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科 別：化學科

作 品 名 稱：瓦斯熱水爐一氧化碳觸媒轉化器之研究

得 獎 獎 項：第一名
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作者簡介



自幼，我即生長於一個溫暖、開明的家庭。家中成員除爸媽外，就只有我一個小孩。父親長時間於船上工作，因此從小到大之多元教育多半受母親薰陶。記得小時候，母親總是費盡心思選擇適合我的讀物，並耐心的陪我閱讀，甚至教我動手做有趣的科學小實驗；透過這種互動式的學習，我不僅養成了喜愛閱讀的習慣，對種種科學現象也漸漸開啟了興趣之門！

摘要

瓦斯熱水爐使用大火時廢氣的 CO 濃度非常高是導致一氧化碳中毒事件的關鍵原因，要解決這個問題觸媒轉化是一種可行的方式。影響觸媒性能的因素中以活性中心的種類最為重要，我們發現對轉化一氧化碳為二氧化碳的反應而言鈷有最好的催化效果，其次分別為：鎳、銅、鐵。最好的載體是三氧化二鋁，鈷的含量使用 10%，煅燒溫度使用 300°C 可兼顧性能與成本。

本研究中所研發的 Co/Al₂O₃ 觸媒具備有實用的潛力，可以在空間速度高達 1000min⁻¹ 的情況下將濃度 14,632ppm 的 CO 百分之百轉化為 CO₂，而僅需 233°C 的反應溫度。因此，應該可以應用在瓦斯熱水爐上以降低一氧化碳中毒的風險。

Abstract

The incorrect usage of a natural gas powered water heater always generates high carbon monoxide concentration in a closed environment. The dangerous CO gas can be fatal to the careless user of the water heater. Catalytic conversion of CO to CO₂ can be a convenient method to solve this problem.

The effect of the support, the supported metal, loading of the metal, reaction temperature, gas concentration, and reactants flow rate on the performance of the CO oxidation catalysts have been investigated. X-ray diffraction, gas adsorption and Infrared spectroscopy were applied to study the characteristics of catalysts.

A 100% conversion of CO to CO₂ can be achieved when 1.46% CO/6% oxygen/N₂ reactants was catalyzed by a 10% Co/Al₂O₃ catalyst at 233 °C with a space velocity of 1000min⁻¹.

This reaction condition is sufficient to remove the entire CO generated by a family-sized natural gas water heater.

壹、研究動機

常在新聞上看到因為使用瓦斯熱水爐不慎導致一氧化碳中毒身亡的可怕消息，面對這種無色、無味、無臭的毒性氣體，我們該怎樣預防它的危害呢？

將瓦斯熱水爐裝置在戶外通風處是避免一氧化碳中毒最直接而有效的方法。但是有時礙於既有空間的限制無法將熱水爐設於室外，或因建築物通風設計不良使得雖在室外仍無法有效擴散廢氣，則一氧化碳中毒的風險仍然無法完全避免。近來有加裝抽氣設備強制排氣的機種出現，但其使用仍需空間配合。想想若是排放於狹窄的巷弄或公寓大樓的天井中，豈不是以鄰為壑互相毒害嗎？

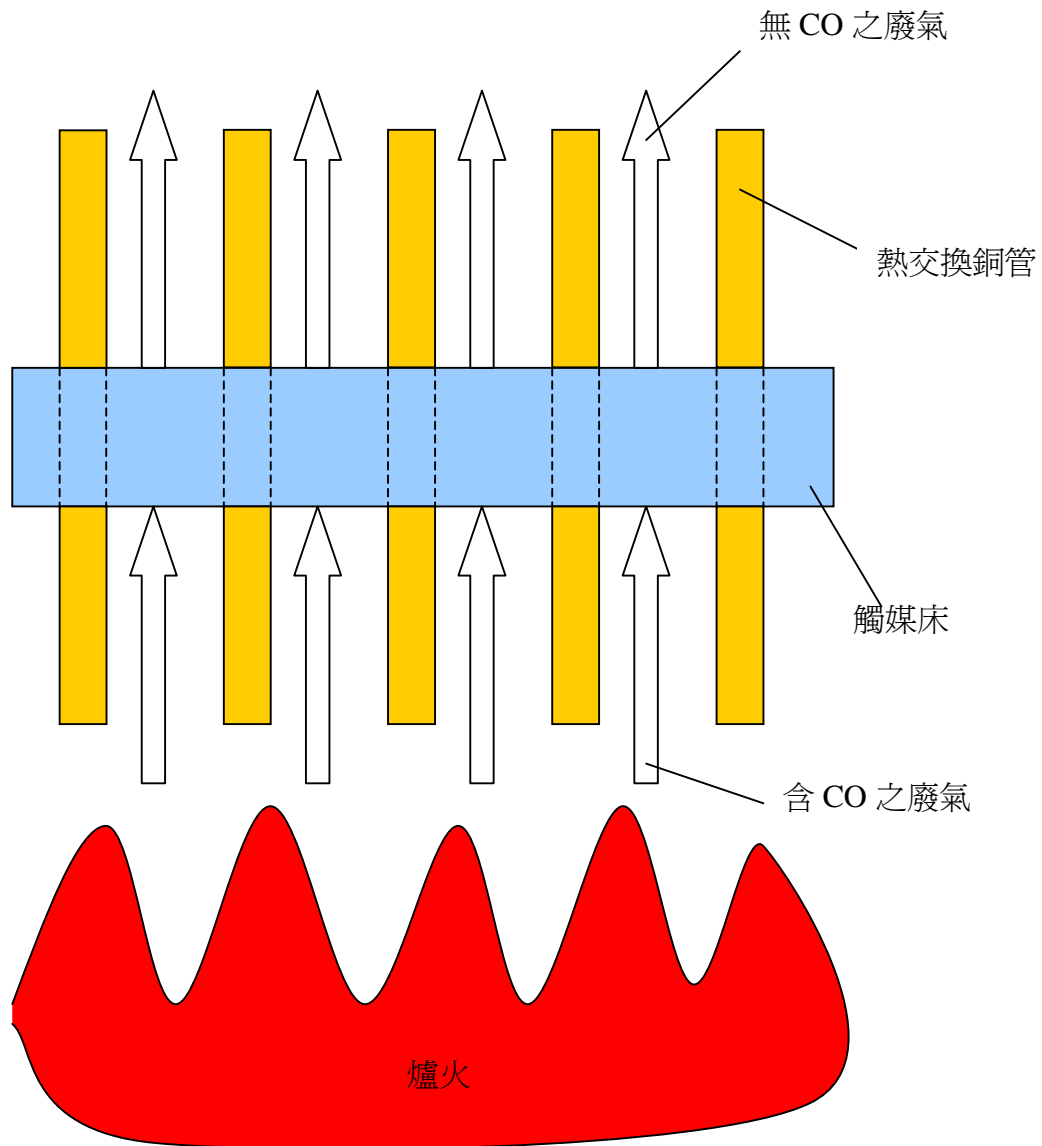
觸媒已被成功的運用在工廠與汽機車廢氣的轉化上，如果也能應用於瓦斯熱水爐，將一氧化碳轉化為毒性遠遠較低的二氧化碳，應該可以大大提昇瓦斯熱水爐的安全性，減少許多無辜生命的損失。

表一 高中教材與本研究的相關性

教材內容	與本研究相關性
物質的變化之氧化還原反應	一氧化碳轉化為二氧化碳之反應原理
物質的質量之莫耳與化學計量	觸媒製作、藥品配製
氣體的性質之理想氣體方程式	燃燒廢氣量及廢氣組成之計算
物質的變化之化學反應速率-活化能	觸媒催化原理、反應速率與溫度之關係

貳、研究目的

本研究的目的是研發高性能的一氧化碳轉化觸媒。我們構想可以把觸媒裝置於瓦斯熱水爐熱交換銅管間的廢氣通道上，如圖一所示。當啟動瓦斯熱水爐時，高溫的廢氣迅速加熱觸媒床達到工作溫度，一氧化碳即被有效率的轉化成二氧化碳了。



圖一 瓦斯熱水爐觸媒轉化器示意圖

參、研究設備及器材

一、反應器

如圖二所示反應器本體為不鏽鋼製，外管內徑 21mm，內管外徑 6.4mm。反應氣體由外管入口進入後向下流動通過預熱段提高溫度，然後到達觸媒床進行反應。觸媒床構造為底部鋪設厚約 0.5 cm 之石英棉，玻璃棉上鋪厚約 0.5 cm 之石英砂，石英砂上填充觸媒。反應氣體穿過觸媒床後在玻璃棉層中轉向進入內管，然後向上流動到達出口，再由鐵氟龍製之導管送至氣體分析儀。氣密鎖入一支 K-type 熱電偶，前端插入至內管底部以測量反應溫度。

反應氣體是以 CO 標準氣體經 N₂ 及空氣適當稀釋配比後調整至所需濃度，並且使 O₂ 濃度為 6%。

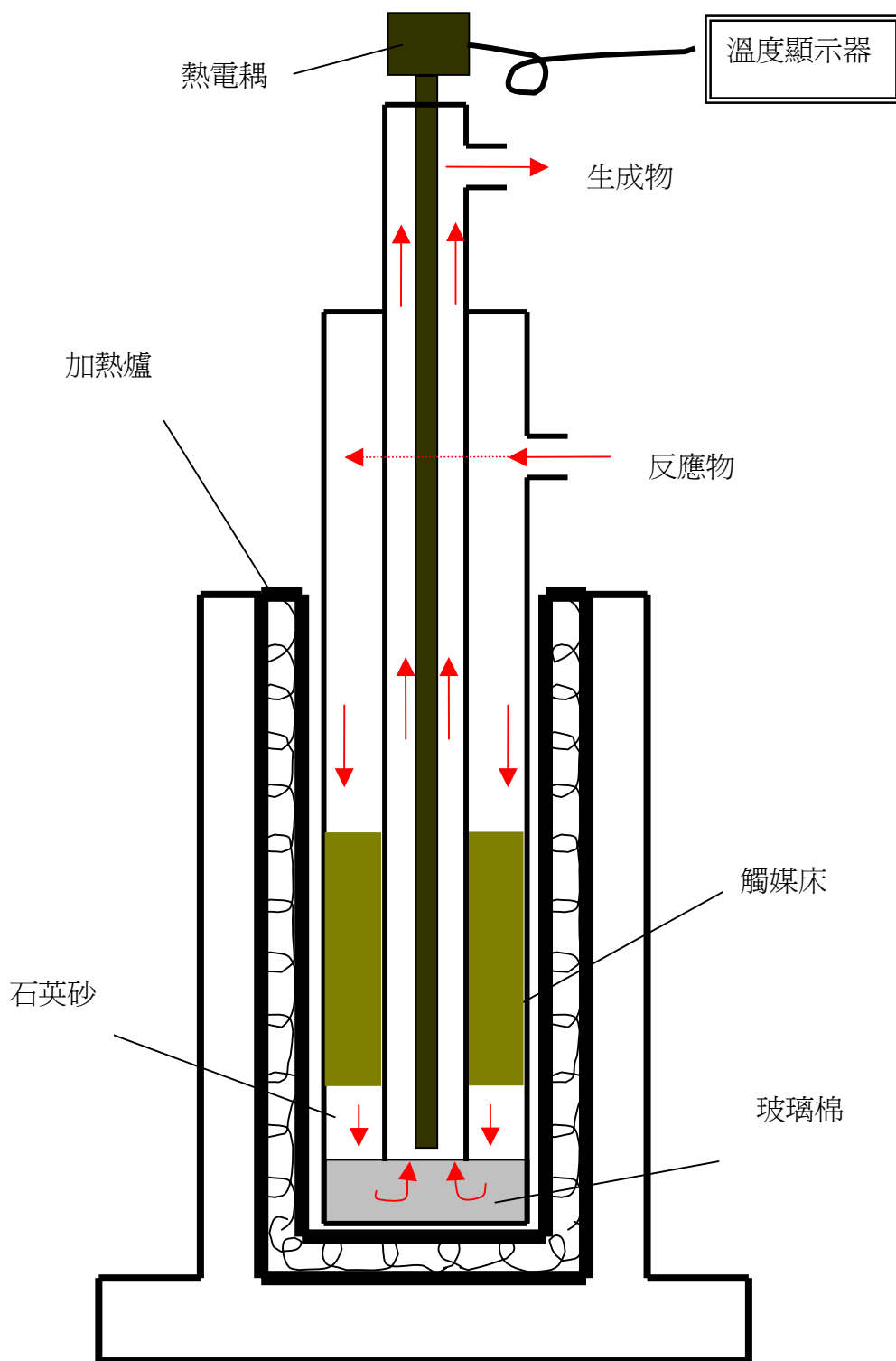
一氧化碳及氧氣濃度分析使用 IMR2000 煙道氣體分析儀（頤樺科技公司代理），氮氣、CO 標準氣體、空氣等高壓氣體鋼瓶供應商為欣和氣體公司。

觸媒床之填充方式為：先將觸媒裝在加蓋之量筒中，輕輕敲至緊密後量取所需體積之觸媒。用漏斗將觸媒倒入反應器中，再輕敲反應器管壁使觸媒均勻分佈。

二、藥品

表二 藥品清單

試藥	英文名稱	分子量	廠牌	等級
Cu(NO ₃) ₂ · 3H ₂ O	Copper(II)Nitrate	241.59	藥理化學工業	試藥一級
Ni(NO ₃) ₂ · 6H ₂ O	Nickel Nitrate	290.79	日本試藥工業	試藥一級
Co(NO ₃) ₂ · 6H ₂ O	Cobalt(II)NitrateHexahydrate	291.03	昭和化學	試藥一級
Fe(NO ₃) ₃ · 9H ₂ O	Iron(III)Nitrate	403.99	日本試藥工業	試藥一級
SiO ₂	Silicon Dioxide	60.08	石津製藥	試藥一級
高嶺土	Kaolin	—	日本試藥工業	試藥一級
TiO ₂	Titanium Dioxide	79.9	日本試藥工業	試藥一級
Al ₂ O ₃	AluminiumDioxide	101.96	日本試藥工業	試藥一級



圖二 反應器示意圖

肆、研究過程或方法

一、觸媒相關知識彙整

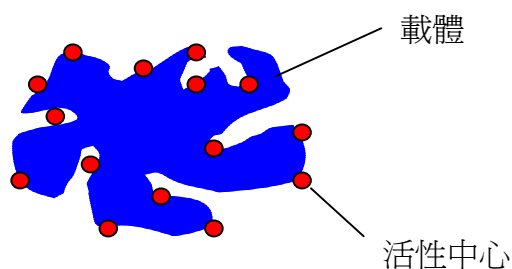
（一）非均相觸媒

觸媒可分為均相觸媒與非均相觸媒，觸媒與反應物不同相時稱之為非均相觸媒，譬如汽車的觸媒轉化器為固體（固相），反應物為氣體（氣相），即是一種非均相觸媒應用的例子。非均相觸媒因易與反應物分離，所以在工業上被廣泛使用。

（二）非均相觸媒結構

觸媒的功效在於降低反應的活化能，因此能增快反應速率。非均相觸媒主要由活性中心與載體所構成。通常是利用適當氧化態的金屬作為催化的活性中心。

載體的主要功用有三：1.提供大的表面積與適當大小的孔洞。2.分散及固定活性中心。3.與活性中心共同完成催化反應。圖三是以粉粒體觸媒來說明觸媒的構造。



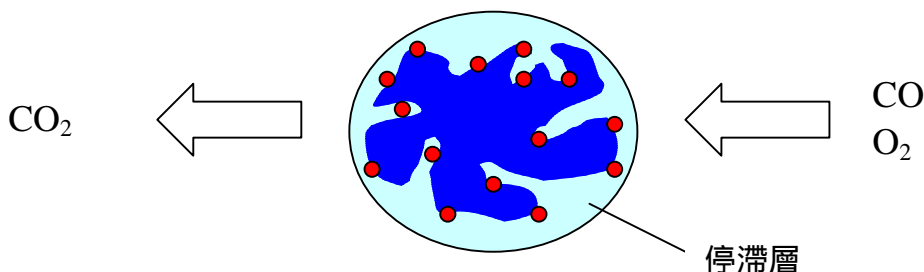
圖三 粉粒體觸媒構造示意圖

（三）觸媒催化反應步驟

異相觸媒進行催化反應可分為七個步驟（以氣/固反應為例）：

1. 反應物由氣流擴散到觸媒表面（通過停滯層）。
2. 反應物擴散通過載體孔洞到達活性中心。
3. 反應物被活性中心吸附。
4. 反應物在活性中心上反應形成生成物。
5. 生成物由活性中心脫附。
6. 生成物擴散通過載體孔洞到達觸媒表面。
7. 生成物由觸媒表面擴散到氣流中。

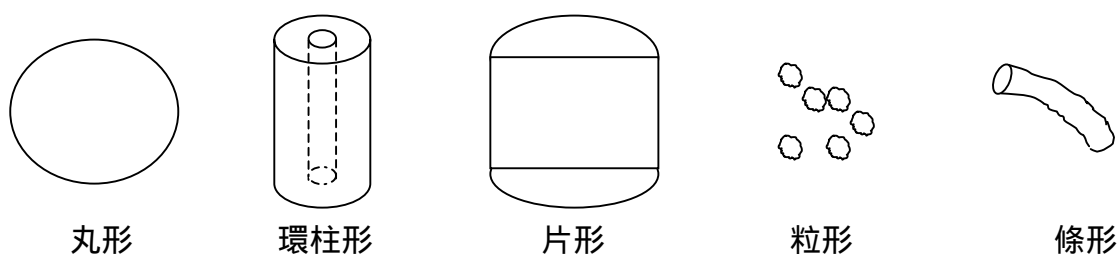
停滯層是靜止停留在顆粒表面上一層很薄的氣體層，而它會形成擴散的阻力。停滯層的厚薄與流體的種類、溫度、黏度、流速以及固體的粒徑、形狀有關。上述七個步驟中速率最慢者為表觀的反應速率決定步驟，如果想要改善觸媒之性能應由其先著手。



圖四 催化反應示意圖

(四) 固定床式反應器

固定床式反應器，是將粒狀觸媒填充在一管子中，反應物由此管流過而與觸媒接觸。由於粒子阻擋了氣體的流動，結果使觸媒床兩端產生了壓力降，所以在入口端必須施加正壓力，或於出口端造成負壓力，以期保持住一定的空間流速。所需壓力的大小，隨空間流速及觸媒床體積的增加、以及顆粒大小的減小而加大。許多不同形狀、大小的觸媒顆粒被使用於固定床式反應器。圖五是一些常見的觸媒形態。



圖五 一些常見的觸媒形態

(五) 空間速度

為比較不同大小、形狀的流動式反應器的性質，或為了將實驗室規模的研究成果放大為實場規模，我們需要一種不受反應器大小、形狀所影響的反應物流量的描述方式。空間速度（space velocity, SV）的定義如下：

$$\text{空間速度 (min}^{-1}\text{)} = \text{反應物流量 (L/min)} \div \text{反應器體積(L)}$$

對於非均相觸媒反應器而言，反應器體積應以觸媒床體積為準，由定義可知一個觸媒床體積 1L 的反應器當反應物流量為 10L/min 時 SV 為 10 min^{-1} ，而一個觸媒床體積 5L 的反應器當反應物流量為 50L/min 時 SV 也是 10 min^{-1} ，因此我們可以藉由空間速度的聯繫來比較這二個反應器的特性。

使用空間速度時必須指明反應物的狀態，例如是在何種溫度、壓力之下的氣體或液體，如此才能正確表達出反應物的流量特性。

二、研究架構

為研發適合處理瓦斯熱水爐廢氣中一氧化碳的觸媒，首先必須瞭解瓦斯熱水爐燃燒及排放一氧化碳的情形，廢氣中氧氣的濃度也很重要，因為氧氣濃度越低越不利於轉化成二氧化碳之反應。

經實際測量某符合 CNS 國家標準之瓦斯熱水爐廢氣組成後發現：當使用小及中火時一氧化碳濃度不高（200ppm 以下），但是當使用大火時，一氧化碳濃度可達 11,000ppm 左右，且氧氣濃度僅略高於 6%。因此，所有測試觸媒性能的實驗均設定在含氧氣 6% 的條件下進行。

觸媒配方及製作程序的篩選使用一次一因子的方式進行，每一階段僅改變一項因子的水準，經由測試評選出最佳的條件。進行的方式如下：

（一）活性中心金屬種類

使用氧化鋁為載體，活性金屬含量為 10%，煅燒溫度為 400°C ，分別製作 Cu、Co、Ni、Fe 等四種不同活性中心金屬之觸媒。經實驗測試催化性能以選出最佳之活性中心金屬。假設選出者為 M。

（二）載體種類

使用 M 為活性中心金屬，M 之含量為 10%，煅燒溫度為 400°C ，分別製作氧化鋁、高嶺土、二氧化鈦、二氧化矽等四種不同載體之觸媒。經測試催化性能以選出最佳之觸媒載體。

假設選出者為 S。

(三) 活性金屬含量

使用 M 為活性中心金屬，S 為載體，煅燒溫度為 400℃，分別製作 M 之含量為 5%、10%、15%、20% 等四種不同金屬含量之觸媒。經測試催化性能並考慮經濟因素以選出最佳之金屬含量。假設選出者為 X%。

(四) 煅燒溫度

使用 M 為活性中心金屬，S 為載體，金屬含量 X%，分別製作 200℃、300℃、400℃、500℃ 等四種不同煅燒溫度之觸媒。經測試催化性能並考慮經濟因素以選出最佳之煅燒溫度。假設選出者為 Y℃。

(五) 觸媒改良

探討影響催化反應速率的因素作為改良觸媒的設計基礎

經上述四個階段評選之結果：以 M 為活性中心金屬，S 為載體，金屬含量 X%，煅燒溫度 Y℃ 即為最佳之觸媒製作方式。

觸媒製作後尚需以接近實際應用狀況之條件加以測試，最主要之變數為空間速度及一氧化碳濃度的變動。經計算瓦斯燃燒速率及過剩空氣量發現為達實用之可行性，觸媒至少需能在空間速度 500min^{-1} ，(即接觸時間 0.12sec) 完成催化反應，能處理之一氧化碳濃度至少應達到 11,000ppm 以上。

三、觸媒製作

觸媒製作程序如下：

1. 稱取所需質量的活性中心金屬硝酸鹽，加入裝有 200mL RO 水的一公升燒杯中，充分攪拌使完全溶解。
2. 稱取所需質量之載體加入前述之燒杯中，使用攪拌器快速攪拌四個小時，讓活性中心成分與載體充分含浸。
3. 將燒杯內容物倒入蒸發皿中，放入 105℃ 之烘箱內，烘至完全乾燥。
4. 將蒸發皿內之固體物取出，磨至能通過 200 mesh 泰勒標準篩之細粉，再置入預設好煅燒溫度之高溫爐中鍛燒 4 小時。
5. 待回復至室溫後，將鍛燒好的觸媒用 200 mesh 泰勒標準篩篩選出粒徑小於 0.074mm 的粉狀觸媒即製作完成。

前述藥品秤重之計算，以製作 50 公克之 $\text{Co}/\text{Al}_2\text{O}_3$ 觸媒（含 Co 重量百分率 10%）為例說明如下：

首先根據 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 分子量為 291.03，又知 Co 的原子量為 58.933，故可以得下列算式：

$$50 \times 10\% = 5 \text{ (g)}$$

$$5 \div 58.933 \times 291.03 = 24.7 \text{ (g)}$$

即知需要秤出 24.7g 的 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 。又，觸媒中 Al_2O_3 佔 90%，故需稱取 45g 的 Al_2O_3 。

伍、結果與討論

一、瓦斯熱水爐燃燒狀況與廢氣組成

本研究的目的是在於研發適合處理瓦斯熱水爐廢氣中一氧化碳的觸媒，因此首先必須瞭解瓦斯熱水爐燃燒及排放一氧化碳的情形，廢氣中氧氣的濃度也是必須關注的重點，因為要將一氧化碳反應生成二氧化碳必須要有氧氣作為氧化劑。

表三是實際測量某符合 CNS 國家標準之瓦斯熱水爐的廢氣組成，從中可發現：當使用小火及中火時一氧化碳濃度都在 200ppm 以下，以這樣的濃度而言，在通風良好的處所應不至於發生重大危害。但是當使用大火時，一氧化碳濃度可達到 10,860ppm，且氧氣濃度只有 6.2 %。由於冬天的時候氣溫較低，用戶大多使用大火燒熱水，因此一氧化碳中毒的事件頻傳。

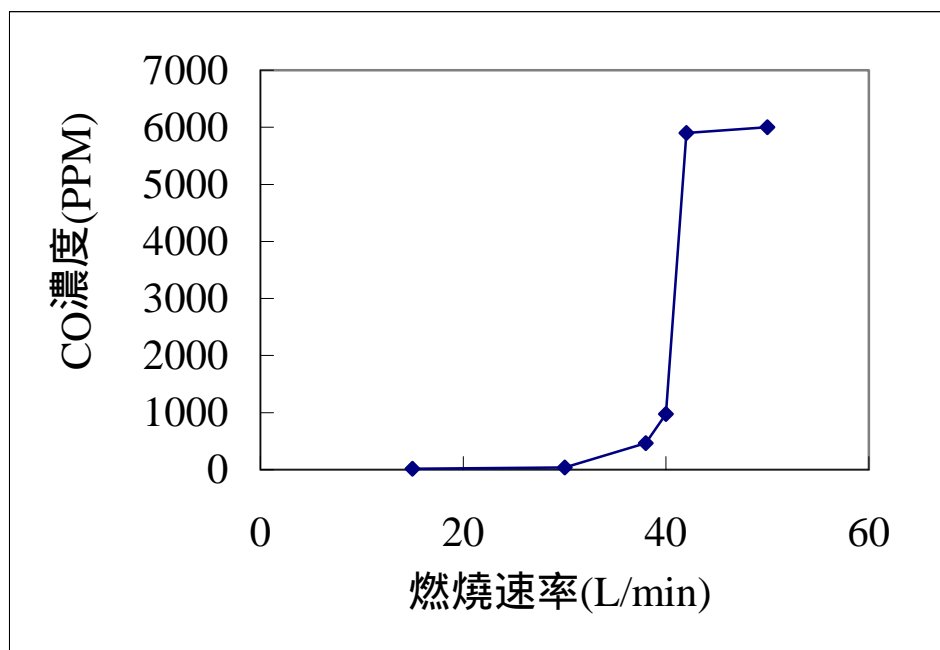
表三 某 CNS 認證廠牌瓦斯熱水爐廢氣實測結果

燃料：天然氣

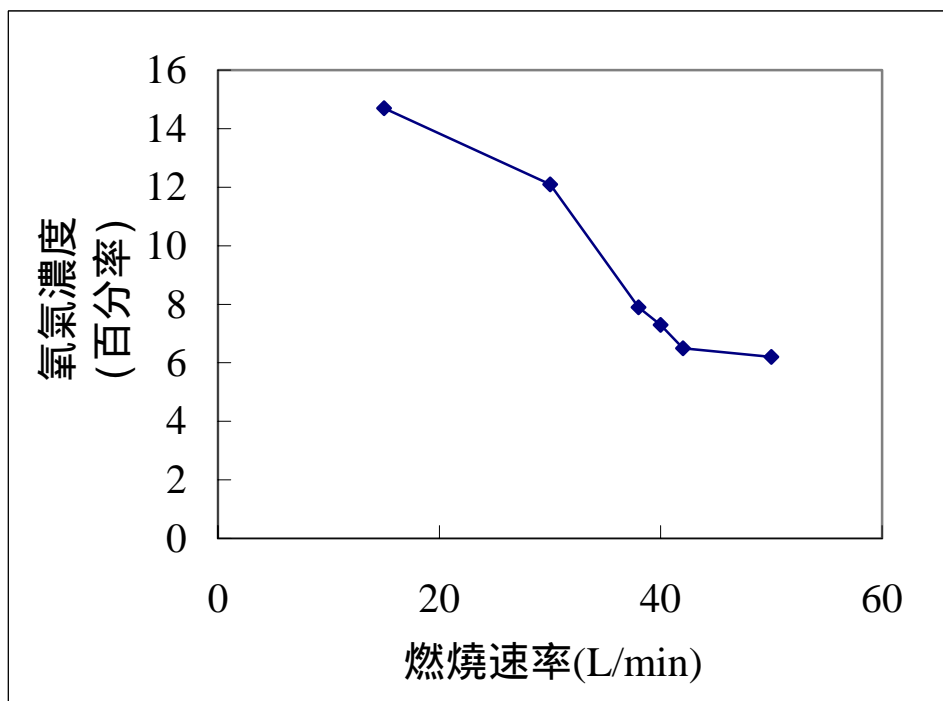
取樣位置：排氣口深入 5 公分

火力	瓦斯燃燒速率 (L/min)	CO (ppm)	O ₂ (%)	廢氣溫度 (℃)
小	15	18	14.7	115
中	30	40	12.1	135
—	38	467	7.9	165
—	40	975	7.3	169
—	42	5900	6.5	173
大	45	10860	6.2	181

當燃料使用越多時，一氧化碳濃度會增高，而含氧量會減低，由圖六及圖七可看出廢氣中一氧化碳上升與氧氣量下降的趨勢。



圖六 廢氣中一氧化碳濃度隨燃燒速率變化圖



圖七 廢氣中氧氣濃度隨燃燒速率變化圖

二、觸媒篩選

製作觸媒最重要的因子有下列四項：

1. 活性中心金屬的種類

活性中心金屬是觸媒催化能力的來源，選出最具催化活性的金屬自然是觸媒研究的第一要務。

2. 載體的種類

載體的主要功能在於提供大的表面積以支撐及分散活性中心金屬，使活性中心金屬能充分與反應物接觸，產生最大的催化效率。此外，載體還具有降低觸媒製作成本的功用。

3. 活性中心金屬的含量

原則上增加活性中心金屬的含量能增加觸媒的性能，但因活性中心金屬必須適度地分散在載體上才能發揮最大的功效，所以，搭載過多的活性中心金屬並不會增加催化效果，反而是一種浪費。

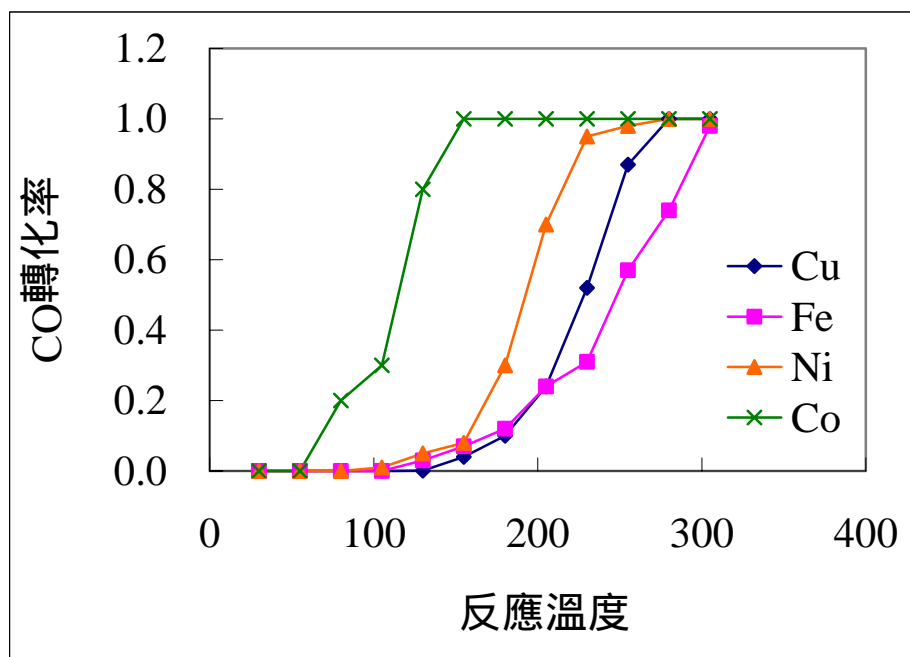
4. 觸媒煅燒的溫度

適當的煅燒溫度可將觸媒原料中的硝酸根熱分解，放出 NO_2 氣體，並使活性中心金屬轉換成正確的氧化物型態，過高的煅燒溫度除浪費能源外，也可能導致活性中心金屬聚集，因而降低分散性影響觸媒性能。

本研究以四個階段來篩選製作觸媒的最佳條件，每一階段探討一項因子，詳細的實驗過程及討論分述於以下諸小節。

（一）活性中心金屬種類篩選

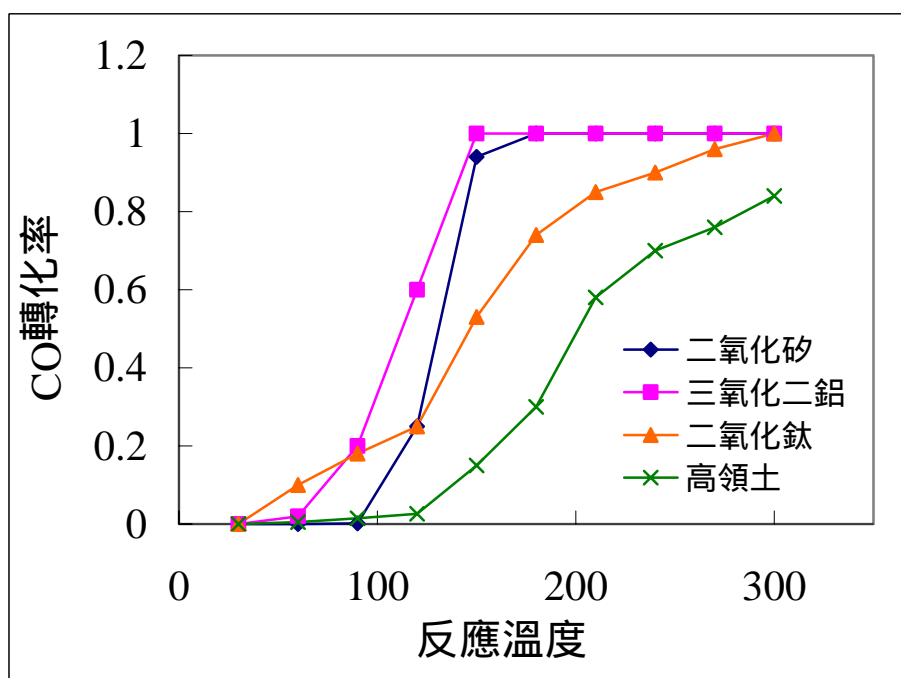
如圖八所示，比較 Cu、Fe、Ni、Co 等四種活性中心金屬，發現以 Co 作為活性中心的轉化效率最佳，在空間速度 50min^{-1} 的條件下，只須 155°C 即可將進口濃度 3764ppm 的一氧化碳完全轉化。其他三種活性中心金屬與之比較均相形遜色，因此，應選擇 Co 作為活性中心金屬是十分明確的。



圖八 各種活性中心金屬催化性能之比較

(二) 載體種類篩選

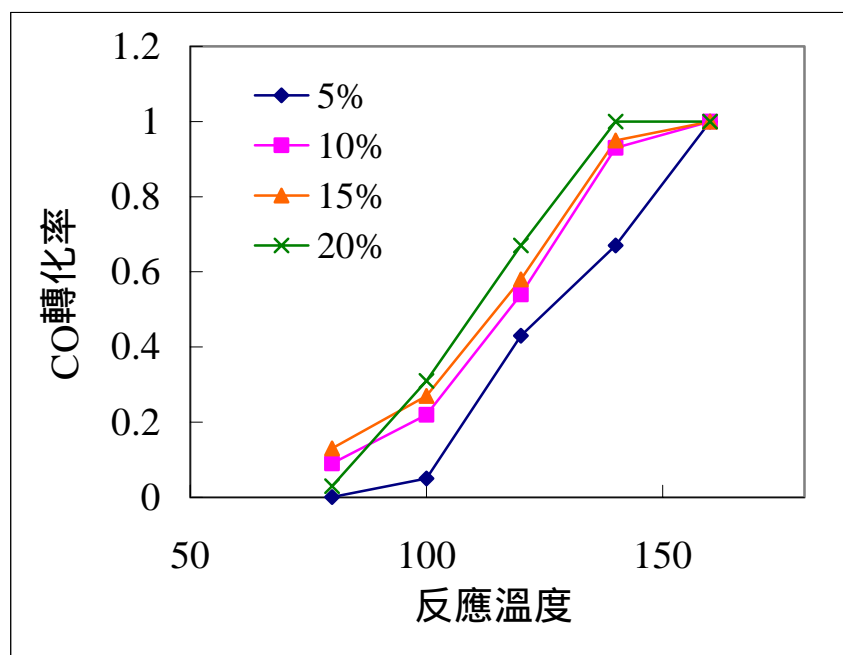
由圖九可以看出四種不同載體的效果由優至劣依序分別為：三氧化二鋁、二氧化矽、二氧化鈦與高嶺土。因此，可確定 $\text{Co}/\text{Al}_2\text{O}_3$ 是最佳的組合。



圖九 鈷搭配不同載體催化效果之比較

（三）活性金屬含量

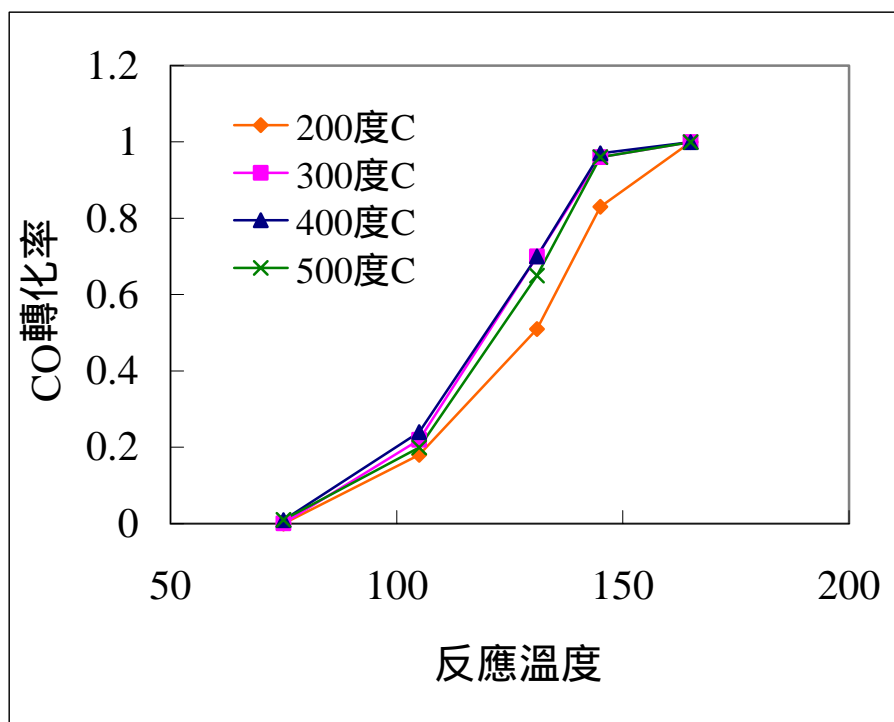
在此階段實驗中，我們調製不同鈷含量的觸媒，並在實驗後發現除了 5% 含量的觸媒效果明顯較差之外，10%、15%、20% 含量的觸媒轉化效率沒有太大的差異。由於硝酸鈷的價格較高，基於成本的考量，選擇使用鈷含量為 10% 的觸媒。



圖十 不同鈷含量之觸媒催化效果之比較

（四）鍛燒溫度

最後我們嘗試改變鍛燒溫度，由圖十一可發現除了以 200°C 鍛燒的觸媒效果較差外，其他三者催化的性能幾乎相等，因為鍛燒溫度越高越消耗能源，所以應選擇使用的鍛燒溫度為 300°C。

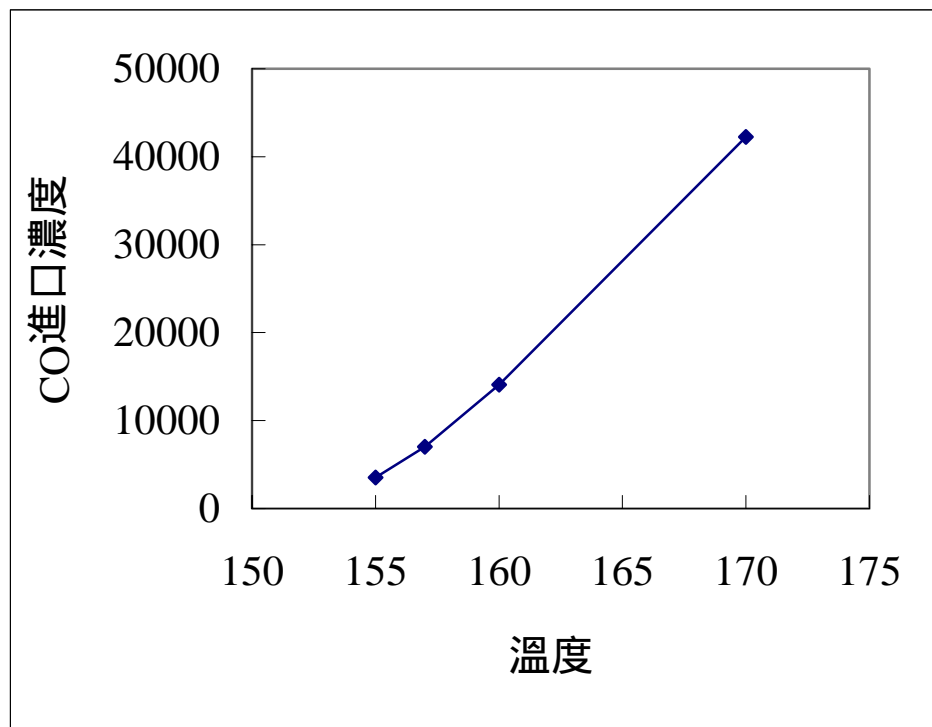


圖十一 不同煅燒溫度對鈷觸媒催化性能的影響

經四階段研究結果得到最佳的觸媒製作條件為：以鈷為活性中心金屬，以三氧化二鋁為載體，鈷含量為 10%，煅燒溫度為 300°C。

三、一氧化碳濃度變化與所需之反應溫度的關係

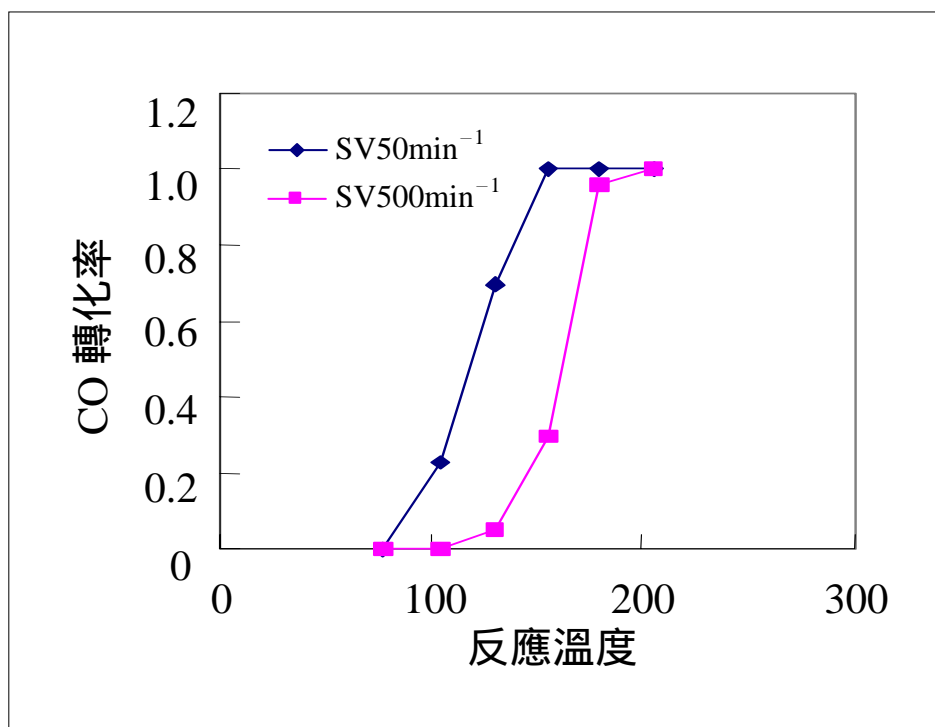
在固定空間流速為 50min^{-1} ，氧含量 6% 之條件下，變化不同的一氧化碳入口濃度，並測量其轉化率為 100% 時所需要的溫度。實驗結果整理於圖十二，由其中可了解到濃度越低時所需要的反應溫度越低，反之則越高。



圖十二 不同 CO 進口濃度達到百分之百轉化率所對應的溫度

四、空間速度變化與所需之反應溫度的關係

圖十三顯示廢氣以空間速度 500min^{-1} 通過鈷觸媒時，欲達到與 50min^{-1} 時有相同的轉化率則所需的反應溫度較高。原因是接觸時間較短，所以必須提高溫度以增加反應速率才能達到相同的效果。



圖十三 不同空間流速下 CO 轉化率比較

五、瓦斯熱水爐燃燒廢氣量計算與觸媒床體積推估

假設燃料消耗速率為 $0.045 \text{ Nm}^3/\text{min}$ (45 公升, 標準狀態), 反應溫度為 180°C (453.15K), 廢氣中氧氣濃度 6%, 計算瓦斯熱水爐燃燒廢氣量並推估所需的觸媒床體積。

【註】 Nm^3 為標準立方公尺, 在 1atm , 0°C (273.15K) 條件下的氣體體積單位

(一) 利用理想氣體方程式 $PV=nRT$ 計算每分鐘燃燒甲烷的莫耳數

理想氣體常數 $R=0.082\text{L} \cdot \text{atm}/(\text{mole} \cdot \text{K})$

反應式為: $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \dots\dots\dots (1)$

$$1 \cdot 45 = n \cdot 0.082 \cdot 273.15$$

$$n=2$$

由(1)式可知理論需氧量莫耳數與甲烷莫耳數比為 1:2, 所以理論需氧量為 4 莫耳。

(二) 計算廢氣量 (以完全燃燒計算)

設每分鐘廢氣量為 X 莫耳, 廢氣中含氧 6% (即 $0.06X$ 莫耳)

$$X = n_{\text{CO}_2} + n_{\text{N}_2} + n_{\text{O}_2} + n_{\text{H}_2\text{O}}$$

$$X = 2 + n_{\text{N}_2} + n_{\text{O}_2} + 4$$

$$X = 6 + n_{\text{N}_2} + n_{\text{O}_2}$$

空氣中氮氧莫耳數比為 4:1, 所以 $n_{\text{N}_2} = (4 + 0.06X) \times 4$

$$X = 6 + 16 + 0.24X + 0.06X$$

$$X = 0.3X + 22$$

$$0.7 X = 22$$

$$X = 31.4$$

(三) 計算每分鐘廢氣體積

$$V = nRT/P = 31.4 \times 0.082 \times 453.15 \div 1 = 1167$$

亦即廢氣體積流量為 1167 L/min (溫度 180°C)

(四) 觸媒床體積推估

空間速度 (min^{-1}) = 氣體流量 (L/min) \div 觸媒床體積 (L)

由表四可知當廢氣量為 1167(L/min)時，若使用空間速度 500 (min^{-1}) 需觸媒床體積 2.33(L)，若使用空間速度 1000 (min^{-1}) 則需觸媒床體積 1.17(L)。實用上此為合理的床體積大小，若空間速度小於這兩者，則所佔用之體積過大，不適合應用在家庭用瓦斯熱水爐上。

表四 特定氣體流量下空間速度與床體積對照表

空間速度 (min^{-1})	氣體流量(L/min)	觸媒床體積(L)
50	1167	23.34
100	1167	11.67
300	1167	3.89
500	1167	2.33
1000	1167	1.17

六、觸媒實用性測試

綜合上述研究，瓦斯熱水爐觸媒轉化器至少需具備下列性能才有實用的價值：

1. 須能將含 11,000ppm 一氧化碳的廢氣轉化至出口濃度小於 200ppm，且如果可能的話一氧化碳排放濃度應該越低越好。
2. 觸媒所需的工作溫度最好能在瓦斯熱水爐內部廢氣可達到的溫度範圍內。
3. 空間速度至少需 500 min^{-1} 以上。

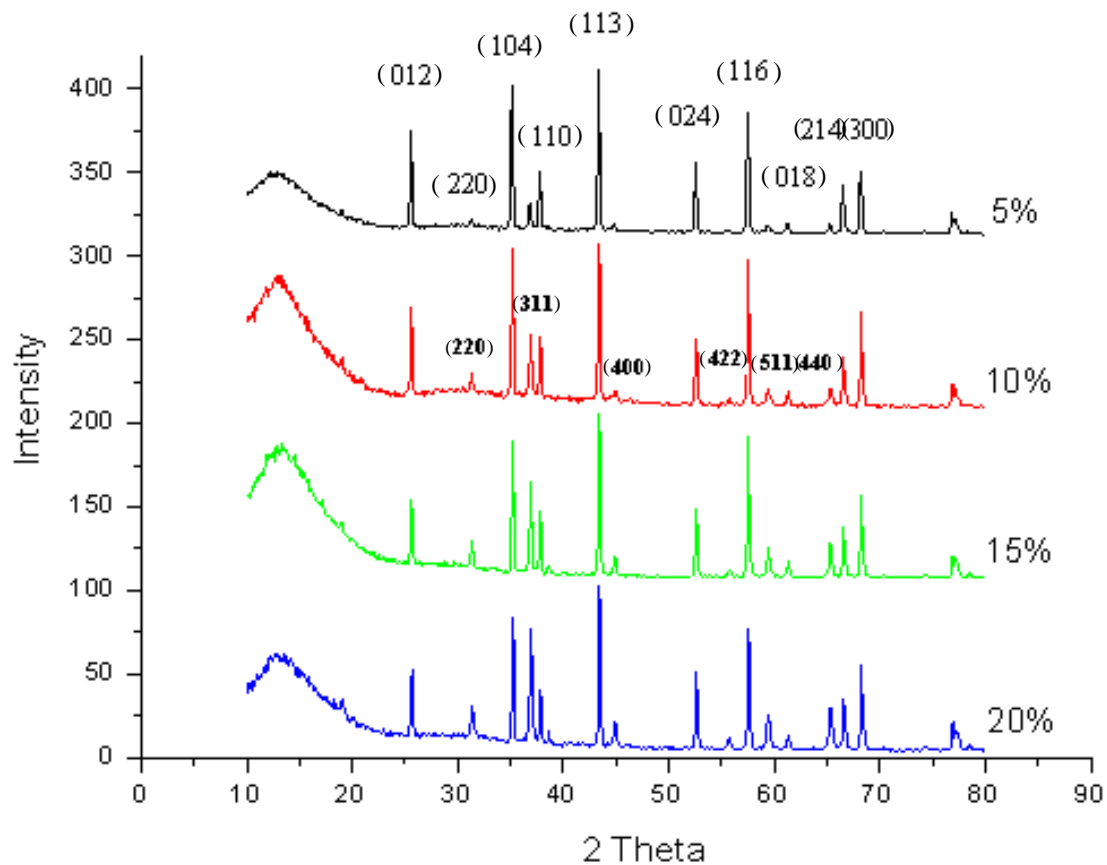
為了瞭解本研究所產製的觸媒其性能是否達到要求，我們測試了幾組嚴苛的實驗條件，結果整理於表五。從中可知此觸媒即使在空間速度高達 1000 min^{-1} 時，亦僅需 233℃ 的反應溫度即可將 14,632ppm 的 CO 百分之百轉化。瓦斯熱水爐熱交換區內輕易即可取得 300℃ 以上的高溫因此，我們所研發的觸媒具有實際應用的可行性。

表五 觸媒性能測試結果

組別	CO 入口濃度 (ppm)	O ₂ 濃度 (%)	空間速度 (min^{-1})	反應溫度 (°C)	CO 出口濃度 (ppm)
1	3547	6	500	206	0
2	3658	6	1000	224	0
3	14632	6	1000	233	0

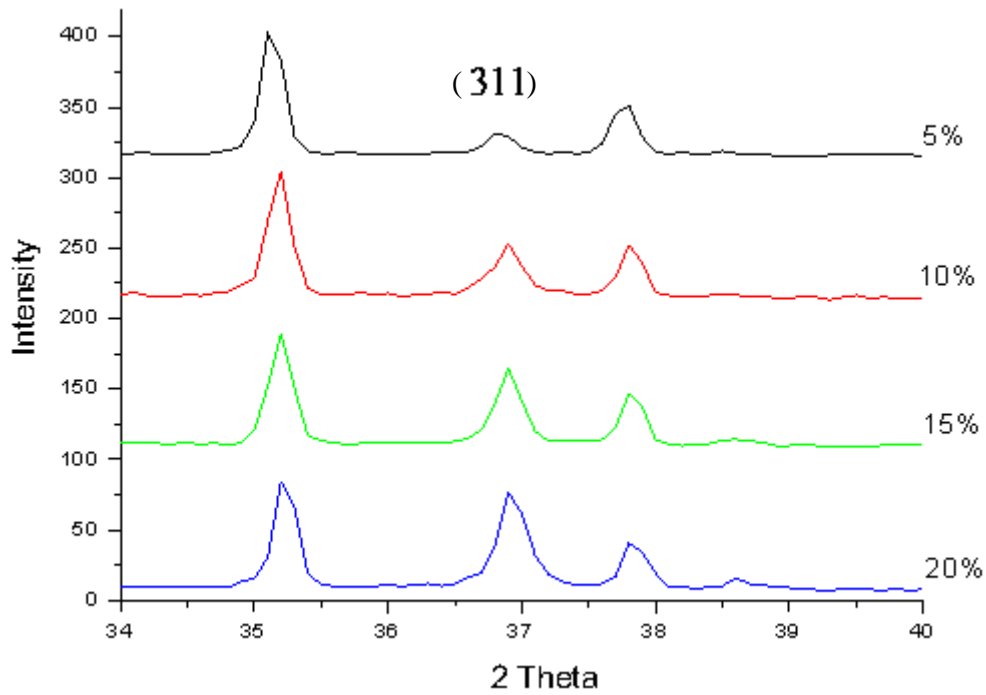
七、觸媒型態的鑑定

爲了瞭解我們所研發之觸媒的性質，作爲一氧化碳氧化觸媒改良的引導方向，我們對鈷系列觸媒做了一系列 X 光繞射譜測量，經與 X 光數據資料庫比對，確認觸媒載體爲 α 型氧化鋁，鈷則以 CoAl_2O_4 之型態散佈於載體上。



圖十四 $\text{Co}/\text{Al}_2\text{O}_3$ 之 X-Ray 繞射圖譜

圖十五為 CoAl_2O_4 主繞射峰(311)範圍之 X 光繞射放大圖。由於各不同鈷濃度樣品之(311)繞射峰都有近乎相等的半波寬，我們知道各不同濃度鈷觸媒的 CoAl_2O_4 晶粒大小都是一樣的。



圖十五 $\text{Co}/\text{Al}_2\text{O}_3$ 之 X-Ray 繞射局部放大圖

陸、結論

經由這次的研究我們發現瓦斯熱水爐使用大火時 CO 的濃度非常高，是導致一氧化碳中毒事件的關鍵原因，要解決這個問題觸媒轉化是一種可行的方式。影響觸媒性能的因素中以活性中心的種類最為重要，我們發現對轉化一氧化碳為二氧化碳的反應而言鈷有最好的催化效果，其次分別為：鎳、銅、鐵。最好的載體是三氧化二鋁，鈷的含量使用 10%，段燒溫度使用 300°C 可兼顧性能與成本。

我們所研發的 Co/Al₂O₃ 觸媒具備有實用的潛力，可以在空間速度高達 1000min⁻¹ 的情況下將濃度 14,632ppm 的 CO 百分之百轉化為 CO₂，而僅需 233°C 的反應溫度，如果藉由燃燒廢氣來加熱，觸媒床可以在點火後很短的時間內達到此一溫度。

經由 X 光繞射的結果，我們知道不同鈷含量的觸媒都有相同的晶體結構及粒徑分布，而造成不同鈷含量觸媒轉化效率不同的主要原因，來自於活性中心濃度的差異，而與觸媒的本質無關。因此，設法增加鈷觸媒活性中心的數目，是改良鈷觸媒催化一氧化碳氧化反應的首要方法。由不同鈷含量之觸媒催化效果之比較(圖十)可知，鈷含量大於 10% 之觸媒活性並無法隨鈷濃度之提升而增加，這個結果表示載體表面可用於分散鈷物種之位置在鈷濃度為 10% 時，就已經被鈷填滿，鈷濃度大於 10% 時只能使鈷堆疊在一起而無法增加鈷觸媒活性中心的數目，因此增加載體表面積以分散表面鈷物種，製造更小的 CoAl₂O₄ 粒子，將更多的鈷活性中心暴露出來，應該可以讓鈷觸媒的催化能力更為加強，以更少量的鈷就可以達成去除熱水器廢氣中一氧化碳的效果。而氧化鋁的種類很多，選用大表面積的氧化鋁作為載體，可以生產更為經濟的 CO 轉化觸媒，我們還在繼續進行一氧化碳在鈷觸媒上的吸收形態及吸附量測量實驗，更深入的探討鈷粒徑變化時反應物在觸媒表面的各種行為。

因此，將來如果有機會繼續發展的話，應該可以開發成一種安全的爐具，以降低一氧化碳中毒的風險，維護社會大眾的健康及生活品質。

柒、參考資料

1. 胡興中編譯。觸媒原理與應用。三版五刷，新科技書局，中華民國九十一年元月十日。
2. 張金海編著。非均相反應觸媒特性與實效應用。修訂再版，復文書局，中華民國八十五年九月。
3. 李明哲編譯。非均相觸媒反應的理論與應用。修訂五版，復文書局，中華民國八十一年二月。
4. 李秉傑、邱宏明、王奕凱合譯。非均勻系催化原理與應用。初版，國立編譯館，中華民國七十七年二月。
5. Huiping Zhang、Xijun Hu (2004)。Catalytic oxidation of carbon monoxide in a fixed bed reactor。 **Separation and Purification Technology**， Volume 34 Page 105-108。
6. Jane B. McCammon, Lyle E. McKenzie, and Michele Heinzman (March 1996)。 Carbon Monoxide Poisoning Related to the Indoor Use of Propane-Fueled Forklifts in Colorado Workplaces。 **Applied Occupational and Environmental Hygiene**， Volume 11, Issue 3, Page 192-198，
7. 蔡欣冀 (民國 93 年)。鈷觸媒之觸媒、特性分析及催化性質之研究。全國碩博士論文資訊網。
8. 吳明玲 (臺北榮總臨床毒物科總醫師) (民國八十五年十二月九號)。提防隱形殺手——氧化碳。自由時報。
9. 科普知識(民國93年7月10日)http://nscnt22.nsc.gov.tw/popular_science_list.asp?popsc_cid=2



照片一 觸媒原料及電子天秤



照片二 觸媒製作-藥品配製



照片三 觸媒製作-攪拌含浸觸媒



照片四 觸媒製作-放入高溫鍛燒爐



照片五 鍛燒時釋放出的 NO_2 氣



照片六 觸媒製作-觸媒成品



照片七 反應器



照片八 煙道採樣器

Optimizing a Catalyst for Elimination of Carbon Monoxide Exhausted from Gas Water Heater

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Introduction

Motivation

To our knowledge, gas water heaters (GWHs) are widely used in many countries despite the fact that they can produce the lethal gas CO when the combustion is not complete. Therefore, the horrible news often hits the headlines that many users of GWH die from inhaling too much carbon monoxide (CO). Fig. 1 shows Taiwan statistic for injuries and fatalities in recent years.

I have always wanted to pursue research that can benefit the world. I wondered if I could develop an approach that would remove the CO from the exhaust of GWHs.

When I looking into the composition of today's catalytic converters, especially the ones used in cars, platinum is the primary active metal adopted. However, platinum is very expensive and presents a major barrier to much wider usage. In this study, I attempted to develop a catalyst based on a lower-cost metal, which can be installed inside a GWH to reduce the CO from the exhaust.

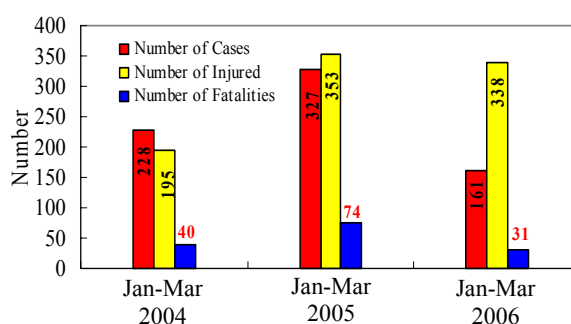


Fig. 1 CO Poisoning Incidence Data

From: Taiwan National Fire Agency, Ministry of the Interior

Analysis of the problem

Formed from incomplete combustion, CO is very detrimental to human health. Exposure to high concentrations of CO (4,000ppm or above) can lead to coma, and even death. Certainly using electric water heaters would not cause CO poisoning, but their enormous demand for electricity is usually an excessive load for buildings; therefore it is not easy to popularize the use of electric water heaters. However, with such benefits as convenient installation, small size and the low cost, about 95% of families in Taiwan use GWH.

Generally speaking, burning fuel in an airtight space is the major factor that causes cases of CO poisoning, and the best way to prevent CO poisoning is to place GWHs in areas with good ventilation. Nevertheless, due to limited space, even if the heater is placed outdoors with poor diffusion of the poisonous gas, CO poisoning accidents cannot be effectively prevented. Though in recent years, a new brand of GWH, which has the function of forcibly emitting the exhaust, has come into use. The newly invented GWH still requires a large space to perfect its functions. In a place with dense population, such a product cannot meet the demands of many residents. Several cases of CO poisoning have occurred even though the GWH is placed in a semi-open space (such as

a veranda, corridor or fire lane), and almost all cases of CO poisonings occur in winter, showing that burning in place with bad ventilation probably was not the only reason for the tragedy. Therefore, the fundamental way to solve this problem is to decrease the concentration of CO in the exhaust itself.

The source of CO is the exhaust of the GWH, so if a GWH is equipped with a catalytic converter (Fig.2) in the exhaust passage, the CO can be converted into CO₂. The converter should be set up around the heat-exchange area. When the fire is ignited, the high-temperature flue gas will heat the catalyst bed up to the working-temperature. The best thing is that the reaction heat can be used in heating to save energy.

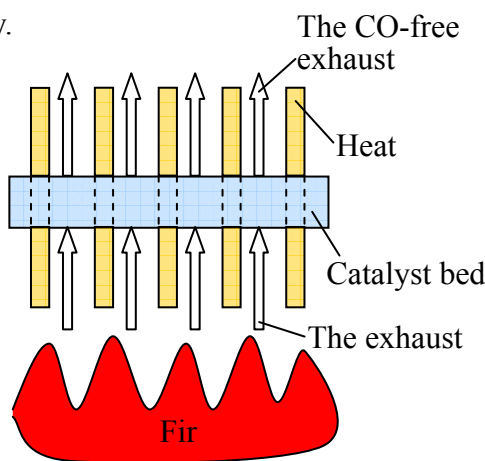


Fig. 2 Diagram of catalytic converter

Background of Catalyst

(1) The heterogeneous catalyst

Catalysts can be divided into homogeneous and heterogeneous catalysts. When the catalyst is in a different state from the reactant, it is called a heterogeneous catalyst. Take the catalytic converter from cars for example: its catalyst is a solid but the reactant is gas, so this is the application of heterogeneous catalyst. As heterogeneous catalysts are easily separated from the reactants, they are used extensively. The efficiency of the catalyst is to reduce the activation of the chemical reaction, so it can increase the rate of reaction. Heterogeneous catalysts are composed of active metal and supporting metal, and they usually use appropriate oxidized metal as the active metal. The major function of the supporting materials is to offer a large surface area and appropriate holes in order to disperse and fix the active metal. Sometimes, the supporting metal also participates in the reaction, finishing the catalytic reaction together with the active metal.

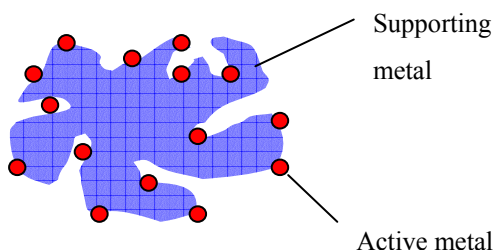


Fig.3 The diagram of powdery catalyst

(2) Steps of Catalytic reaction

The catalytic reaction of heterogeneous catalyst can be divided into seven steps (take gas/solid for instance):

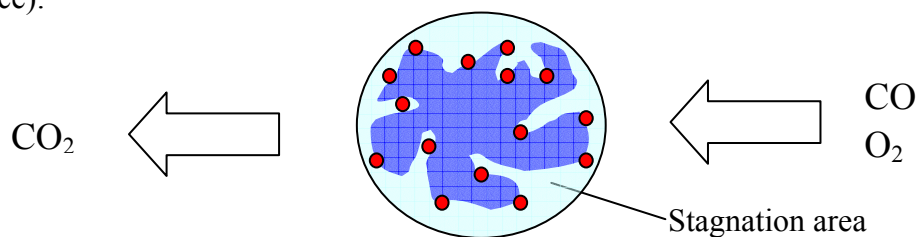


Fig. 4 Diagram of catalyzed CO conversion

1. The reactant spreads from air current to catalyst surface
2. The reactant spreads through the holes in the supporting materials to reach the active metal
3. The reactant is absorbed by the active metal
4. The reactant reacts with the active metal and then forms the products
5. The product takes off from active metal
6. The product spreads through the hole of supporting metal to reach the catalyst surface
7. The product spreads from catalyst surface to the air current.

Of the above seven steps, whichever has the lowest speed is the one that determines the step of reaction rate. With regards to a heterogeneous catalyst, the physical factors (specific surface area, aperture size, spreading...etc) and chemical factors (absorbency, active metals) therefore play an important role. To influence the catalyst preparation and performance, many operation parameters such as the type and content of active metal, support, and calcination temperature are deterministic. A successful catalyst preparation must harmonize all kinds of factors to optimize the catalyst performance.

(3) Space Velocity

In order to turn this laboratory research to the practical uses, we need a description of the reactant flow, independent of the size and shape of the reactor. In a heterogeneous catalytic reaction, the space velocity (SV) is to be formulated as follows:

$$\text{Space velocity (min}^{-1}\text{)} = \text{Reactant flow (L/min)} \div \text{Catalyst bed volume (L)}$$

For instance, when the flow of reactant is 10 L/min, with the reactor containing 1L of catalyst, the space velocity is 10 min^{-1} . However, when the flow of reactant is 50 L/min, with the reactor containing 5L of catalyst, the space velocity is also 10 min^{-1} ; therefore, we can compare the characteristics of these two reactors in term of space velocity. The most important parameter in scaling up the equipment is space velocity.

The heat exchange area of the family-sized GWH is suitable for about 5 liters of catalyst bed, so the catalyst volume used must be less than this. In other words, the necessary catalyst volume cannot exceed 5 liters, or it doesn't have the feasibility of application, and a catalyst with a better performance should be selected.

Materials and Methods

Determining the Composition of Exhaust from GWH

In order to understand the degree of CO production when using GWH, a gas analyzer is used to measure the exhaust from five different brands.

Experimental Plan

A one-factor-at-a-time experimental plan was performed to search for a suitable catalyst. Four different active metals (cobalt, copper, iron, and nickel), four different supports (silicon oxide, aluminum oxide, titanium oxide, and kaolin- $\text{Al}_4[\text{Si}_4\text{O}_4](\text{OH})_8$), metal-to-support ratios (loads of 5% to 20%), and calcination temperatures (200 to 500°C) were studied in order to develop a catalyst for the conversion of CO.

Preparation of Catalyst

The processes of catalyst preparation are as follows: first, weigh the required nitrate of active metal, and place it in a 1-L beaker with 200 ml of RO water, mixing until the metal nitrate is fully dissolved. Second, measure out the necessary weight of supporting materials and add it to the beaker containing the solution, mixing them for six hours with an agitator, in order to saturate the active metal with the supporting materials. Transfer the contents into an evaporator, and dry in an oven at 105 °C. Take the resultant solid out of the evaporator; rub it to fine powder through a 200 mesh Taylor's standard sieve, and then calcined it for 4 hours in a chamber furnace, with the temperature set in advance. After cooling to room temperature, a sieve is used to filter the calcined catalyst in order to collect a powdery catalyst with a particle size smaller than 0.074mm.

Fig. 5 is the flowchart of catalyst preparation and testing. The chemicals used in this work are listed in table 1.

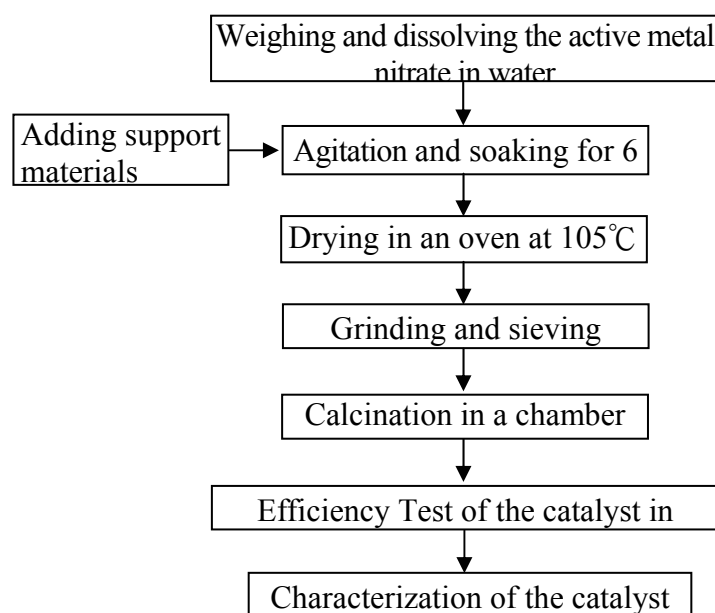


Fig.5 The flowchart of catalyst preparation and test

Table1. Chemicals used in this work

Copper (II) Nitrate	Nickel Nitrate
Iron (III) Nitrate	Cobalt (II)Nitrate
Aluminum oxide	Silicon Dioxide
Titanium Dioxide	Kaolin
10% -CO standard gas	

Catalytic reaction apparatus and procedure

Fig. 6 presents the setup for the catalytic reaction. The reaction gases are mixed with standard gases 10%-CO, N₂ and air, to yield the required chemical composition. The reactor is made of stainless steel with a double pipe structure. The reaction gas enters from the inlet of the outer pipe and flows down. The reaction is performed on the catalyst bed, which is at the bottom of the space between the outer and inner pipes. The catalyst bed has, in order from bottom to top, a 0.5cm layer of quartz wool at the bottom, a 1 cm layer of quartz sand, a 10cm³ volume of catalyst, and another 1cm layer of quartz sand. The reaction gas passes through the catalyst bed and transfers into the inner pipe. Finally, the gas leaves the reactor and passes out the vent. A K-type thermocouple is placed from the top of the inner pipe to the bottom of the inner pipe to measure the reaction temperature. The reactor is placed in a furnace to maintain the reaction temperature. The furnace can accurately set and control the wall temperature to within 0.1°C. Under fixed

conditions (inlet gas composition, space velocity and furnace temperature), the reaction system reaches a steady state. The reaction temperature reaches a specified value by appropriately adjusting the furnace temperature. The concentrations of CO and O₂ are measured using a gas analyzer (IMR2000, Germany).

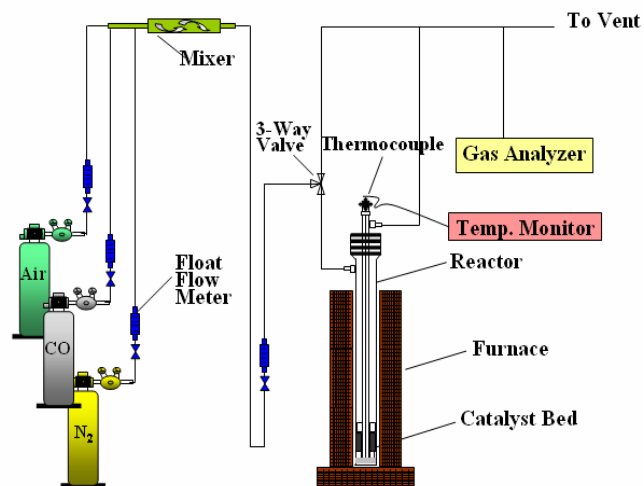


Fig. 6 The schematic diagram of the catalytic reaction experiment apparatus

Characterization of Catalyst

Specific surface area analyzer (BET), energy dispersive spectrometer and X-ray diffraction meter were used to characterize the catalyst.

Testing Catalyst Practicability

The performance of catalysts is evaluated at an oxygen concentration of 6%, a CO concentration of 0.35% or 1.5%, and a space velocity at 500 or 1,000min⁻¹.

Result and Discussion

Determining the composition of exhaust from GWH

Table 2 and Table 3 display the data of five GWHs; we have found that when fuel consumption increases, CO concentration rises as O₂ concentration decreases. The measurement results show that the CO concentration is negligible under low or medium power output conditions; nonetheless, under high power output conditions, the concentration of CO can reach as high as 10,860 ppm, while that of O₂ is as low as only 6.2%. Thus it could be speculated that due to lower temperatures in winter, many people use higher power output to heat water for home use; consequently, the incidents of CO poisoning still occur.

Table 2 CO concentration of exhaust from GWH

Unit: ppm					
Power output	GWH		(* : LNG ** : LPG)		
	A*	B*	C*	D**	E**
Low	19	11	18	33	25
Medium	65	32	40	55	57
High	7348	2854	10860	4922	5672

Table 3 Composition of exhaust from GWH-C

Fuel: Natural gas			
Power output	Fuel supply rate ,L/min	CO, ppm	O ₂ , %
Low	15	18	14.7
Medium	30	40	12.1
-	38	467	7.9
-	40	975	7.3
-	42	5900	6.5
High	45	10860	6.2

The Optimum Conditions for producing the Catalyst

(1) Selection of active metal

As shown in Fig. 7, of four different active metals (Cu, Fe, Ni and Co) when Co is used as the active component, the conversion efficiency is the best. The Co catalyst completely converts the CO at a concentration of 4,000 ppm to CO₂ at a space velocity of 50 min⁻¹ at 155°C. The other active metals seemed to be inferior. Co was therefore chosen as the active metal for the catalyst.

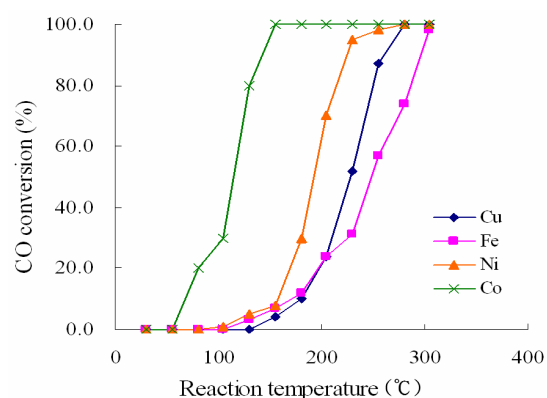


Fig. 7 The comparison of the catalytic activity of various metals

(2) Determination of the supporting material

The effects of the different supporting materials are shown in Fig.8. The order of effectiveness, from the best to the worst, of the Co catalyst with four different supports is as follows: aluminum oxide, silicon dioxide, titanium dioxide, and Kaolin. It indicates that Co/Al₂O₃ is the best combination.

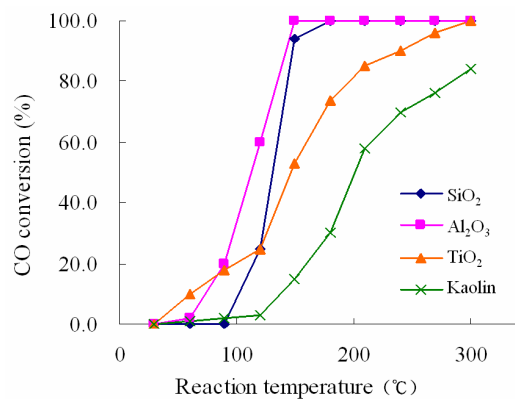


Fig. 8 The support effect on the catalytic activity

(3) Selection of ratio of active metal/support

Fig. 9 shows that, minor differences were observed in the catalytic conversion efficiency between the 10%, 15% and 20% ratios. Considering the cost, the catalyst containing 10% Co was chosen for the following experiments.

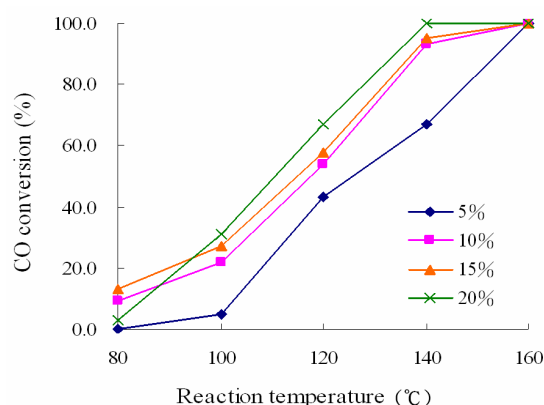


Fig. 9 The comparison of the content of Co

(4) Calcination temperature settings

Fig. 10 shows that above 300°C, catalytic efficiency was almost uniform. The higher calcination temperature used, the more energy was consumed; hence, 300°C was used as the optimum calcination temperature.

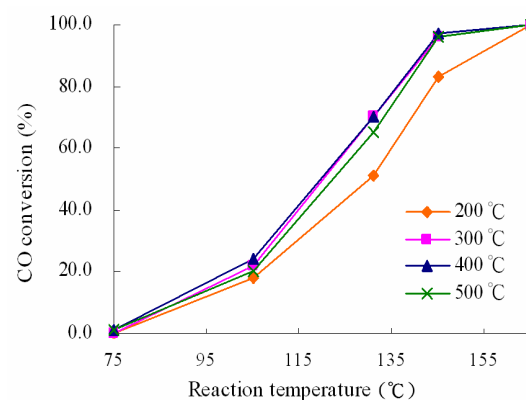


Fig.10 The comparison of calcination temperature

Summary:

Here are the optimum condition for producing the catalyst: 1) Co as the active metal; 2) aluminum oxide as the support; 3) a 10% Co content, and 4) a calcination temperature of 300 °C.

Characterization of Catalyst

X-ray Diffraction Spectra (XRD) (Fig. 11) showed that calcination temperature and type of support did not influence the crystallized form of Co (it remained as Co_3O_4). Combining the data of specific surface area and surface element proportions, Table 4 indicates that the percentage of Co_3O_4 cover on the catalyst surface increased with the amount of metal loading, while the catalyst performance decreased with the specific surface area. Table 5 shows that the different amount of surface area provided by various supports is the main factor influencing the catalyst performance.

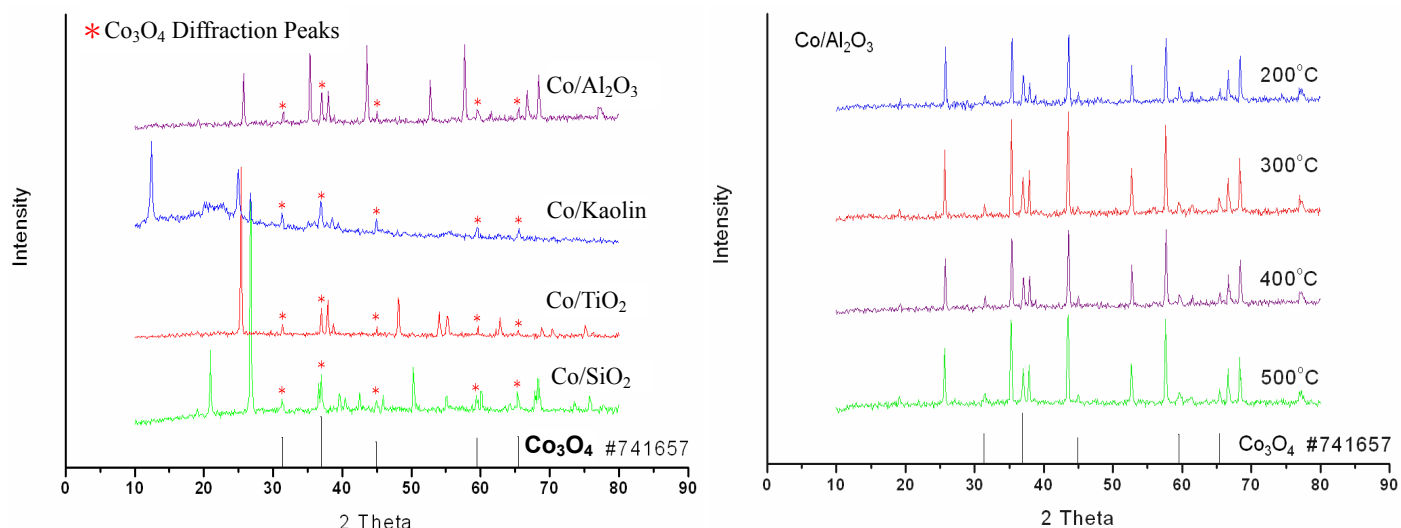


Table 4 Characteristics of Co/ Al₂O₃ catalyst with different Co content

Percentage of Co Content	5%	10%	15%	20%
Percentage of Co on Catalyst Surface*, %	13.35	49.28	56.55	76.48
BET-Specific Surface Area, m ² /g	25.2	26.77	18.51	5.84
The data were obtained by an energy dispersive spectrometer (EDS). Co% + Al % = 100%				

The Scanning Electron Microcopy (SEM) images displayed in Fig. 12 verify the presence of porous holes with the loading of Co catalysts at 5% and 10%, but the holes are practically blocked with Co_3O_4 aggregates when the loading of Co is 15% and 20%.

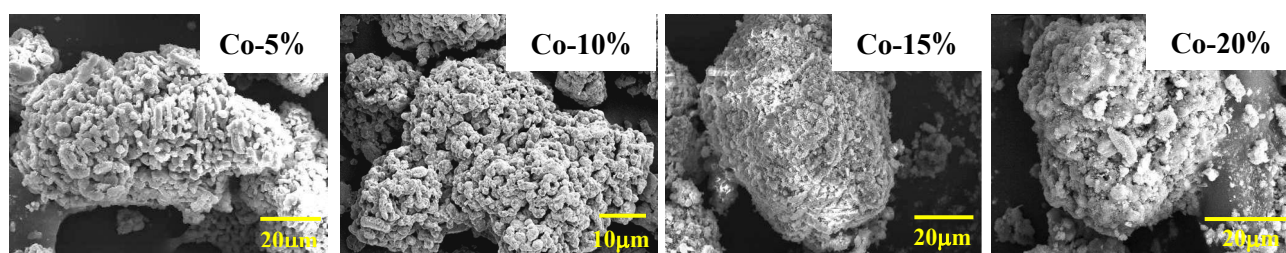


Fig. 12 The SEM photographs of Co/ Al₂O₃ catalyst with different Co content

Table 5 shows that various supports providing different amounts of surface area is the main factor influencing the catalyst performance.

Table 5 BET-specific surface area of Co-catalyst of various supports

Support	Al ₂ O ₃	SiO ₂	TiO ₂	Kaolin
BET-Specific Surface Area, m ² /g	26.77	20.81	13.32	2.73

The specific surface area of the catalyst in the research is 26.77 m²/g.

Strategies to Improve the Performance of the Catalyst

1. Look for the active metal that has better catalytic ability than Co, or combine two kinds, or more, of metal in order to improve catalyst performance.
2. Try different supporting materials or change the manufacture method in order to achieve a larger surface area.

Applications

Catalyst practicability

To determine whether the catalyst can satisfy the application requirements, several experiments have been made, as summarized in Table 6. It indicates that 100% conversion of CO can be achieved when 15,000 ppm CO is catalyzed at 233°C at a space velocity of 1,000 min⁻¹. Since the temperature in the heat-exchange area of GWH can easily go up higher than 300 °C, the catalyst developed in this research has demonstrated its high suitability for particle application.

Table 6 Catalyst practicability test

Space Velocity, min ⁻¹	Inlet CO, ppm	Inlet O ₂ , %	Reaction Temperature, °C	Outlet CO, ppm
500	3,500	6	206	0
1,000	3,500	6	224	0
1,000	15,000	6	233	0

The exhaust calculation of GWH and estimation of the catalyst volume

Suppose that the fuel (natural gas) burns at 0.045 Nm³/min (under high power output conditions), the reaction temperature is 233°C (506.15K), and the concentration of the oxygen in the exhaust is 6%, calculation shows that the flow rate of the exhaust is around 1,300 L/min, i.e. it takes 1.3 L for the catalyst bed under a space velocity of 1,000 min⁻¹. Such a volume is suitable to be placed in a family-size GWH.

Conclusion

High carbon monoxide concentration in the exhaust of GWH, which is generated during the incomplete combustion when the GWH is used under high power output conditions, has been found to cause accidental deaths. Catalytic conversion can be a convenient method to solve this problem.

To determine the most suitable catalyst for converting carbon monoxide to carbon dioxide, certain factors, including different active metals and supporting materials, loading of active metals and different calcination temperatures have been investigated. It is found that of four metal nitrate substances, cobalt displays higher catalytic performance than nickel, copper, and iron. Aluminum oxide is the most suitable support and the best cobalt loading is found to be 10%. The most practical calcination temperature is found to be 300°C. The best combination of all four variables reveals high applicability at low cost.

In the presence of 15,000 ppm carbon monoxide, the conversion rate reaches 100% at a space velocity of 1000 min⁻¹ at 233°C. Therefore, if the catalyst is heated with the exhaust, it can reach to the required temperature in a short period of time.

The practical feasibility of the Co/Al₂O₃ catalyst developed in this work has been demonstrated; therefore, it has potential to be implemented in GWHs to safeguard public health.

Bibliography

1. G. C. Bond (1987) "Heterogeneous Catalysis: Principles and Applications", oxford university press, Great Britain.
2. M. V. Twigg (1989) "Catalyst Handbook", Wolfe Publishing Ltd, London.
3. Jinhai Zhang (1996) "Heterogeneous Reaction Catalyst: Characteristic & Application", Fu Wen publishing, Taiwan.
4. Huiping Zhang, Xijun Hu (2004) "Catalytic oxidation of carbon monoxide in a fixed bed reactor" *Separation and Purification Technology*, Volume 34. P. 105-108.
5. J. B. McCammom, L. E. McKenzie & M. Heinzman (1996) "Carbon Monoxide Poisoning Related to the Indoor Use of Propane-Fueled Forklifts in Colorado Workplaces" *Applied Occupational and Environmental Hygiene*, Volume 11. Issue 3, P.192-198.
6. J. S. Smith; S. Brandon: Morbidity from Acute Carbon Monoxide Poisoning at Three Year Follow-up., *Br. Med. J. 1*:318-321,(1973).

評語

將觸媒轉化器之原理，應用於瓦斯熱水爐很有創意，是一個解決使用熱水器中毒的一個解決方法，在一些金屬化合物中找到鈷是最好的金屬，數據也顯示可以證明其氧化一氧化碳的功效，作品中分析的方法明確也可以應用在實務上相當有價值。未來對於毒化現象或實際放置於熱水爐的結構可再開發是具有發展潛力的題目。