相沉澱法之探討(homogeneous precipitation method)

傳統共沉澱方法為工業上製備 CZA 觸媒時廣泛使用的方法，在配製 Cu, Zn, Al 之硝酸鹽溶液後藉由緩緩加入鹼源之方式(例如：氫氧化鈉、碳酸鈉等)提升其 pH 值。然而共沉澱方法在反應過程中會造成嚴重濃度梯度問題，進而影響產生觸媒之均勻度，因此本實驗試圖以均相沉澱方法改善此缺點。均相沉澱法與共沉澱法的主要差異在於加入鹼源的方式，而前者採取利用加熱尿素水解產生之 OH 改變溶液的 pH 值，反應式如下所示：

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_4^+ + HCO_3^- + OH^-$$
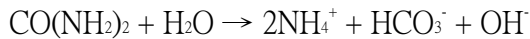
在均相沉澱法實驗中，由於我們於加熱之前將尿素溶於 CZA 之硝酸鹽溶液，因此在反應進行時，尿素分子在水中呈均勻分布並隨溫度提升產生 OH⁻，減少濃度梯度的問題。

首先，我們進行對照組：傳統共沉澱方法實驗，再與均相沉澱法的結果做比較。

貳、 共沉澱方法(co-precipitation method)

以 Na_2CO_3 滴定銅鋅鋁硝酸鹽水溶液並控制酸鹼值至 pH=7~pH=8 之間，再將沉澱物以抽氣過濾方式取出，經熱處理後得所要粉體。

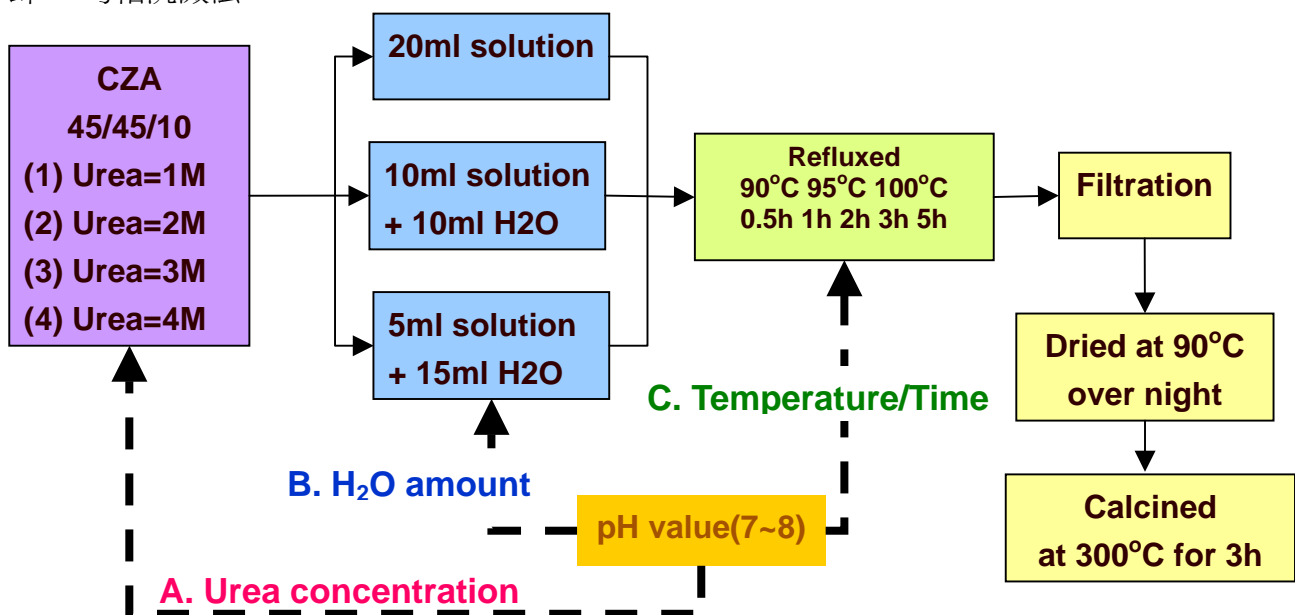## 參、 均相沉澱法預備實驗(homogeneous precipitation method)

一、 目的

觀察 $Cu^{2+}, Zn^{2+}, Al^{3+}$ 三種金屬離子在不同酸鹼值環境中沉澱狀態，並探討最佳條件。

二、 實驗方法

將 Cu,Zn,Al 三種金屬硝酸鹽溶於水中，於室溫或 363K 環境中以 NaOH 改變其酸鹼值，並記錄沉澱情形。

肆、 均相沉澱法

由文獻中得知以共沉澱方法製備CZA觸媒時，當Cu/Zn/Al氧化物比率 45/45/10(weight

percent wt%)之觸媒有較佳的反應結果。於是在接下來的實驗中我們們採取此比率使用均相沉澱方法製備 CZA 觸媒，並比較兩種方法之差異。

一、 均相沉澱法之預備實驗

1. 目的

　　為使製備 CZA 觸媒時能有效控制活性金屬之比例，觀察 $Cu^{2+}, Zn^{2+}, Al^{3+}$ 三種金屬離子在不同溶液及酸鹼值環境中之沉澱狀態，並探討最佳沉澱條件。

2. 實驗方法

　　將 Cu、Zn、Al 三種金屬硝酸鹽溶於 100mL 水中，於室溫或 363K 環境中以 NaOH(0.5M)改變其酸鹼值，每 1~2 pH 值取一小瓶溶液(20mL)，並記錄沉澱情形。

二、 調整尿素濃度：

　　由預備實驗的結果得知，當反應環境酸鹼值介於 pH=7~pH=8 之間時，可有效控制製備過程中沉澱金屬比例。於是接下來我們嘗試以調整尿素的濃度控制反應環境的酸鹼值，試圖達到 pH=7~pH=8 之間的要求。

三、 調整水的濃度：

　　由於得知前項實驗反應結果不如預期，必須加入高濃度的尿素才能將酸鹼值控制在 pH=7~pH=8 之間，因此在接下來的實驗中我們改變研究方向，尋求不同的方法調整酸鹼值。

　　在尋找不同方法時，我們想到尿素水解的反應中有 OH⁻ 生成，因此添加水促進水解反應可以提高反應環境的酸鹼值，且水自身的酸鹼值約為 7，同樣可以提高反應環境酸鹼值。因此決定調整溶液中水的濃度，並控制反應後溶液酸鹼值至 pH=7~pH=8 之間。

四、 調整反應溫度與反應時間：

　　在確定最佳反應的酸鹼值條件、反應溶液中水濃度後，接下來的實驗探討反應時間與反應溫度對反應情形與酸鹼值的影響。

五、 分析：

1. SEM (scanning electron microscope)：

　　藉由掃描式電子顯微鏡觀察所製作之 CZA 觸媒於不同條件中微觀的形貌。

2. XRD(X-ray diffraction)：

　　利用 XRD 繞射分析所得之圖譜，與標準圖譜相比對，藉以得知所製作之觸媒中含有的化合物種類與結構。

3. TPR(Temperature Programming Reduction)分析：

　　可決定樣品上還原性基的總數。可得知觸媒自身還原反應時的溫度、反應性氣體的濃度與反應的溫度區間。

4. GC (Gas Chromatograph) ─ 氣相層析儀：

　　　　將經甲醇重組反應後的氣體通入 Column 中，藉由其內填充物與攜帶氣體(He,Ar)的性質將氣體中的物質分離。

	Column	Carrier gas	Analysis
A	Porapak Q	He	CO_2, CH_3OH, H_2O
B	Molecular sieve 13X	He	CO, CH_4
C	Molecular sieve 13X	Ar	H_2

　　　　在甲醇重組反應過程中使用氣相層析儀即時分析反應產生的氣體，可得到不同的分析圖譜，其中不同氣體分子的滯留時間及訊號強度可用於判斷氣體的種類和濃度。

5. ICP (inductively coupled plasma Optical Emission Spectrometry) 感應耦合電漿光學放射光譜儀

　　　　以電感耦合電漿(ICP)作為離子源，將元素在 ICP 中離子化，以分析溶液中微量元素的儀器。

六、 添加 Ce, Zr 的反應情形：

　　　　為了降低產氫過程中一氧化碳產生量，我們設計實驗，探討在 CZA 觸媒中加入 Ce 與 Zr 元素的反應情形。

1. 目的：

　　　　探討均相沉澱法合成 CZA 觸媒中添加 Ce, Zr 金屬的反應結果。

2. 實驗方法：

　　　　配製尿素濃度為 3M 條件下，Cu/Zn/Al/Ce/Zr 金屬氧化物比例分別為 45/45/10/0/0, 45/45/0/10/0, 45/45/5/5/0, 45/45/5/2.5/2.5, 45/45/0/5/5 的溶液並進行 TPR 測試。

　　　　由於反應結果顯示相較之下 Cu/Zn/Al/Ce/Zr 金屬氧化物比例為 45/45/0/10/0, 45/45/0/5/5 的催化劑之還原溫度高於其他三種約 20℃，因此我們設計實驗，對催化劑製備的反應過程進行進一步的探討。

1. 目的：

　　　　進一步探討均相沉澱法合成 CZ 觸媒中添加 Ce, Zr 金屬製備過程中反應情形。

2. 實驗方法：

A. 配製尿素濃度為 3M 條件下，Cu/Zn 濃度分別為 0.005M/0, 0/0.005M, 0.005M/0.005M ，Cu, Zn, Ce, Zr 金屬氧化物比例分別為 40/40/10/10, 40/40/10/0, 40/40/0/10 的溶液。

B. 將上述溶液分別分裝入 25 管 10mL 離心管，並將管蓋蓋緊以減少水量蒸發對反應的影響。

C. 將 25 管離心管以超音波震盪機震盪加熱至 90℃ 反應，每 5 分鐘取出一管後放入冰浴使其立即停止反應。
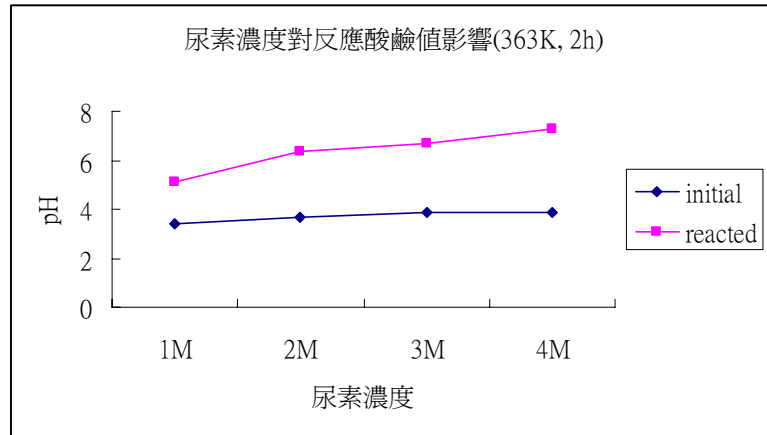
D. 重複以上步驟至 50 分鐘後改相隔 10 分鐘取出一管。
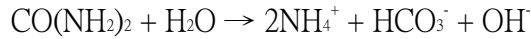
E. 測量並記錄 25 管反應後 pH 值並分析反應結果。
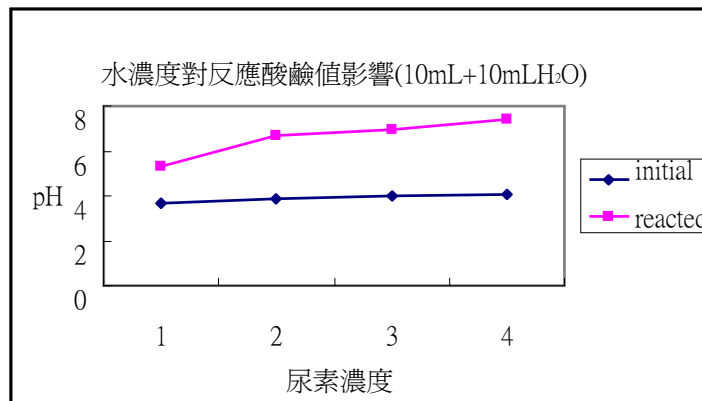
結果與討論

壹、改變酸鹼值

一、 調整尿素濃度

尿素濃度 1M~4M 溶液原始酸鹼值皆低於 pH=4，反應後溶液酸鹼值則有明顯的上升。然而即使溶液濃度最高可達 pH=7.28，消耗尿素的量仍然太多，效率不盡理想，因此接下來的實驗改採不同變因調整反應環境的酸鹼值。

二、 調整水的濃度

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_4^+ + HCO_3^- + OH^-$$

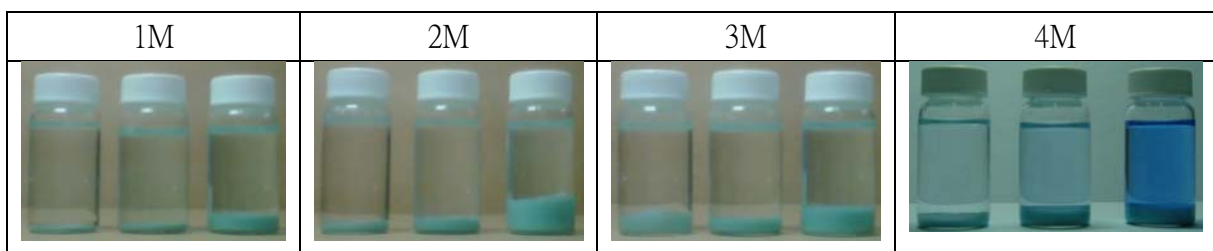由於尿素水解的反應式中，水為反應物，且其 pH 值為 7，反應後亦有 OH 基生成，因此我們推測添加水可有效提高反應環境的酸鹼值。為了達到酸鹼值介於 7~8 之間的效果，此部分實驗配置水濃度不同之溶液，並控制溫度於 363K 持溫反應兩小時。

首先取 10mL 的原溶液，添加 10mL 的水進行反應。由圖表中可以得知，反應前後各種尿素溶液酸鹼值皆明顯上升，且反應後的酸鹼值高於原先未加水的溶液。其中，加入 10mL 水的 4M 尿素溶液在反應後酸鹼值高達 pH=7.43，符合 pH=7~8 之間的要求。

水濃度對反應酸鹼值影響 (5mL+15mL H2O)
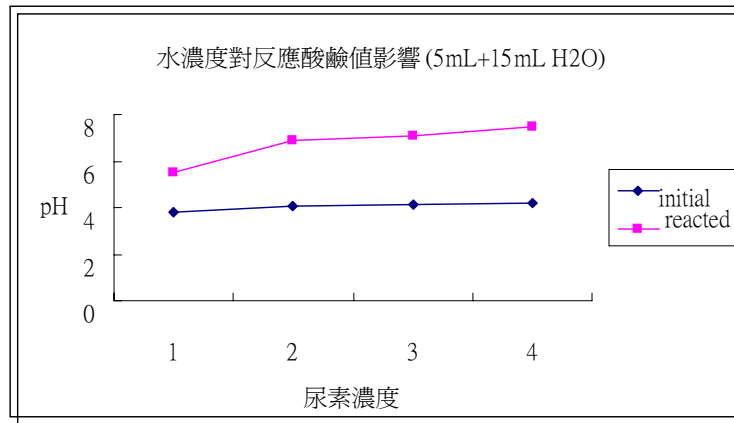
　　在 5mL+15mL H_2O 的反應中，依然可以得知反應前後各種不同濃度尿素溶液的酸鹼值均呈現明顯上升，且在同一濃度溶液中，加入水之溶液酸鹼值明顯高於未加水及加水 10mL 的結果。而在反應後，3M 與 4M 的濃度分別是 pH=7.11 與 pH=7.46，均符合所期望 pH=7~pH=8 範圍之間。

Urea conc(added)	20mL		10mL+10mL H_2O		5mL+15mL H_2O	
	initial	reacted	initial	reacted	initial	reacted
1M	3.43	5.13	3.64	5.32	3.80	5.48
2M	3.68	6.33	3.88	6.69	4.05	6.90
3M	3.84	6.72	4.01	6.96	4.16	7.11
4M	3.90	7.28	4.08	7.43	4.19	7.46

↑由右而左分別為 20mL, 10mL+10mL H_2O, 5mL+15mL H_2O 之圖片

　　由上述照片可知，在 4M 的反應情形中，10mL+10mL H_2O 與 5mL+15mL H_2O 兩個反應後溶液皆帶有藍色，推論是銅離子再度溶於溶液中的結果，這代表產生的沉澱物中金屬比例和反應物比例相較發生改變，難以維持其最佳比例，因此不選擇這兩種反應條件。而 4M, 20mL 與 3M, 5mL+15mL H_2O 兩種條件比較之下，由於兩者的酸鹼值差小於 0.2，而尿素量使用量卻相差很多，因此決定選取 3M, 5mL+15mL H_2O 條件為最佳反應條件。

三、 調整反應溫度與反應時間

上述實驗結果中，選取 3M, 5mL+15mL H_2O 為最佳反應條件，因此接下來將針對此條件，探討不同反應溫度與時間的反應情形。

5mL +15mL H_2O	90℃ 2h	90℃ 5h	95℃ 2h	95℃ 3h	100℃ 0.5h	100℃ 1h	100℃ 2h
2M					7.15		8.53
3M	7.11	7.97	7.63	8.09	7.53	8.22	8.56
4M							8.6

1. 100℃ 反應：

首先提高反應溫度至 100℃ 並進行持溫兩小時之反應，得知 2M, 3M 的反應酸鹼值均高於 pH=8.5，遠遠高於所期望的 pH=7~8 之間，於是在接下來實驗中進行修正。藉由縮短反應時間，分別進行 0.5 和 1 小時的實驗，得知反應後的酸鹼值與持溫兩小時的反應結果相較有明顯的降低，由此可推論反應溫度的高低及時間的長短皆能影響溶液的酸鹼值，溫度越高、時間越長酸鹼值越高。

2. 修正 2M 條件測試：

即使先前實驗中已確認 3M 為最佳尿素反應濃度。但由於在 100℃ 的實驗中得知，改變尿素濃度會對酸鹼值造成影響，因此再次修正實驗，添加尿素濃度為 2M 之溶液，恆溫 100oC 持溫 0.5 小時。得知與 100℃ 2h 的結果相較，其酸鹼值有明顯的下降，且落在設定的 pH=7~pH=8 範圍內。

3. 90℃ 反應：

由於在前項實驗中得知延長反應時間會提高溶液酸鹼值，因此我們推測在較低反應溫度也能以此方法提高溶液酸鹼值。因此在接下來的實驗中再次修正反應條件，進行恆溫 90℃ 持續 5 小時的實驗。由結果圖表可以得知，恆溫 90℃ 持續 5 小時的反應結果酸鹼值在 pH=7~8，符合期待的酸鹼值 pH=7~pH=8 之間。而由於 90℃ 恆溫 5 小時的 pH 值接近 pH=9, 因此我們降低反應時間，進行 90℃ 2h 之反應，得知其 pH 值為 7.11。

4. 恆溫 95℃：

就持續 2 小時，尿素濃度 3M 的反應比較，在 90℃ 與 100℃ 的反應結果相差太大 (分別為 pH=7.11, pH=8.56)，因此將實驗的反應溫度調整為恆溫 95℃，分別進行反應時間為 2 小時與 3 小時的實驗，並觀察其反應結果。由結果可以得知，與反應 3 小時相較，95℃ 持續兩小時的反應酸鹼值為 7.63，且反應時間較短，符合經濟效益，顯然是較好的條件。

90℃ 5h	95℃ 2h	95℃ 3h	100℃ 0.5h	100℃ 1h	100℃ 2h
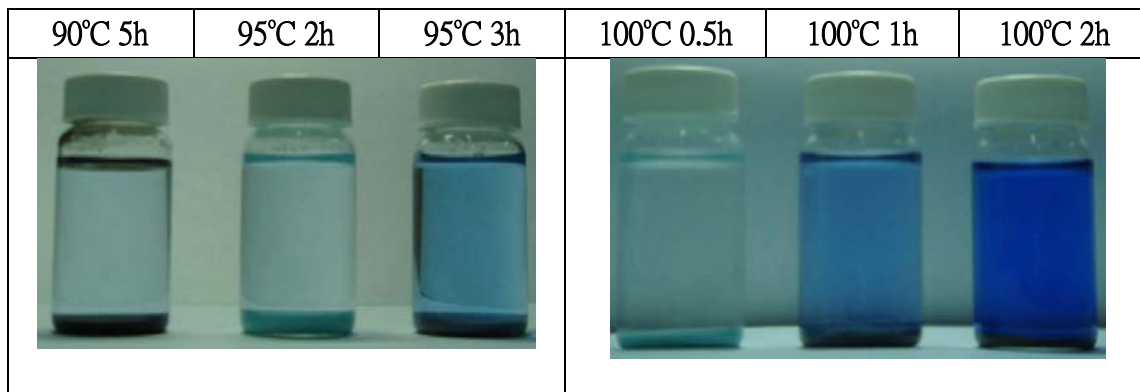
5. 溶液沉澱情形分析：

　　就溶液沉澱比較可以得知，95℃ 3h, 100℃ 1h, 100℃ 2h 三種條件下反應後的溶液非澄清透明，而帶有藍色，推測是銅離子再度溶於溶液中的結果，可能造成金屬組成比例與最初預設值不同，故不取這三組數據。

6. 討論：

　　綜合上述結果，可以得知反應溫度對溶液酸鹼值的影響較反應時間大，因為當反應溫度由 90℃ 增加至 100℃ 時，酸鹼值增加了 1.45，而當反應時間延長為 5h 時，酸鹼值則僅增加了 0.86。另外在 90℃ 持續五小時的反應中，因反應時間太長，較不符合經濟效益。100℃ 持續 0.5hr 的反應即使可以達到極佳的酸鹼值要求，但由於 100℃ 水會有劇烈的沸騰現象，即使有迴流管裝置還是會對反應造成影響，且由 XRD 分析可得知其觸媒結構因反應時間太短而尚未反應成我們所希望的化合物。因此，相較之下，選擇尿素濃度 3M，恆溫 95℃ 持續 2 小時為最佳反應條件。
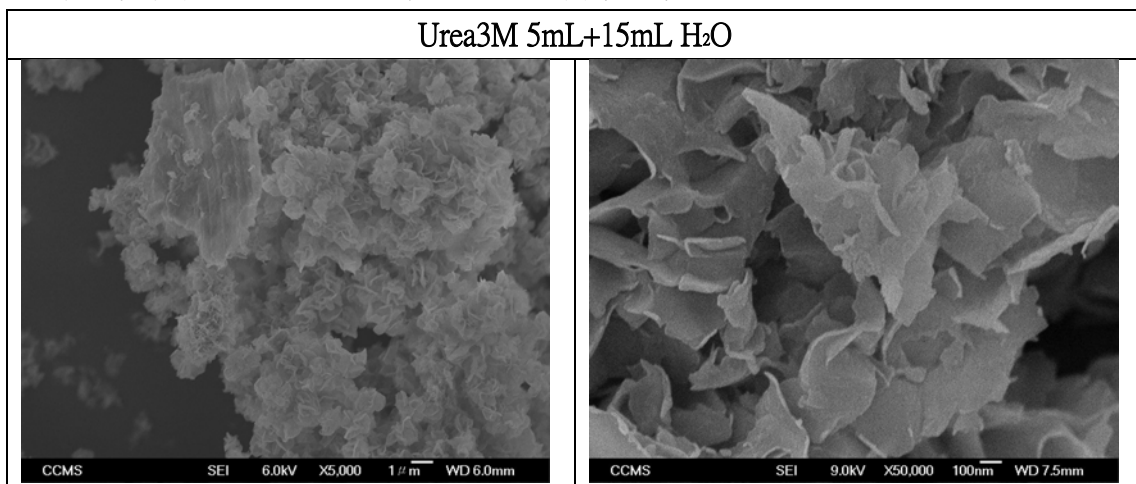
貳、觸媒特性分析

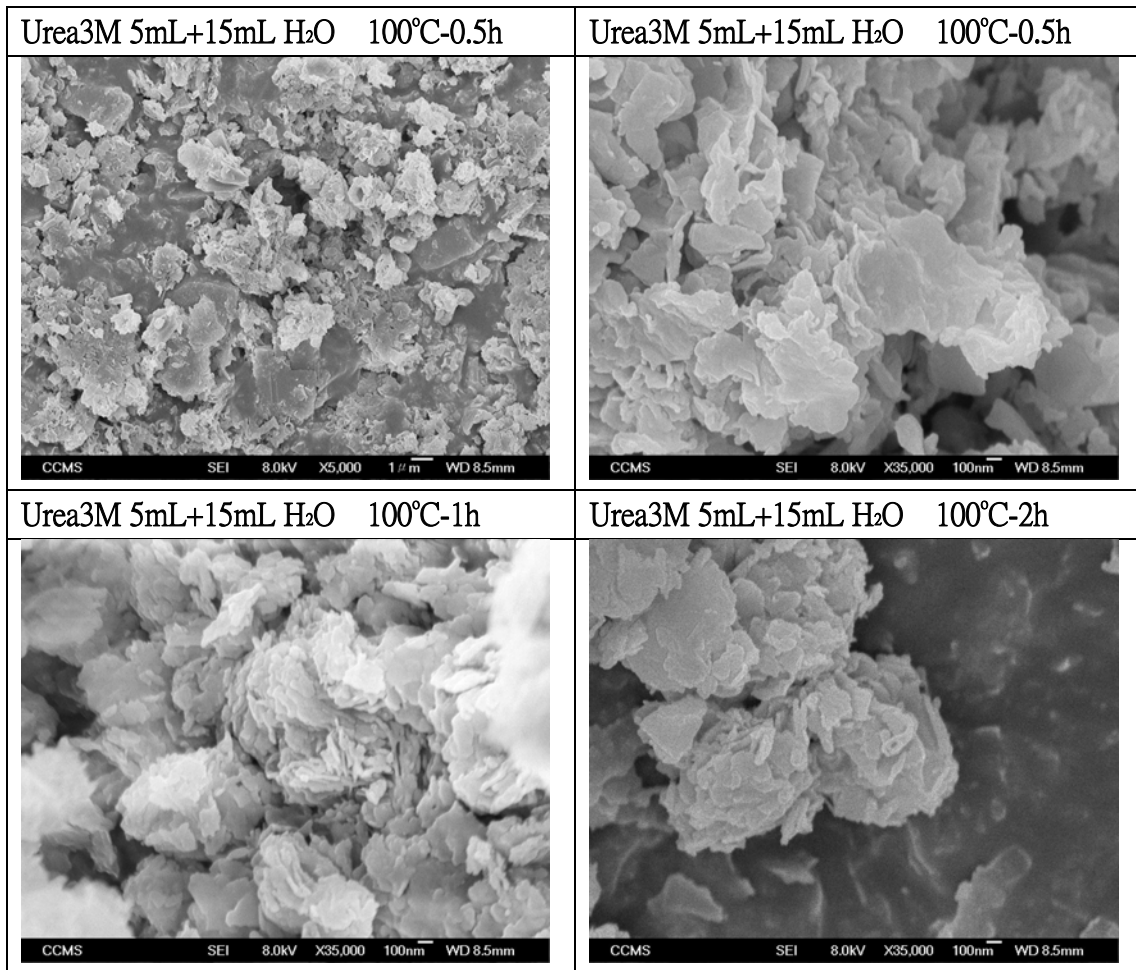在完成上述實驗後，將不同條件下製備的溶液以抽氣過濾法過濾，其沉澱物經烘乾後製成粉末，而後進行熱處理，並透過以下分析探討沉澱物的性質。

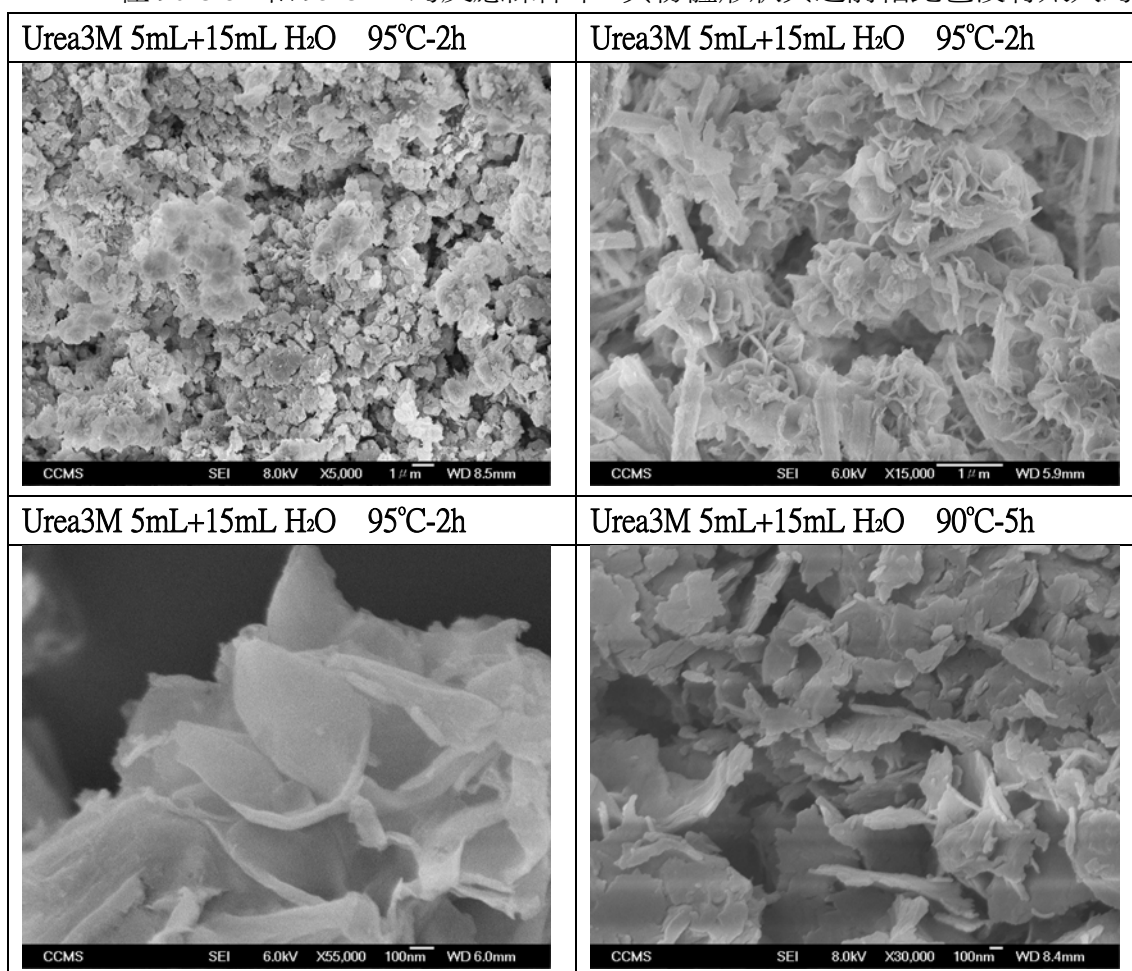一、 SEM 圖譜

由 SEM 圖譜中可以得知，隨著尿素濃度由低到高時的表面狀態，大約是偏長條狀到趨近於破碎小塊狀的結構。

Urea1M 20mL	Urea2M 20mL
Urea3M 20mL	Urea4M 20mL
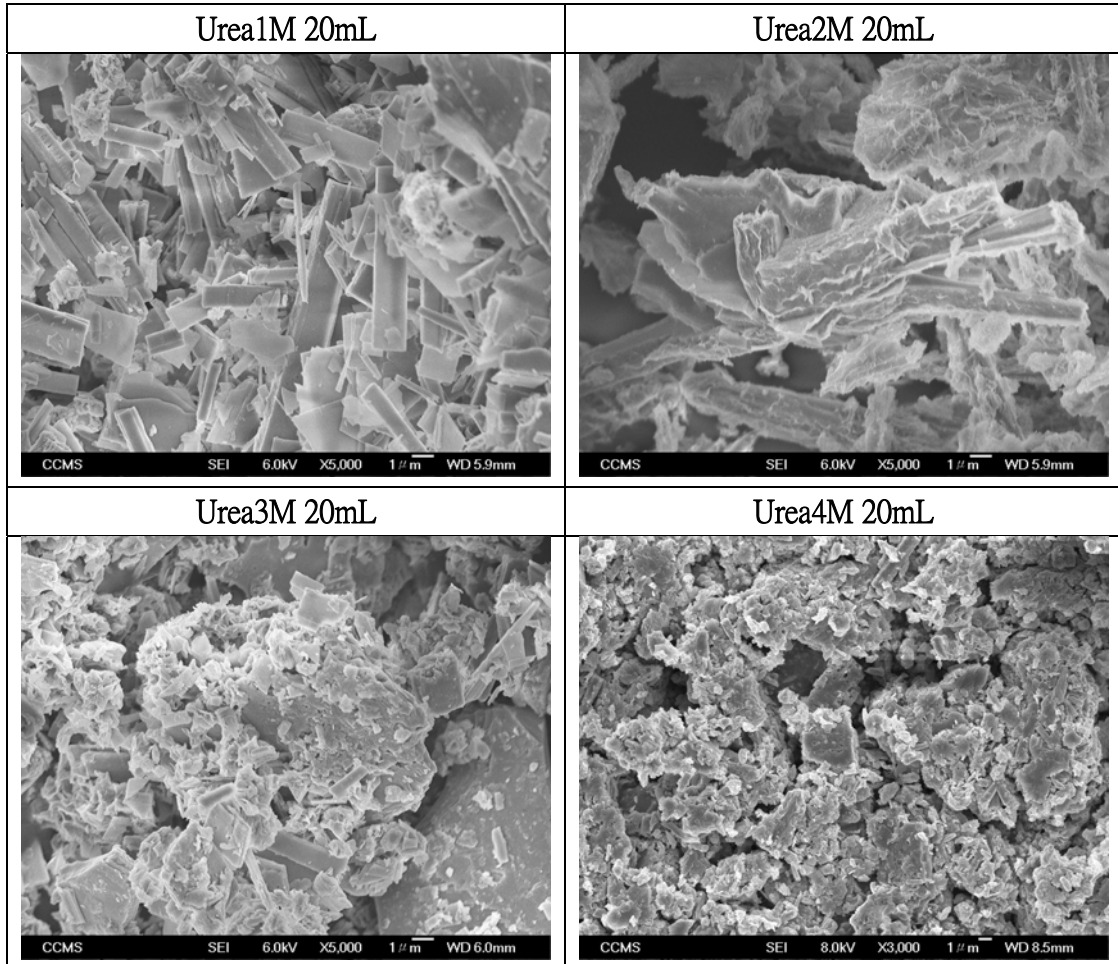
水濃度較高之溶液，觸媒表面趨近於片狀結構。

Urea3M 5mL+15mL H₂O	

在 100℃ 的反應溫度下，不同反應時間的粉體外觀看起來相當類似，均呈現破碎的片狀結構。

Urea3M 5mL+15mL H₂O　100℃-0.5h	Urea3M 5mL+15mL H₂O　100℃-0.5h
Urea3M 5mL+15mL H₂O　100℃-1h	Urea3M 5mL+15mL H₂O　100℃-2h

在 90℃-5h 和 95℃-2h 的反應條件下，其粉體形狀與之前相比也沒有太大的變化。

Urea3M 5mL+15mL H$_2$O　95℃-2h	Urea3M 5mL+15mL H$_2$O　95℃-2h
Urea3M 5mL+15mL H$_2$O　95℃-2h	Urea3M 5mL+15mL H$_2$O　90℃-5h

　　爲了與傳統合成方法作比較，我們選擇均相沉澱法中的最佳合成條件合成的觸媒與共沉澱法的觸媒作比較。

Catalyst name	Base source	Synthesis condition
CP-CZA(共沉澱法)	Na$_2$CO$_3$	RT
HP-CZA(均相沉澱法)	Urea = 3M 5mL+15mLH$_2$O	95℃ 2h

CP-CZA (precursor)	HP-CZA (precursor)
CP-CZA (after 300℃ heating)	HP-CZA (after 300℃ heating)
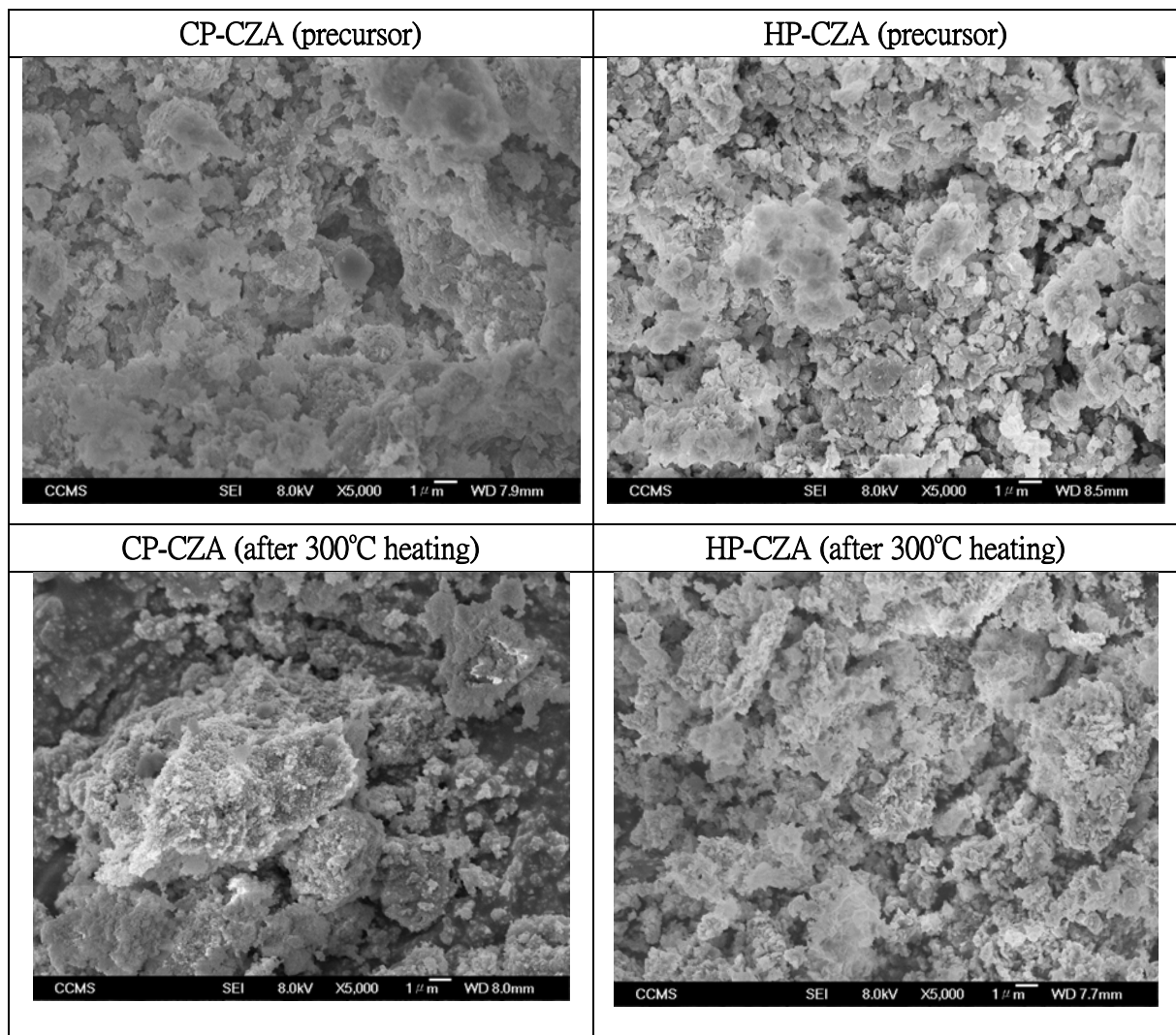
比較 CP-CZA 與 HP-CZA 兩種方式合成的粉體得知，均相沉澱法所合成的粉體呈分散花朵狀的結構，粒徑較小，而共沉澱法的粉體在經過 300℃ 熱處理後有嚴重聚集現象。

二、 XRD 圖譜：
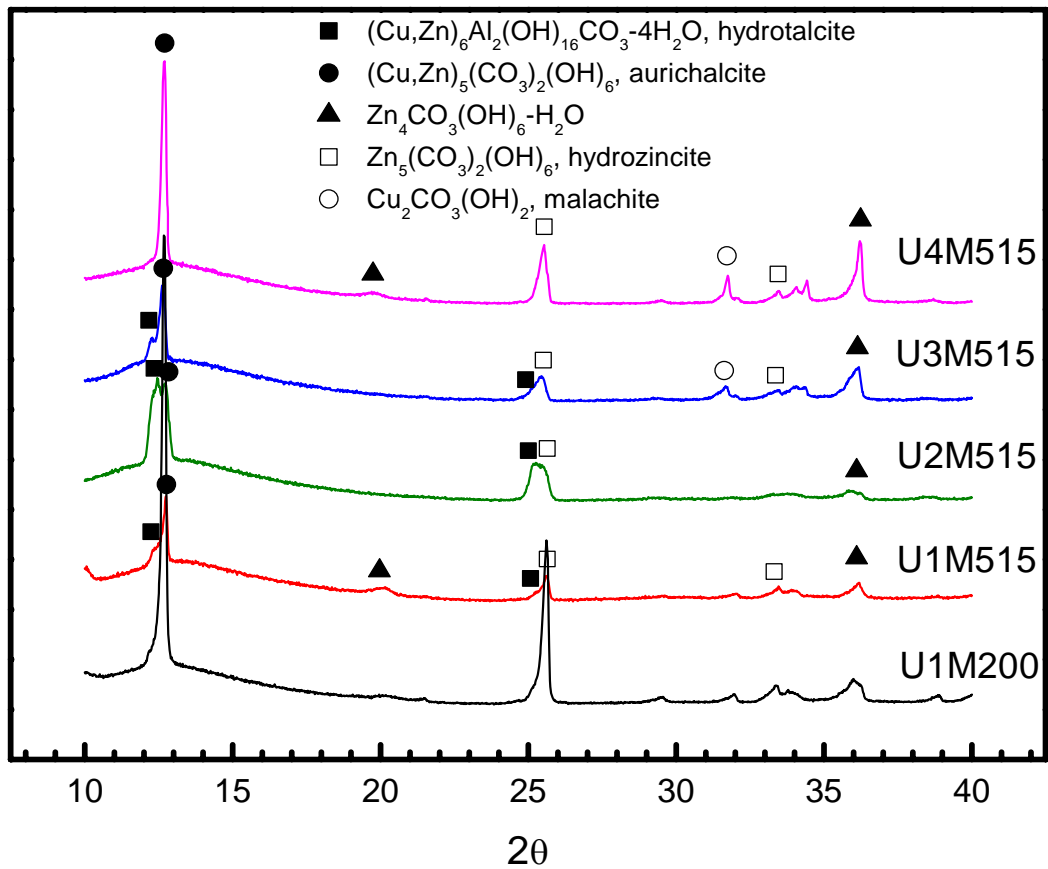
上圖是不同尿素濃度經由 XRD 繞射分析所得出的圖譜，藉由與標準圖譜的比對，得知會產生下列數種化合物：

$(Cu,Zn)_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, hydrotalcite

$(Cu,Zn)_5(CO_3)_2(OH)_6$, aurichalcite

$Zn_4CO_3(OH)_6 \cdot H_2O$

$Zn_5(CO_3)_2(OH)_6$, hydrozincite

$Cu_2CO_3(OH)_2$, malachite

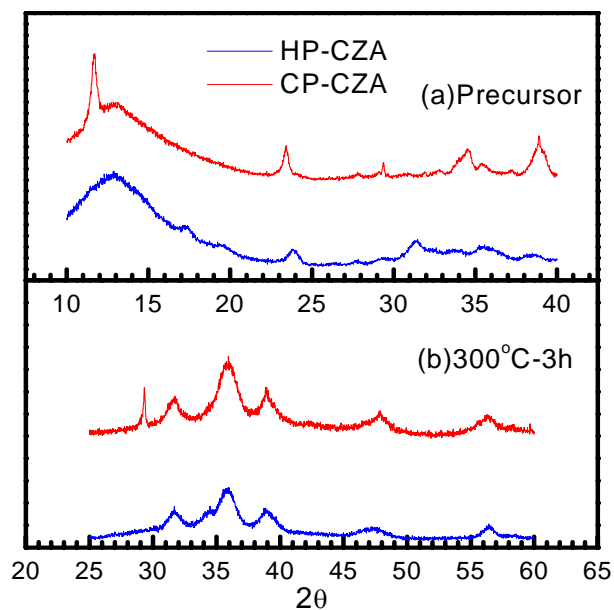在尿素濃度為 1M 的條件下，可以得知在繞射角 13° 左右的繞射峰的訊號強度，遠遠大於其他條件，而由 SEM 的結果可得出其形狀為長條狀。
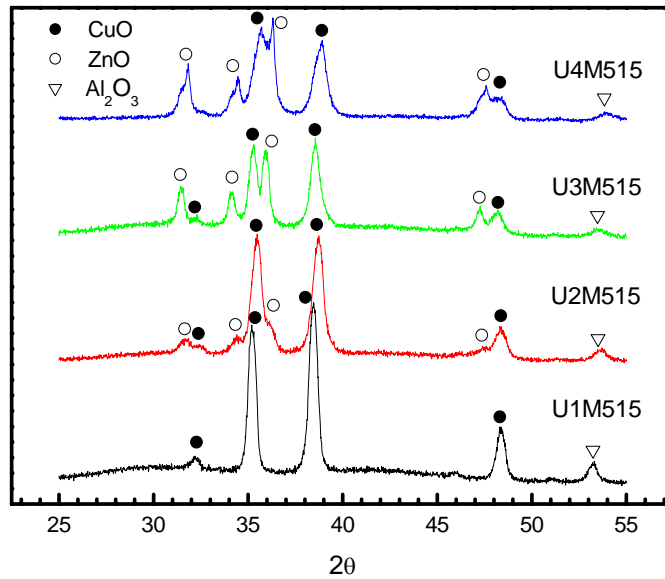
上圖是 300℃ 持溫 3 小時熱處理的 XRD 結果，可得知大部份均是 Cu、Zn、Al 相關氧化物結構。其中 U1M515 的條件下，並沒有發現 ZnO 的繞射峰訊號，推測可能是酸鹼值較低，鋅離子的沉澱量不足所致。
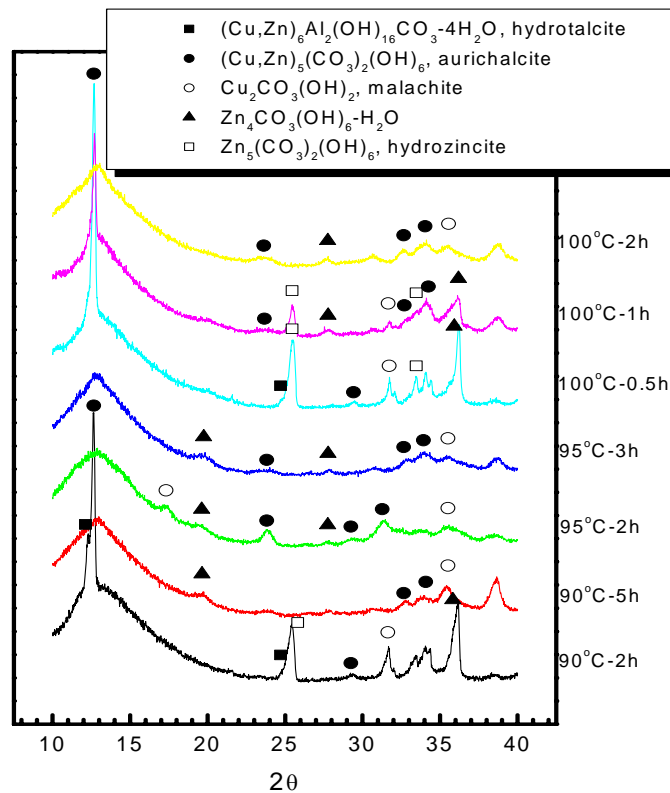
由圖表中比較得知，酸鹼值相同的綠色(95℃-2h)、紅色(90℃-5h)、深藍(95℃-3h)、粉紅(100℃-1h)四曲線，產生的化合物有相似的組成，繞射峰寬度較寬，峰形較不明顯，由 SEM 分析也可得知其表面結構較破碎。
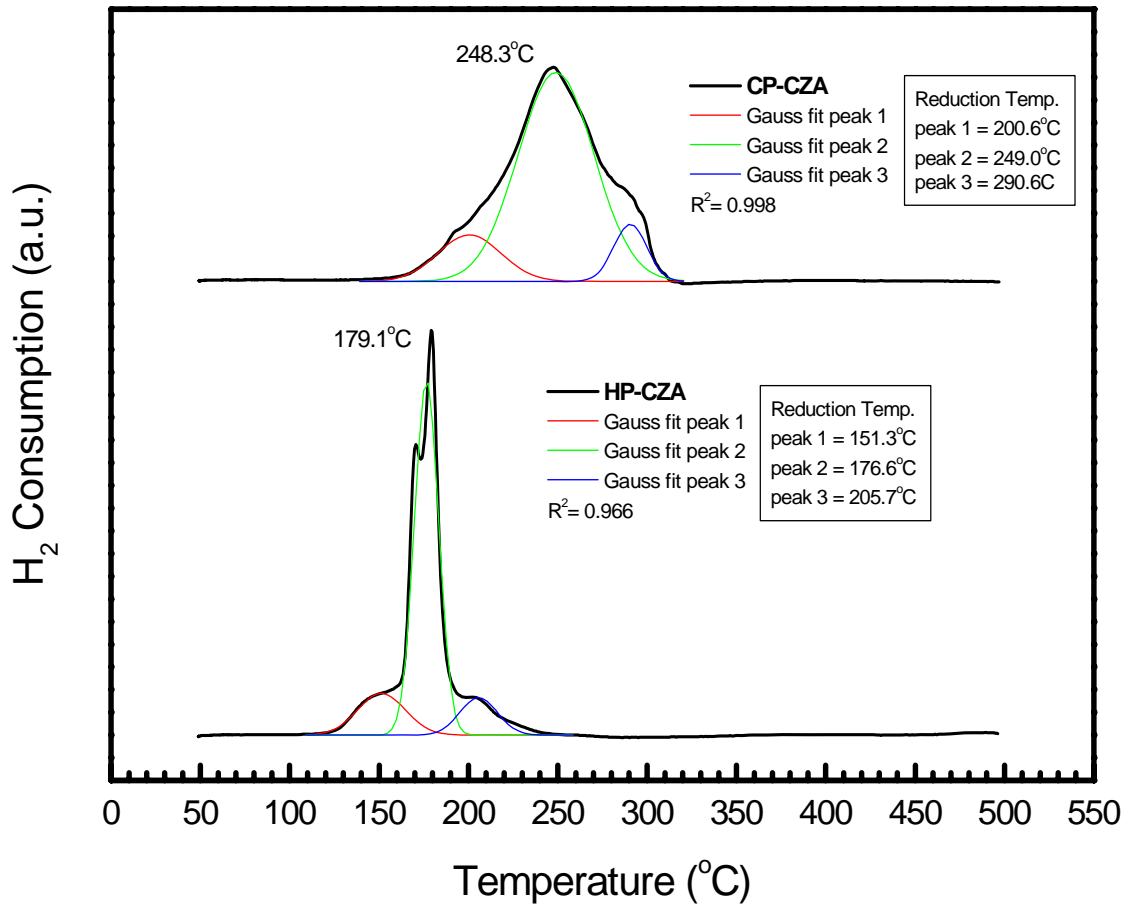
由其他曲線的比較可以得知，當反應時間縮短時，繞射峰的峰形較明顯，可由此得知反應時間的長短會影響結構的變化。

CP-CZA 曲線為利用 Na_2CO_3 以傳統共沉澱方法製備觸媒的分析結果。透過繞射譜數據資料庫比對可得知與均相沉澱法製出的觸媒結構相似，且其圖譜分析結果近於 90℃ 恆溫反應五小時所得的結果。

經過 X 光繞射譜測量與數據資料庫比對後，可得知圖譜中主要的組成是 CuO 與 ZnO。另外以均相沉澱法製備的觸媒，相對共沉澱法而言其繞射峰的寬度較寬，可知其粉體粒徑大小較小。

三、 觸媒活性測試： TPR (Temperature Programming Reduction)圖譜：

由圖譜可知均相沉澱法製備的 CZA 觸媒還原溫度(179.1℃)較共沉澱法(248.3℃)低，代表均相沉澱法製備的觸媒有較高的活性。

由峰的寬度比較可得知均相沉澱法製作之觸媒分析的結果寬度較窄，代表均相沉澱法製備的觸媒在較小的溫度區間內就可還原，反應較易進行。

圖表中顯示非高斯對稱曲線，經過分析後得知 Cu 的化學環境相當複雜，至少有三種上述不同的反應環境。

參、甲醇重組反應：

在進行活性測試前，先透過還原反應將氧化銅還原為金屬銅，使其具有活性。還原條件為在 $H_2/N_2 = 10\%$的環境下於 350℃ 持溫 2 小時，之後再於 250℃ 下進行甲醇重組反應。

在反應過程中使用氣相層析儀即時分析反應產生的氣體，可以得到不同的分析圖譜，由其中不同氣體分子的滯留時間及訊號強度可以判斷氣體的種類和濃度。

GC	Column	Carrier gas	Analysis
A	Porapak Q	He	CO_2, CH_3OH, H_2O
B	Molecular sieve 13X	He	CO, CH_4
C	Molecular sieve 13X	Ar	H_2
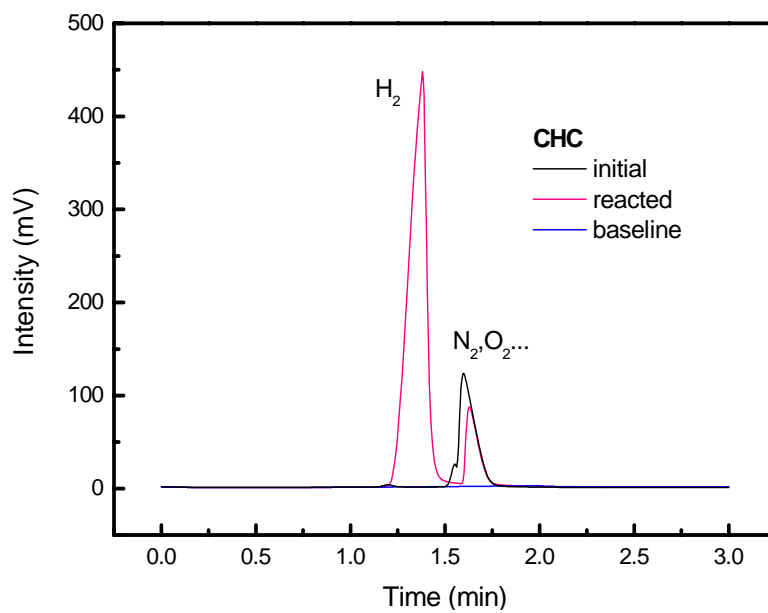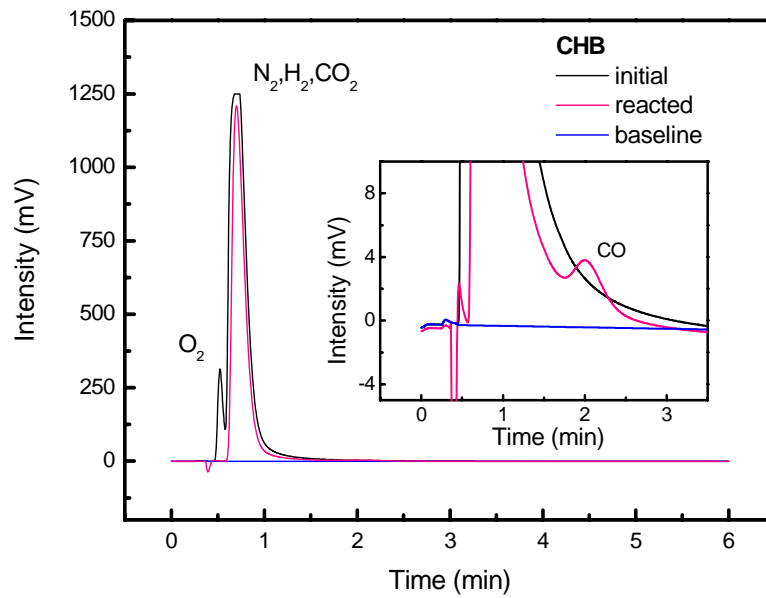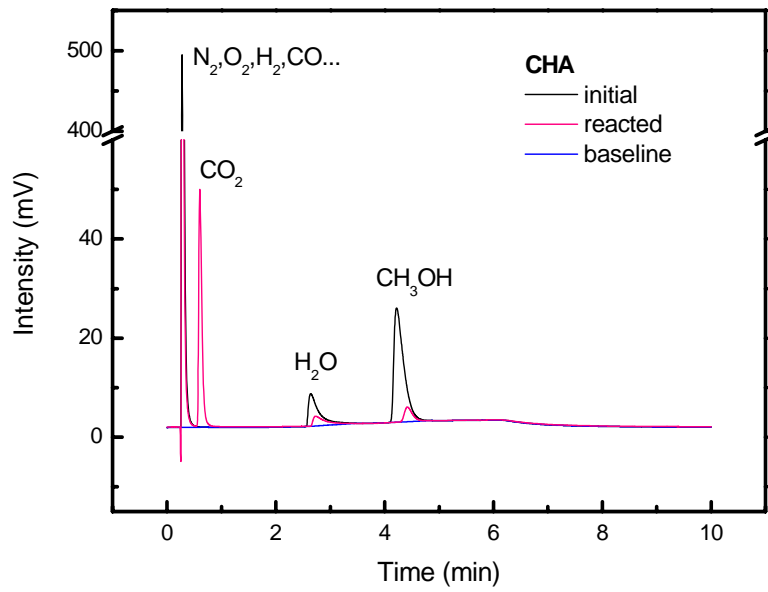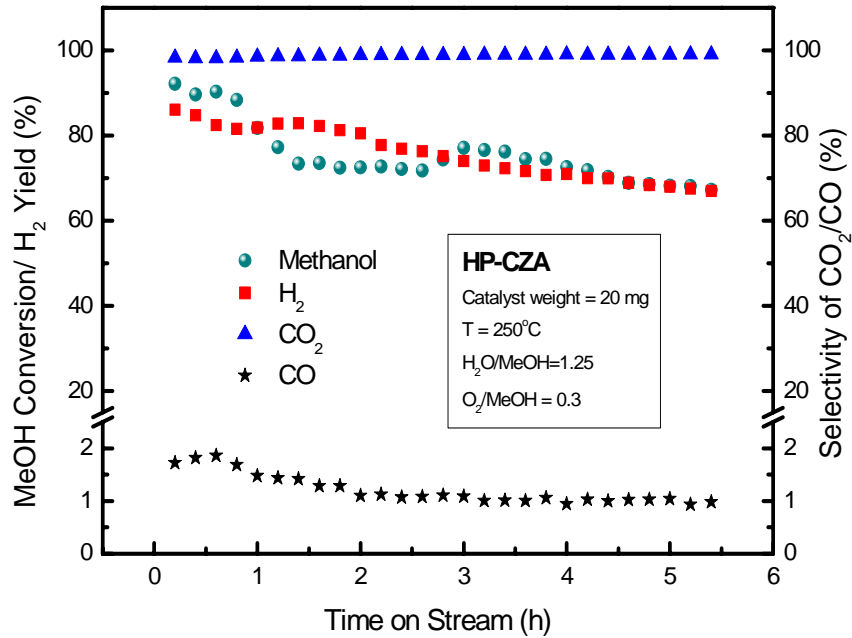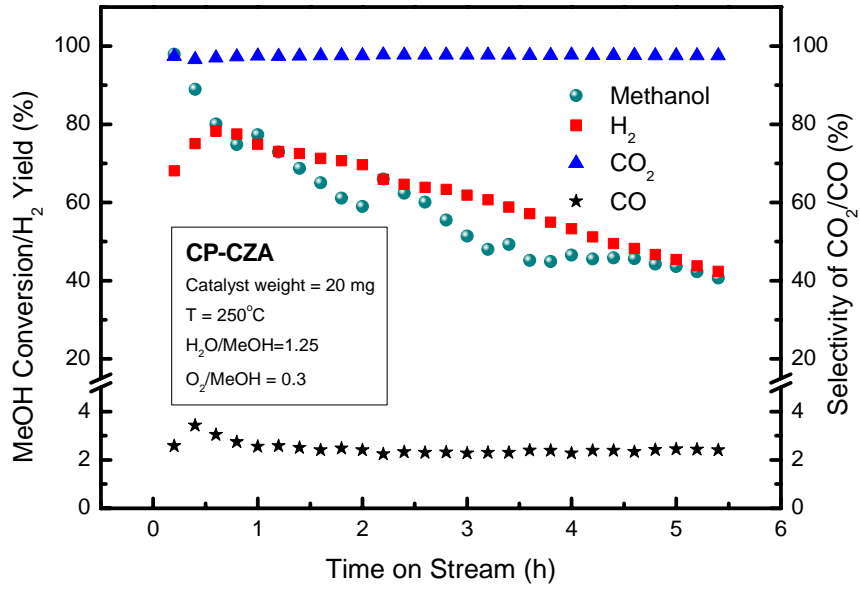
反應的結果如上圖所示，其中

甲醇轉化率 $Conversion = \dfrac{initial - remained}{initial} \times 100\%$

氫氣產率 $Yield = \dfrac{real\ H_2\ concentration}{ideal\ H_2\ concentration} \times 100\%$

CO/CO$_2$選擇率 $Selectivity = \dfrac{CO/CO_2\ concentration}{Methanol\ reacted} \times 100\%$

Catalyst	Synthesis pH value	Specific surface area(m^2/g)	Methanol conversion (%)	H₂		Selectivity (%)		CO (ppm)
				Yield (%)	(mmol/sec-Kg$_{cat}$)	CO_2	CO	
CP-CZA	7.77	47.3	58.6	61.6	592.1	97.5	2.5	2214
HP-CZA	7.63	78.5	72.8	73.0	772.6	98.8	1.2	1328

反應的結果可以整理成上表，由表中可看出 HP-CZA 和 CP-CZA 相比反應結果較佳，且甲醇轉化率、氫氣產生率和 CO2 的選擇率均較高，表示以均相沉澱法所合成的觸媒擁有較佳的催化活性。

肆、添加 Ce, Zr 的反應情形：
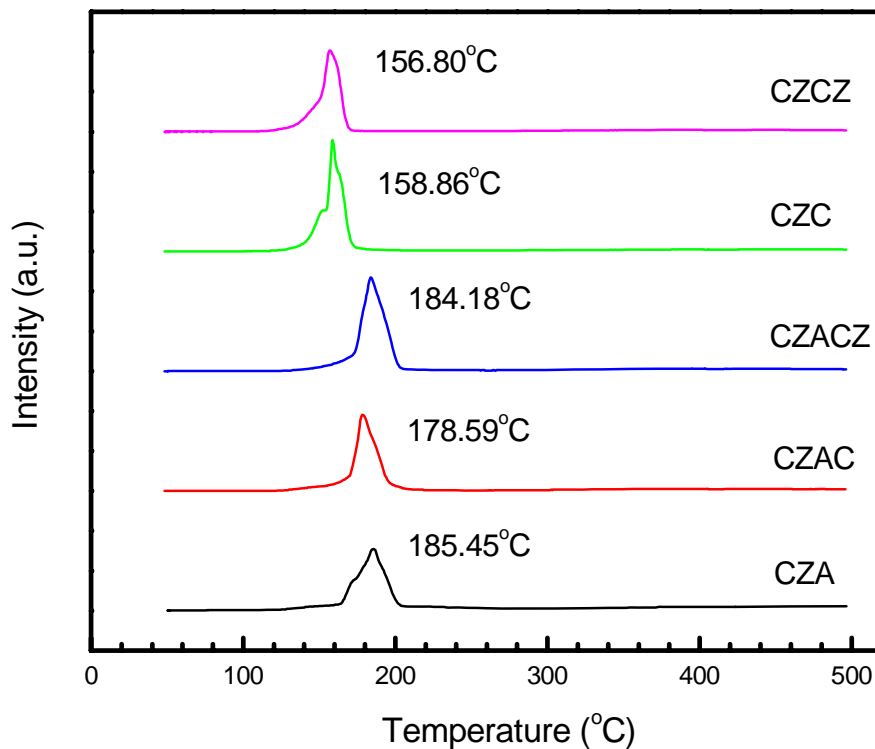
	Cu	Zn	Al	Ce	Zr
CZA	45	45	10	0	0
CZAC	45	45	5	5	0
CZACZ	45	45	5	2.5	2.5
CZC	45	45	0	10	0
CZCZ	45	45	0	5	5

TPR 圖譜中，不含鋁的催化劑 CuZnCe 和 CuZnCeZr 與含鋁的催化劑 CeZnAl, CeZnAlCe, CuZnCeZr 相較之下有明顯較低的還原溫度，由此可以推測其有較高的活性。於是我們設計相關實驗，進一步分析 CuZnCeZr 與 CuZnCe 兩種催化劑製備時觸媒反應情形。

以下三圖為 CuZn 與 CuZnCeZr 觸媒製備過程中 pH 值對時間變化情形。
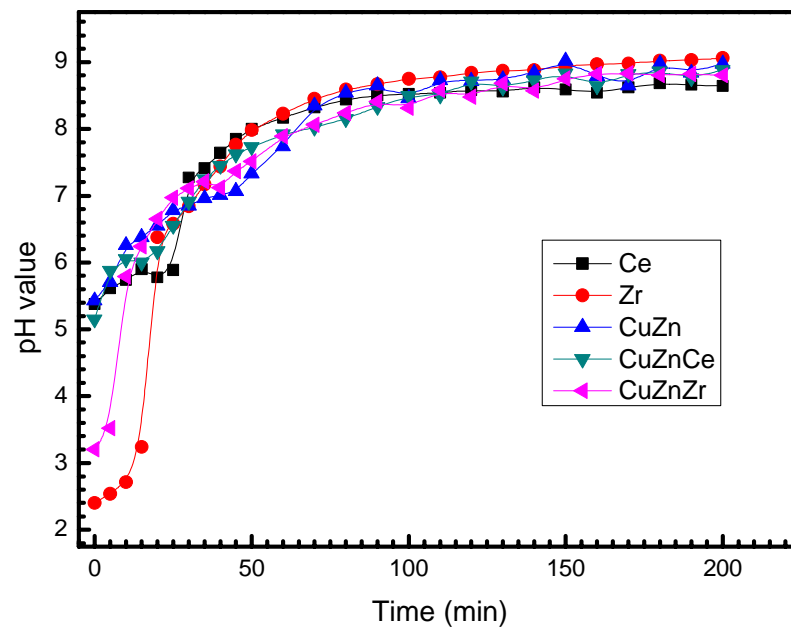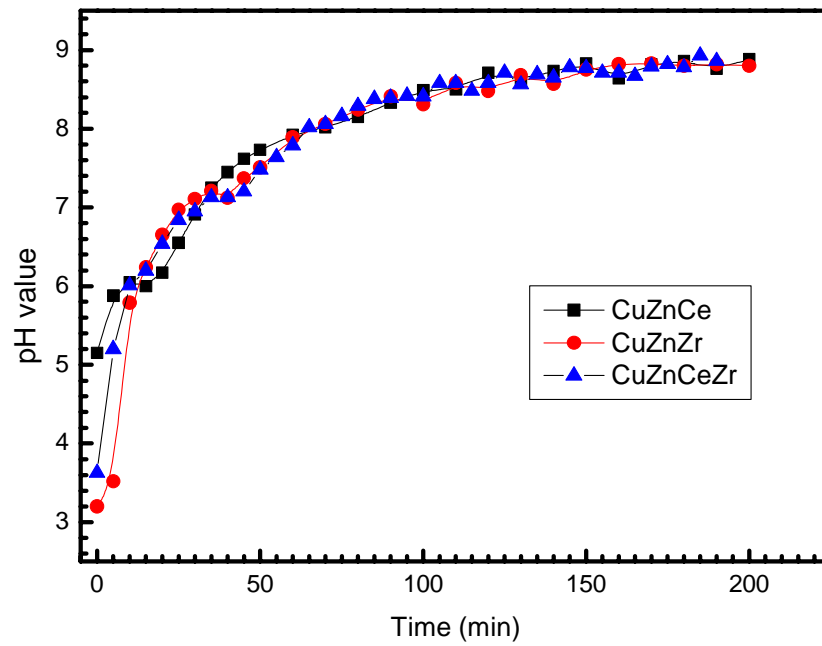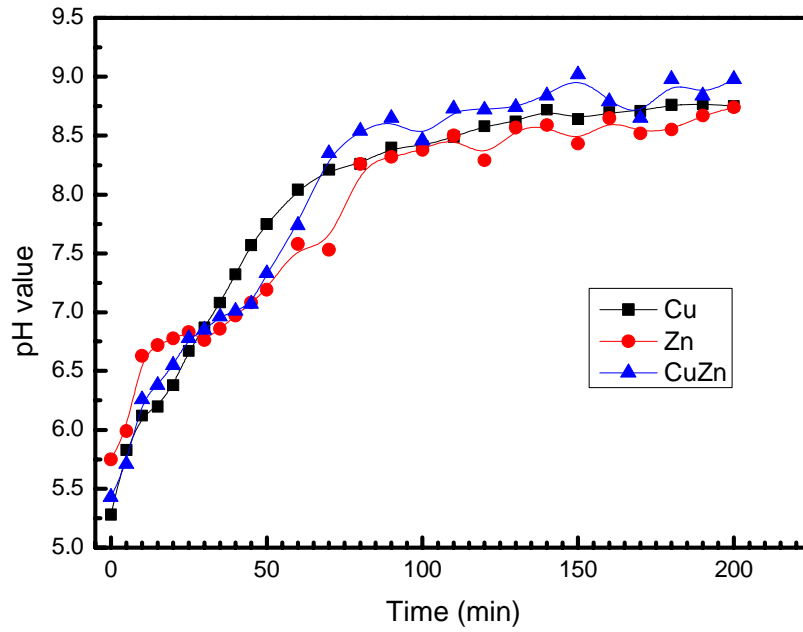
在反應過程中，尿素分子水解放出 OH⁻離子使溶液 pH 值上升。由圖表可得知，當溶液 pH 值約為 pH=6 與 pH=7 時，pH 值上升的情形有停滯現象，因此我們推測是因為水解反應放出的 OH⁻離子與溶液中的金屬離子反應，產生沉澱。

Inductively coupled plasma (by percentage%)

Urea	1M	2M	3M	4M			3M	CP
T/C t /h	90°C 2h						95°C 2h	RT 2h
H_2O	20-0				10-10	5-15	5-15	
Cu	82.3	73.7	64.2	43.2	41.9	40.1	45.7	43.1
Zn	16.3	20.7	29.7	46.8	47.3	48.3	44.8	46.2
Al	1.4	5.6	6.1	10.0	10.8	11.6	9.5	10.7

由 ICP 圖表分析可得知，當尿素濃度增加或所添加水量增加時，Cu 與 Al 的重量百分比隨之減少，而 Zn 的重量百分比則呈現上升情形。而我們所選擇的均相沉澱最佳條件：95°C 2h, 5mL urea + 15mL H_2O 與共沉澱法製備催化劑之 Cu/Zn/Al 重量比皆接近最初預設值，顯示兩種方法同樣能合成比例與預設值相近 CZA 觸媒。

六、結論

壹、尿素濃度、水量、反應溫度、反應時間四種變因均可改變均相沉澱反應進行時的化學環境，其中反應溫度對酸鹼值的影響最大。

貳、在製備的 CZA 觸媒反應中，均相沉澱法以尿素濃度 3M，恆溫 95℃ 持續 2 小時為最佳反應條件。

參、與共沉澱法相較，均相沉澱法製備之 CZA 觸媒有以下優點：
　　還原溫度較低(179.1℃)，顯示 HP-CZA 觸媒的高活性。
　　觸媒粒徑較小。
　　於較小的溫度區間內便可還原，反應較容易進行。

肆、甲醇重組反應：與共沉澱法相較，均相沉澱法製備之 CZA 觸媒進行甲醇重組反應有較高的甲醇轉化率(72.8%)、氫氣產生率(73.0%)、比表面積(78.5%)。和 CO_2 選擇率(98.8%)。

伍、均相沉澱方法所製備之高效能 CZA 觸媒除可有效提高甲醇重組反應的氫氣產生率，提供氫能燃料電池使用，亦可應用於工業上合成高均勻性多成份材料。

七、參考文獻

[1] H. Scott Fogler, "Elements of Chemical Reaction Engineering," 3rd ed. Prentice Hall PTR, 1999.

[2] 汪建民編著，「材料分析」，四版，中國材料科學學會，中華民國九十四年三月。

[3] C. N. Satterfield, "HETEROGENEOUS CATALYSIS IN INDUSTRIAL PRACTICE", 2nd ed. McGraw-Hill, New York, 1991

[4] William D. Callister, "Materials Science and Engineering", John Willey & Sons.

[5] 王瑞祥，葉君棣，「鉑催化劑進行甲醇重組反應來製造氫氣」，全國碩博士論文資訊網，中華民國九十五年七月。

[6] 陳永杰，葉君棣，「以金觸媒催化甲醇重組反應製造氫氣」， 全國碩博士論文資訊網，中華民國九十五年七月。

[7] T. Shishido, Y. Yamamoto, H. Morioka, K. Takaki ,K. Takehira, *J. Appl. Catal. A*, 263 (2004) 249.

[8] T. Shishido, Y. Yamamoto, H. Morioka, K. Takehira, *J. Mol. Catal. A:Chem*, 268 (2007) 185.

評語

本研究以 Cu/Zn/Al 的塩類進行均相共沉澱，合成過程針對尿素濃度，加入水量，溫度，反應時間改變變因，獲得的催化劑用在甲醇還原的反應上，顯示有較好的轉化率。本研究過程完整，目標清晰，主題前瞻性可以連結燃料電池的發展，應該是很好的國際科展作品，可能在金屬的選擇上有更強的論點與理論背景。

Efficient Hydrogen Production

Using Cu-Zn-Al Catalysts Prepared by

Homogeneous Precipitation Method

CH014

Yi-Han Su

Taipei First Girls High School, Taipei, CHINESE TAIPEI

Abstract

In industry, high-activity catalyst is desirable for methanol reforming reaction in order to generate hydrogen efficiently. In this project, multi-composition Cu-Zn-Al catalyst was synthesized by homogeneous precipitation (HP) method with urea treatment. In comparison with those obtained from conventional co-precipitation method, our technique offers an opportunity to improve the homogeneity of metal mixing and to increase the surface area of catalysts. By adjusting urea concentration, water amount, reaction temperature and time, various hydrotalcite-like compounds are obtained. The optimized catalysts having flower-like morphology, exhibited high surface area (78.5 m^2/g, as determined by Brunauer-Emmett-Teller method), and a lower reduction temperature. The HP-method derived Cu-Zn-Al catalyst exhibited higher methanol-conversion, hydrogen-production-rate and CO2-selectivity under methanol reforming reaction at 523K compared with those derived by co-precipitation method. To further improve the catalytic performance of the Cu-Zn-Al, Ce and Zr were employed to modify the support. The Ce/Zr-modified catalysts did show higher activity, as evidenced by a 20K lower reduction temperature and more than 85% of methanol conversion. Our method can be generalized for the synthesis of other multi-composition materials with high homogeneity.

Acknowledgements

First of all, I wish to express the deepest appreciation to my advisor, Dr. Li-Chyong Chen, for her guidance and patience throughout this work. I also gratefully thank my classmates, for their support and many stimulating discussions.

Especially, I wish to express the deepest appreciation to other researchers for their guidance and patience during the experiment at advanced material laboratory of the academic sinica.

Finally, I am grateful to my families and my good friends for their encouragement, support and love during the research.

1. Introduction

Due to the energy crisis, an effective alternative energy is essential to replace the dwindling supply of petroleum. In comparison with other energy generation techniques, hydrogen fuel cell is one of the most environmentally cleaner sources; however, the supply and storage of hydrogen are enormous obstacles for hydrogen industry. In order to solve this problem, the reforming reaction of methanol is considered as an attractive way for hydrogen supply, also thanking to its ease of handling and synthesizing from various feedstock. For catalytic process, extracting hydrogen from methanol can be performed by oxidative steam reforming, which combines the endothermic steam reforming reaction and the exothermic partial oxidation reactions. By appropriate system design, favorable hydrogen production rate as well as no external heat can be achieved.

For methanol reforming reaction, copper based catalysts are the most extensively used ones, such as Cu-Zn-Al (CZA) oxide system, due to the low cost and high activity. The dispersion of active Cu metal and the surface area for such catalysts play crucial roles on the catalytic activity and stability. Most groups adopted co-precipitation (CP) method to prepare CZA catalysts. However, this method has serious concentration gradient of hydroxide ions during the addition of base source, which would result in the poor mixing of precipitates. In order to improve the uniformity of precipitates, the homogeneous precipitation (HP) method was employed in this research. Urea would hydrolyze and release hydroxide ions homogeneously in the solution without concentration gradient. To obtain the better precipitation conditions, four parameters -- urea concentration, water amount, heating temperature and time -- were discussed. For CZA catalyst system, the correlations between the morphologies and crystal structures of precipitate precursors and catalytic performance would vary from different synthesized methods. CP-derived CZA catalyst was, thus, prepared as a comparison. In addition, the possibility of applying HP method on synthesizing multi-compositional compounds and improving the catalytic performance of CZA catalyst were also discussed.

2. Experimental

2.1 Preliminary experiments

In order to observe the precipitation reactions under different pH value conditions and reaction temperature, the features of metal ions were discussed. The pH values of distilled water with different metal nitrates dissolved were controlled by addition of NaOH, and the experiments of reaction temperature were carried out at room temperature and 373K.

2.2 Preparation of the catalysts

The precursors of the catalysts with varying composition are prepared by urea method. Aqueous solution of metal nitrate and urea were mixed at room temperature and followed by heating at appropriate temperature for hours. During the preparation progress, the urea was forced to hydrolyze and resulted in generation of the hydroxide. Since the effect of the concentration gradient may be reduced, it is highly expected the homogeneous precipitation method can afford catalysts with high homogeneity than the conventional precipitation method. The reflux method was adopted during the heating process as reducing the influence of boiling in the precipitation. The precipitates were then separated, washed with distilled water and finally dried at 363K for overnight. Calcination of the precursors was performed at 573K for 3h in air, and the oxides were then pressed, crushed and sieved. For the reactions above, the ratio of weight percent for metal oxides was kept constant as 45/45/10.

As controls, the solutions were mixed together and added dropwise to a continuously stirred solution of Na_2CO_a. Later the obtained precursors were crushed into powder, dried at 363K for overnight and finally calcined in air at 573K for 3h.

2.3 Characterization of the catalysts

2.3.1 X-ray diffraction

X-ray powder diffraction patterns were collected in the 60° and 0.0164 step size. In order to understand the state of catalyst after calcination and reaction, the peak position was compared to XRD reference book. The line broadening at half-height of maximum reflection was used to calculate the average crystallite thickness.

2.3.2 BET Surface Area Measurement

The BET apparatus determined the surface area by employing the technique of adsorbing one component from a flowing mixture. Before the experiment, the sample must be degassed for 2 hrs ($<$ 5 μmmHg) to get rid of water and impurity at catalyst. The process of adsorption and desorption were monitored by measuring the change in the thermal conductivity of the gas cell, and then a mixture of gas was passed the cell.

2.3.3 Temperature-Programmed Reduction (TPR)

The appropriate amount of sample was held between two quartz wools. The reactor effluent was monitored immediately downstream by using a thermal conductivity detector (TCD), which was stabilized to a linear baseline following changes in carrier gas. Temperature-programmed reduction experiments were conducted to compare the reducibility of the fresh catalyst. Next, 20 mg of sample was placed in a quartz fixed bed reactor and a high-purity flow of 10 vol.% H_2/Ar mixtures was passed through the bed. The consumption of hydrogen was monitored by TCD cell and the result was recorded by a computer.

2.3.4 Equipment for the Reaction

The methanol solution (H_2O/MeOH=1.25) were fed into the evaporator unit and thereby methanol solution could be vaporized and fully mixed; then carrier gas, Helium (He), is able to carry vapors into reaction tube to process methanol steam reforming. The feed rate was kept 2 mL/hr. After the reaction unit, analyzed on-line by means of the Gas Chromatography (China Chromatography 9800), equipped with thermal conductivity detector (TCD).

3. Results and discussion

3.1 Precipitation of the metal ions

Table. 1 pH values of reacted solutions under different concentration of urea and amount of water prepared by homogeneous precipitation method.

Urea conc (added)	20 mL		10 mL+ 10 mL H_2O		5 mL+ 15 mL H_2O	
	initial	reacted	initial	reacted	initial	reacted
1M	3.43	5.13	3.64	5.32	3.80	5.48
2M	3.68	6.33	3.88	6.69	4.05	6.90
3M	3.84	6.72	4.01	6.96	4.16	7.11
4M	3.90	7.28	4.08	7.43	4.19	7.46

Table. 2 pH values of reacted solutions under different concentration of urea and amount of water prepared by homogeneous precipitation method.

5mL +15mL H_2O	90°C 2h	90°C 5h	95°C 2h	95°C 3h	100°C 0.5h	100°C 1h	100°C 2h
2M					7.15		8.53
3M	7.11	7.97	7.63	8.09	7.53	8.22	8.56
4M							8.6

For the preliminary experiments of copper, zinc and aluminum ions, amount of precipitates increase with the pH values, and shows a significant declination as the pH values are above 8(data are not shown). Hence, it was confirmed that the pH between 7 and 8 are the most suitable values for the precipitation progress, which can allow the complete precipitation.

3.2 Conditions of urea concentration and water amount

In our study, the influence of the catalysts under high urea concentration was discussed as the concentration of metal ions were kept constant. However, since the water both has its pH values higher than the initial solutions and works as the reactant in the hydrolyzation, it is expected that the pH values can be efficiently adjusted by addition of water with varying quantity. Also, addition of water may be favorable way for adjusting pH values thanks to its ease of handling. For the reasons above, the precipitation processes for different urea concentration and water amount were carried out at 363K for two hours.

The results of precipitation progress over series of the precursors are shown in Table. 1. The pH values of the initial solutions increases with the amount of water and the concentration of urea, and also for the reacted solutions. After two

Table. 3 Inductively coupled plasma (ICP) results for the
hp-CZA and cp-CZA prepared under different synthesis conditions.

Urea	1M	2M	3M	4M			3M	CP
T/.C t /h	90°C 2h						95°C 2h	RT 2h
H_2O	20-0				10-10	5-15	5-15	
Cu	82.3	73.7	64.2	43.2	41.9	40.1	45.7	43.1
Zn	16.3	20.7	29.7	46.8	47.3	48.3	44.8	46.2
Al	1.4	5.6	6.1	10.0	10.8	11.6	9.5	10.7

series of reactions, significant enhancements of the solutions in the pH values were both observed, and the pH values are up to 7 as solutions with four molar ratio of urea

and when 3 times water was added to the 3M solution. In comparison, the addition of water is more sensitive than under different urea concentration, suggesting a better way for adjusting the pH values. Also, the blue solutions were observed as 4M urea is added under varying water quantity while the condition of 3M urea diluted by 3 times water shows colorless.

Precursors prepared under urea of 3M and diluted by 3 times water, was considered to be the better one for reasons below: First, it was reported that the aurichalcite and hydrotalcite-like compounds are favorable phases in comparison with other structures formed in the hydrolysis reactions, owing to the higher dispersity. Secondary, compared with the two reacted 3M and 4M solutions with favorable pH values, intense blue colors was observed over the solution of 4M. The feature strongly suggested the reduction in the copper level, owing to the formation of copper complexes in the solution proved by UV visible (data are not shown). Third, the ICP results (Table. 2) further proved that the ratio of metal precipitates close to the initial value, which was reported as the better one. Thus, the chosen synthesis condition was used in the following experiments.

3.3 Conditions of reaction temperature and reaction time

Experiments for reaction temperature and reaction time were performed as the conditions of water amount and urea concentration were kept constant as the chosen one. The results of precipitation progress over series of the precursors are shown in Table. 3. The pH values of reacted solutions both increase with long reaction time and high reaction
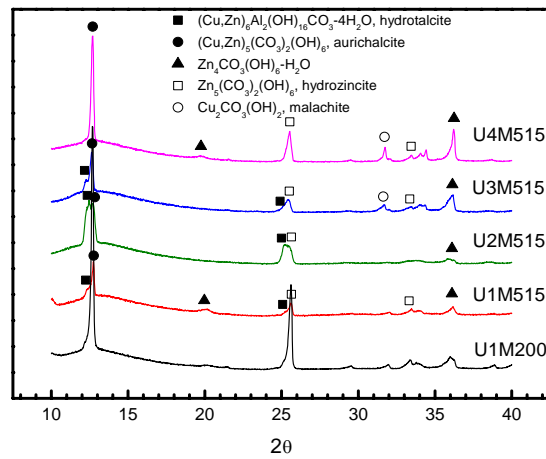
Fig. 1 X-ray diffraction (XRD) figure of precursors prepared under different concentration of urea and amount of water.
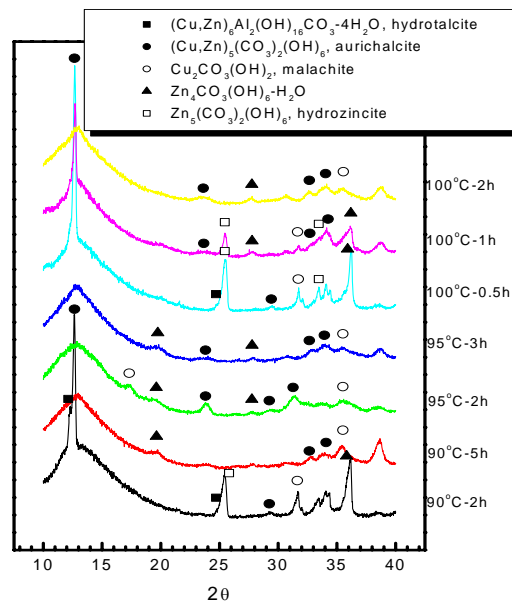

Fig. 2 X-ray diffraction (XRD) figure of precursors prepared under different reaction temperature and time.

temperature. In addition, it is also observed that reaction temperature is more sensitive to the pH values in comparison with reaction time. Results of the reacted solutions indicated that the pH values were above 8 mostly when the blue solution colors are obtained, which were unfavorable for the precipitation. Also, it is also suggested that reactions performed under 373K are inconvenient for our catalysts due to the difficulty of handling over the water amount in liquid state. Thus, heating at 363K for two hours is chosen to be the better synthesis condition.

3.4 Structure of the CZA precursors and the catalysts

X-ray diffraction (XRD) patterns of the precursors synthesized by different urea concentration and water amount were shown in Fig. 1. The peaks of aurichalcite and hydrotalcite-like compounds were observed under initial solution of 3M urea diluted by three times water, suggesting preferable structures with high dispersity can be obtained from the chosen condition. Moreover, a significant increase of the intensity was showed in the precursors prepared from 1M urea.
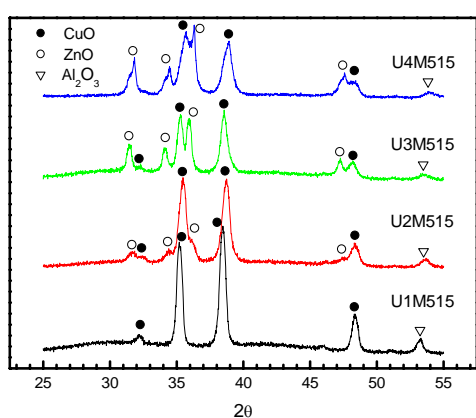

Fig. 3 X-ray diffraction (XRD) figure of compounds prepared under different concentration of urea and amount of water after heat treatment of 573K.
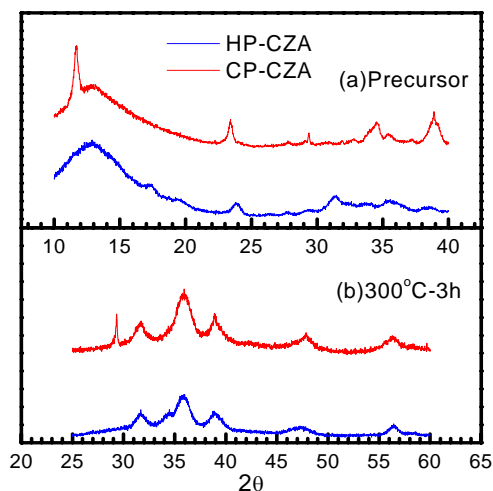
Fig. 4 X-ray diffraction (XRD) figure of compounds prepared by HP and CP method before and after heat treatment of 573K.

The phases formed after the experiments for varying reaction temperature and reaction time were shown in Fig. 2. Among the precursors obtained from different reaction temperature and reaction time, better structures were observed under 363K for 5 hr, 368K for 2 hr and 368K for 3 hr due to the dispersity reason; however, 368K for 2 hr was chose as the preferable condition both due to the appropriate pH values and colorless solution.

XRD pattern of compounds after heat treatment was shown in Fig. 3.   After calcination for three hours, the diffraction lines indicated the formation of copper, zinc and aluminum oxide. A phase of zinc oxide was absent in compounds prepared from 1M urea diluted by three times water, which may due to the lower pH value. For the Fig. 4, structures of hp-CZA are similar to cp-CZA both before and after the calcination, while the broader peaks of hp-CZA were observed.

3.5 Morphology of the CZA precursors and the catalysts

The SEM images of the precursors prepared from different conditions are shown in figure 5. Observation of the precursors clearly shows the formation of the bar-shape structure were obtained from three molar urea. Fracture surface of the structures were indicated when the molar ratio increase. For the precursors prepared from large amount of water addition, the particles are assembly of plate-like structures, which is unfavorable for the larger specific surface area. Under the conditions of 373K, the particles showed fracture surface when reaction time is variable. After the calcination at 573K, catalysts prepared by homogeneous precipitation showed flower-like shapes on its surface, which may responsible for the larger specific surface area, while the particles of control groups obtained from conventional precipitation method showed serious aggregation. Thus, it is strongly proved that the serious aggregation during the sintering can be reduced by preparation of homogeneous precipitation method.
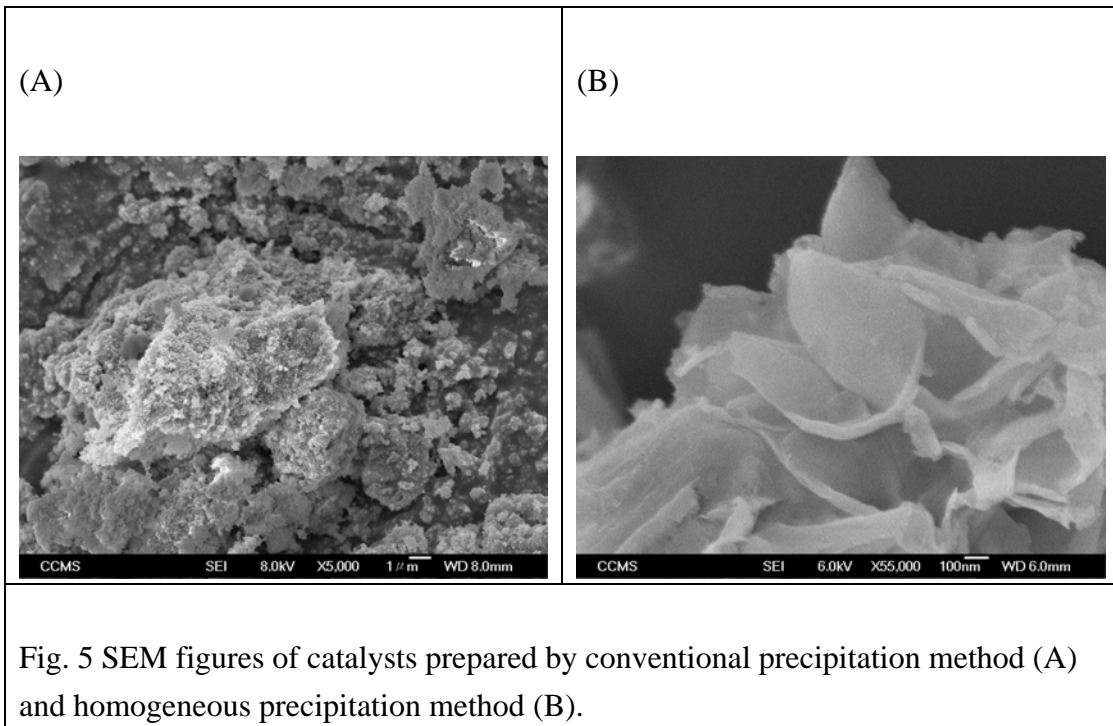
Fig. 5 SEM figures of catalysts prepared by conventional precipitation method (A) and homogeneous precipitation method (B).
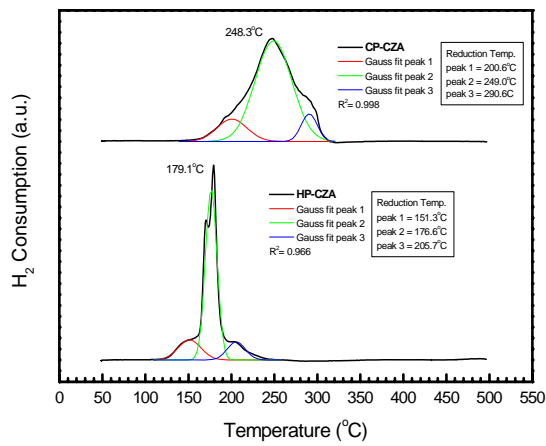

Fig. 6 The temperature programmed reduction (TPR) profile of HP and CP-catalysts.

3.6 The temperature programmed reduction process of CZA catalysts

The TPR profile of the catalysts prepared by HP and CP method was shown in Fig. 6. Catalysts prepared by HP method show obvious lower reduction temperature than the control groups, which may result in higher activity. Compared with hp-CZA, wider temperature range was needed for cp-CZA during the reaction, strongly suggesting a decrease of the homogeneity over the particles. Over the reduction processes, the systems over the catalysts prepared both by CP and HP method were complicated.

3.7 Dispersity for the CZA catalysts

Since the HP method can be used to generate the hydrolysis ions homogeneously, it is highly expected that catalysts prepared by homogeneous precipitation method can exhibit high homogeneity. The SEM mapping figures (Fig. 7) of CZA and CZCZA both indicated that the homogeneous precipitation method is able to afford highly dispersed metal particles, which may result in stable activity over the reforming reaction of methanol.
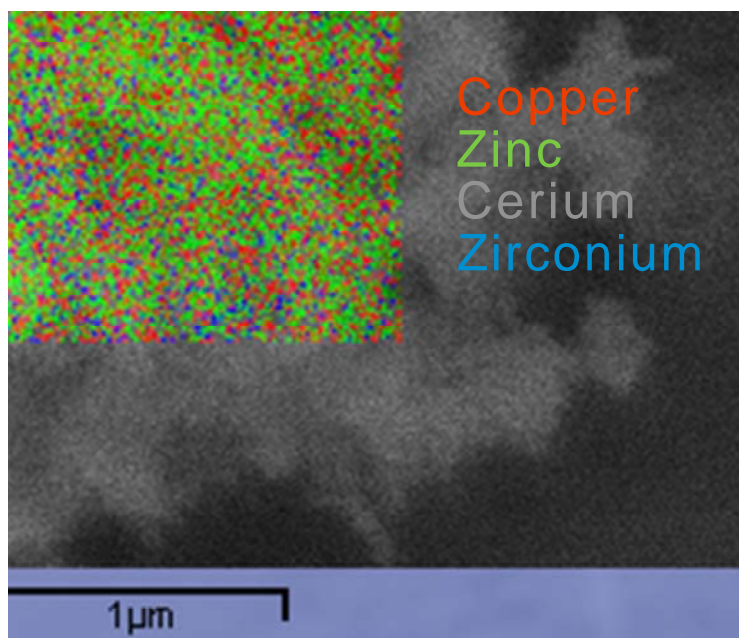

Fig. 7 The SEM mapping of CuZnCeZr precursors.

3.8 Methanol reforming reaction over the CZA catalysts

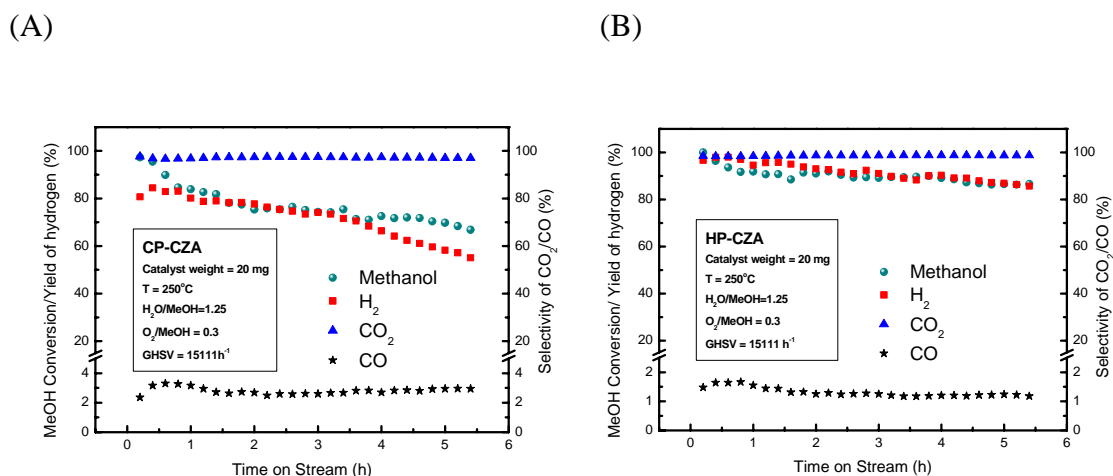(A)   (B)

Fig. 8 Steam reforming of methanol over HP-CZA (A) and CP-CZA (B).

The results of the steam reforming of methanol over the CZA catalysts prepared by CP and HP method were shown in Fig. 8. Over the reactions, catalysts prepared by HP method showed obvious higher methanol conversion than the control groups. The phenomenon may refer to the effect of aggregation during the sintering were reduced as the particles are highly dispersed HP method. Significant enhancements of the yield of hydrogen production and selectivity of carbon dioxide were also exhibited, suggesting the homogeneous precipitation method can afford highly catalytic activity over the methanol reforming reaction.

3.9 Addition of cerium and zirconium for the CZA catalysts

In order to reduce the carbon monoxide side-product which can cause the catalyst poisoning, cerium and zirconium were incorporated to the supports of the CZA catalysts in the methanol reforming reaction. As a result, catalysts with varying compositions were synthesized by homogeneous precipitation method.

For precursors without Al components and for catalysts with cerium and zirconium, apparently lower reduction temperature was exhibited (Fig. 9), which may

result in higher activity. The yield of hydrogen production and methanol conversion increased in the absence of aluminum over the catalysts modified by cerium and zirconium (Fig. 10), owing to the formation of spinel structure with inherently high thermal stability. Modification of cerium can greatly enhance the conversion of methanol and yield of hydrogen production, and also for catalysts with zirconium added. In addition, catalysts with cerium exhibit obvious lower selectivity of CO, which may due to the oxygen storage capacity.

Incorporation of zirconium can further improve the catalytic ability, for the yield of hydrogen production up to 98% and methanol conversion up to 96%. In addition, apparent decrease in the selectivity of carbon monoxide is observed, owing to the inhibition of the thermal sintering of CeO_2 by Ce-Zr mixed oxides formation.
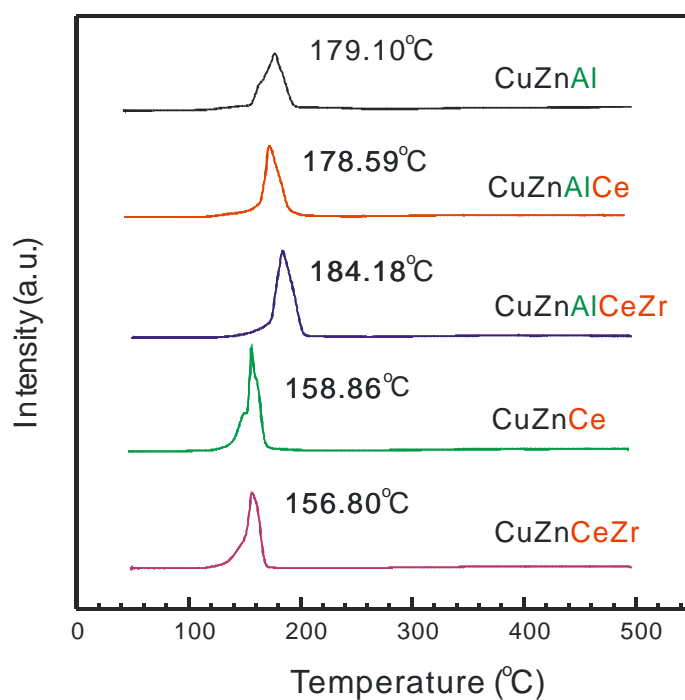

Fig. 9 Temperature programmed reduction (TPR) profiles of different catalysts prepared by HP method.
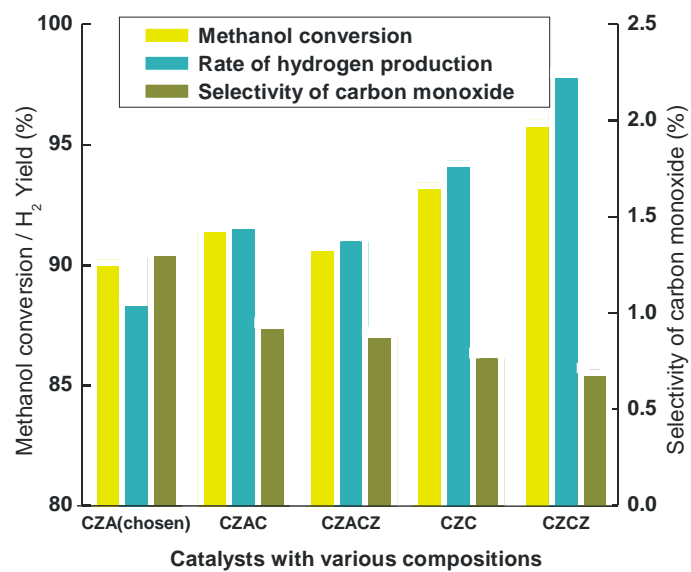
Fig. 10 The results of methanol reforming reaction over the catalysts of different compositions.

4. Conclusion

Under adequately controlled conditions, the reactivity of catalysts prepared by homogeneous precipitation method was studied over the reforming reaction of methanol. CZA catalysts obtained by homogeneous precipitation method exhibit higher dispersity, lower reduction temperature as well as favorable structure in comparison with the conventional precipitation method. In particular, presence of flower-like shape suggests that the homogeneous precipitation method can afford larger specific surface area. For the catalytic reaction over reforming of methanol, catalysts prepared by homogeneous precipitation method perform better in methanol conversion, yield of hydrogen production and higher carbon dioxide selectivity in comparison with conventional precipitation. In the absence of aluminum, lower reduction temperature and better performance over reforming of methanol was observed. Further modification of cerium and zirconium can also improve the catalytic ability; for 20 milligrams catalysts loading, higher methanol conversion and yield of hydrogen production were exhibited.

5. References

[1] H. Scott Fogler, "Elements of Chemical Reaction Engineering," 3rd ed. Prentice Hall PTR, 1999.

[2] C. N. Satterfield, "HETEROGENEOUS CATALYSIS IN INDUSTRIAL PRACTICE", 2nd ed. McGraw-Hill, New York, 1991

[3] William D. Callister, "Materials Science and Engineering", John Willey & Sons.

[4] T. Shishido, Y. Yamamoto, H. Morioka, K. Takaki ,K. Takehira, *J. Appl. Catal. A*, 263 (2004) 249.

[5] T. Shishido, Y. Yamamoto, H. Morioka, K. Takehira, *J. Mol. Catal. A:Chem*, 268 (2007) 185.

[6] S. Murcia-Mascaros, R. M. Navarro, L. Gomez-Sainero, U. Costantino, M. Nocchetti, J. L. G. Fierro, *J. Catal*, 198 (2001) 338.

[7] Galo J. De A. A. Soler-Illia, Roberto J. Candal, Alberto E. Regazzoni, Muguel A. Blesa, Chem. Mater, (1997) 9 184.

[8] Roberto J. Candal, Alberto E. Regazzoni, Migual A. Blesa, *J. Matar. Chem.,* 1992, 2(6), 657