

# Effect of Cu Loading to Catalytic Selective CO Oxidation of CuO/CeO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>

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Received May, 2013

## ABSTRACT

This work studied CuO/CeO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> with wt% Ce:Co ratio 95:5 for selective CO oxidation with effect of wt% Cu loading. The catalysts were prepared by co-precipitation. Characterizations of catalysts were carried out by XRD and BET techniques. The results showed a good dispersion of CuO for 5 wt% Cu loading catalysts and showed high specific surface area of catalyst. For selective CO oxidation, both 5CuO and 30CuO catalysts could remove completely CO in the presence of excess hydrogen at 423 K and 20CuO could eliminate CO completely at 443 K. Moreover, considering the selectivity to CO oxidation, the 5CuO catalyst has shown the highest selectivity of 85% while the 30CuO catalyst obtains the selectivity of 65% at the reaction temperature of 423 K.

**Keywords:** Selective CO Oxidation; CuO/CeO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>; Cu Loading; Ce:Co Ratio; Co-precipitation

## 1. Introduction

Proton-exchange membrane fuel cell (PEMFC) has interest with automotive and residential application because of low operating temperature, high power density and rapid start up. Hydrogen is an ideal fuel for PEMFC. In many practical cases hydrogen can be produced by steam reforming, following by water gas shift reaction [1]. The presence of 1vol%CO in hydrogen steam gas poisons to Pt-anode of PEMFC [2]. Among the different methods for removal CO, selective CO oxidation reaction is the preferred methods because this method used oxygen for CO oxidation and high efficiency for remove CO [3]. An efficiency of catalyst for reaction must be active and selective to avoid parallel H<sub>2</sub> oxidation.

In the recent year, the CuO-CeO<sub>2</sub> catalyst has been proposed as a promising catalyst due to its low cost and high catalytic performance when compared with gold or platinum catalysts [4,5]. The cobalt-based catalyst has been reported shown good activity, selectivity at low temperature and H<sub>2</sub>O resistance [6]. A large number of studies catalyst preparations, the co-precipitation method are the preferred method to high specific surface area of catalyst and high activity for CO oxidation [7].

In this study, The CuO-CeO<sub>2</sub> catalysts promoted with Co<sub>3</sub>O<sub>4</sub> were prepared by co-precipitation with different wt% Cu loading and define wt% Ce:Co ratio 95:5. The characterizations of catalyst were carried out by BET and XRD techniques, in order to correlate catalyst properties to catalytic performance. The performances of catalysts

were tested by selective CO oxidation.

## 2. Experimental

### 2.1. Catalysts Preparation

The catalysts CuO/CeO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> with wt % Ce/Co ratio of 95:5 were prepared by co-precipitation. Aqueous solutions of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were mixed. Aqueous Na<sub>2</sub>O<sub>3</sub> 0.1 M used as a precipitating agent was added drop-wise until a pH of 9 was attained. The resulting precipitate was aged at room temperature for 2 h, then filtered, washed several times with deionize water and dried at 110°C overnight. The obtained samples were calcined at 500°C for 5 h. The prepared catalysts were denoted as XCuO. The X shows the wt% Cu loading

### 2.2. Catalyst Characterization

All catalyst powders were characterized for their surface area, average pore diameter and average crystal-liter sizes. Specific surface area ( $S_{BET}$ ) of catalysts was determined with adsorption-desorption isotherms of N<sub>2</sub> at 77 K using Autosorption-1C from Quantachrome. Prior to N<sub>2</sub>-physical adsorption measurement, catalysts were degassed under N<sub>2</sub> gas purged at 473 K for 12 h. The adsorption isotherms were tested at 10<sup>-5</sup>< p/p<sub>0</sub><1.0. Using the nitrogen adsorption isotherm, BET equation was used for calculation of specific surface area using values between 0.05 and 0.30. X-ray diffraction measurement was made

using a Bruker AXS model D 8 Discover equipped with a Cu K $\alpha$  radiation (40 kV, 40 mA) with a nickel filter. Diffraction intensity was measured in the 2 $\theta$  ranges between 20° and 80°, with a step of 0.02° for 8 s per point. The mean crystallite sizes of oxides were determined from the X-ray line broadening measurements, using the Scherrer equation.

### 2.3. Catalytic Performance

The selective CO oxidation in the H<sub>2</sub>-rich gasses was carried out in a quartz reactor inserted in a vertical furnace. The reaction mixture consisted of 1% CO, 1% O<sub>2</sub> and 50% H<sub>2</sub> (volume fraction) with He as a balance gas. The flow rate of gas mixture was 40 cm<sup>3</sup>·min<sup>-1</sup>, equivalent to space velocity 75,000 cm<sup>3</sup>·gcat<sup>-1</sup>·h<sup>-1</sup>. The catalyst bed temperature was measured by means of a thermocouple inserted in the furnace. Product and reactant analyses were conducted by a GC-3600CX gas chromatograph. The molecular sieve was used to separate CO, O<sub>2</sub> and CO<sub>2</sub>. Water was trapped before the gases entering the GC.

The CO conversion and selectivity for CO oxidation were calculated from the concentration of CO and O<sub>2</sub> at inlet and outlet of the reactor as shown in equation (1) and (2).

$$\text{CO conversion} = \frac{\text{CO}_{\text{inlet}} - \text{CO}_{\text{outlet}}}{\text{CO}_{\text{inlet}}} \times 100\% \quad (1)$$

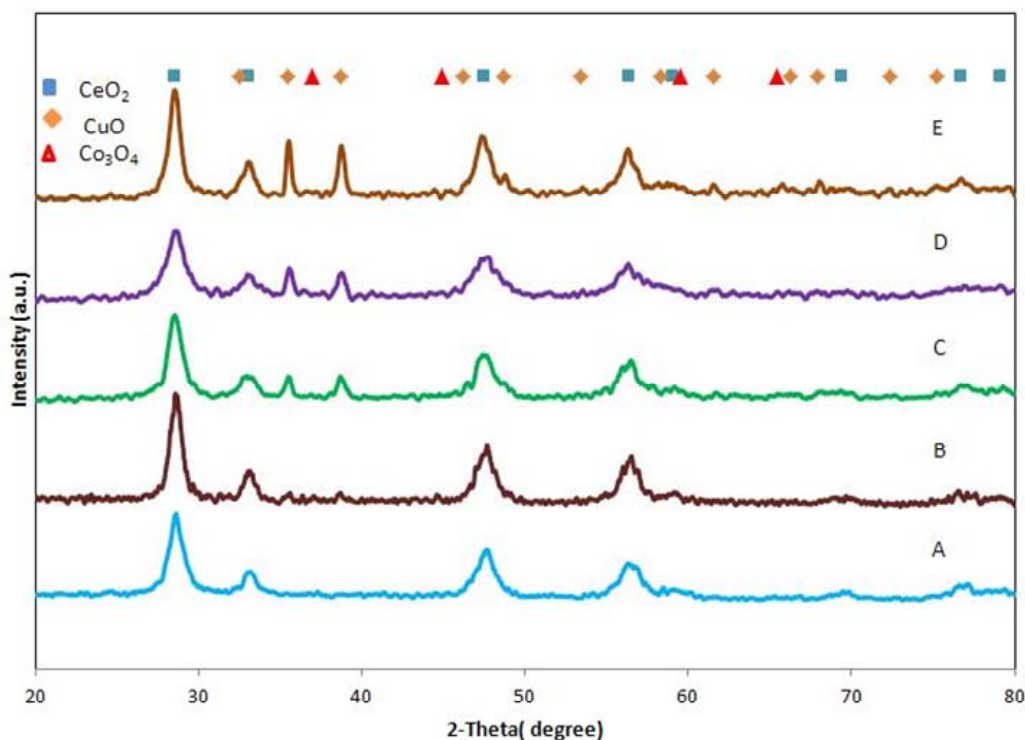
$$\text{selectivity} = \frac{\text{CO}_{\text{inlet}} - \text{CO}_{\text{outlet}}}{2 \times (\text{O}_{2\text{inlet}} - \text{O}_{2\text{outlet}})} \times 100\% \quad (2)$$

## 3. Results and Discussion

### 3.1. Catalyst Characterization

The powder X-ray diffraction was applied to investigate the structure of the CuO/CeO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> catalysts. **Figure 1** shows the XRD patterns of the sample. All samples shown the presence of CeO<sub>2</sub> in the fluorite-type cubic crystal structure, with the diffraction peak at 2 $\theta$  of 28.55°, 33.08°, 47.48°, 56.34° and 76.70°. Strong two diffraction peaks of CuO are exhibited the high crystalline structure of monoclinic tenorite-phase CuO in the 20CuO, 30CuO and 40CuO at 2 $\theta$  = 35.46° and 38.73°. For 10CuO, the diffraction peaks of CuO are weak in the XRD patterns, suggesting that CuO is highly dispersed on the fluorite CeO<sub>2</sub> support. Accordingly, no CuO peaks are observed for 5CuO, probably due to very low metal loading and its high dispersion [8]. For diffraction peaks of Co<sub>3</sub>O<sub>4</sub> in all samples not recognize due to very low of Co<sub>3</sub>O<sub>4</sub> promoted to catalysts. The average crystalline sizes of catalyst were calculated by Scherer's equation. The average size of CeO<sub>2</sub> are about 7-10 nm and CuO are more than 10 nm (**Table 1**).

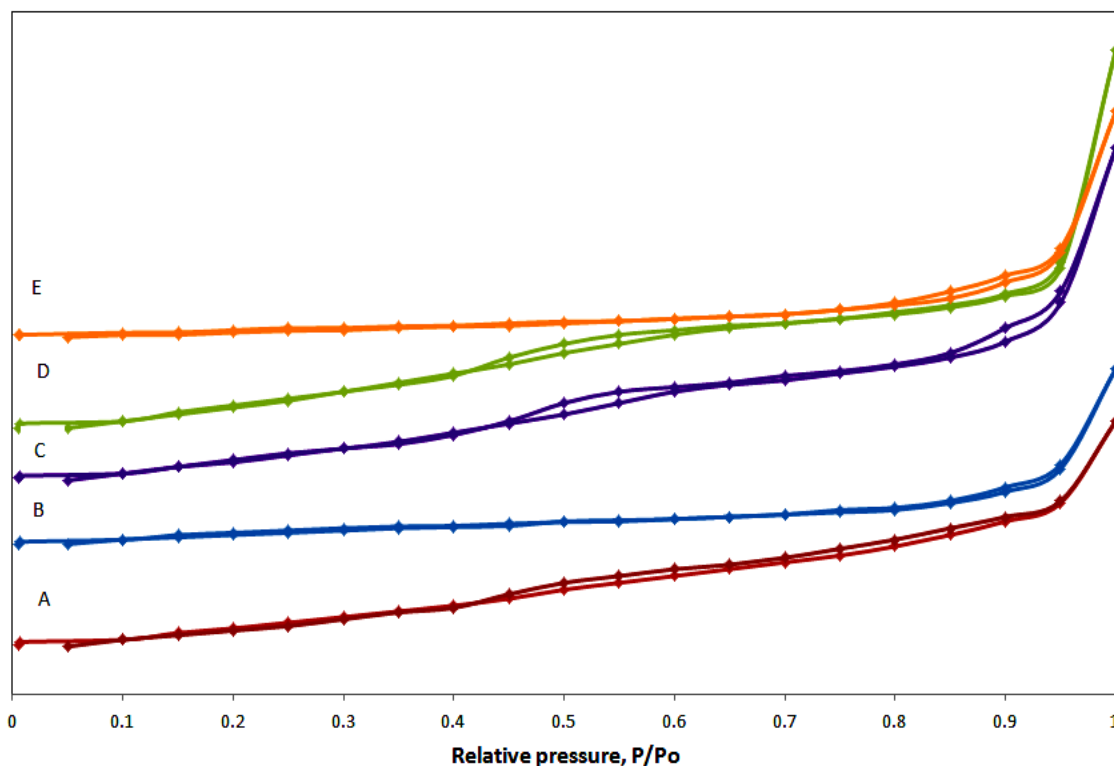
The isotherm of the catalysts at different wt% Cu loading reveals a typical type IV sorption behavior, representing the predominant mesoporous structure characteristic as shown in **Figure 2**.



**Figure 1.** XRD patterns of the catalysts (A) 5CuO; (B) 10CuO; (C) 20CuO; (D) 30CuO; (E) 40CuO.

**Table 1. The properties of CuO/CeO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> catalysts.**

Catalysts	Crystalline size			S <sub>BET</sub> (m <sup>2</sup> ·g <sup>-1</sup> )	d <sub>pore</sub> (nm)	Phase detected
	d <sub>CuO</sub> (nm)	d <sub>CeO2</sub> (nm)	d <sub>Co3O4</sub> (nm)			
5CuO	-	7.9	-	105.4	6.9	CeO <sub>2</sub> /Cubic
10CuO	-	9.5	-	73.3	8.4	CeO <sub>2</sub> /Cubic
20CuO	14.7	7.9	-	121.2	8.7	CuO/monoclinic, CeO <sub>2</sub> /Cubic
30CuO	13.7	7.1	-	136.5	8.8	CuO/monoclinic, CeO <sub>2</sub> /Cubic
40CuO	23.5	10.2	-	31.3	21.0	CuO/monoclinic, CeO <sub>2</sub> /Cubic

**Figure 2. Isotherms of the catalysts (A) 5CuO; (B) 10CuO; (C) 20CuO; (D) 30CuO; (E) 40CuO.**

The volume of N<sub>2</sub> adsorbed on the catalyst surface decreases with increasing CuO up to 40 wt%, which indicates that coverage of CuO decreases the specific surface area of the sample [9]. The S<sub>BET</sub> of CuO/CeO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> catalysts were calculated by Brunauer Emmett-Teller (BET) method using data from N<sub>2</sub> adsorption-desorption isotherm with in between 0.05-0.35 and the results are reported in **Table 1**.

High surface area is usually helpful to enhance catalytic activity due to more surface active centers exposed to reactants. The sample prepared by co-precipitation exhibits the highest specific surface area all the samples. The 30CuO catalyst with the highest BET surface area displays the best CO PROX performance, indicating that the BET surface area is possibly one of the important influencing factors on the catalytic performance of CuO/CeO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> catalysts. Generally, high BET surface area

is favorable to the dispersion of Cu species, enhancing the interaction between ceria and Cu species. [10]

### 3.2. Catalytic Performance

The catalytic performance of the catalysts was accomplished in the CO-PROX reaction by using a synthetic gas (1% CO, 1% O<sub>2</sub>, 50% H<sub>2</sub>, He balance). **Figure 3**, obviously indicates that the catalyst presents higher catalytic activity at lower temperature in the presence of excess hydrogen. The CO conversions of catalysts are the function of temperature. CO conversion increases with an increase in reaction temperature and further increasing in reaction temperature decreases CO conversions. The maximum CO conversion for 5CuO is 100.0% at the reaction temperature in the range between 423-443 K, 10%CuO is 98.1 at 463 K, 20CuO is 100.0% at 443 K, 30CuO is 100% at the reaction temperature in the range between

423-443 K and 40CuO is 98.5% at 463 K. At the increase temperature, CO conversion decreases. This may be due to high competition between H<sub>2</sub> oxidation and CO oxidation or reverse water gas shift reaction [11].

The selectivity can be seen in **Figure 4**, the selectivity for CO oxidation is 100% over the catalysts at reaction temperature lower than 403 K for 5CuO, 20CuO and 30CuO and lower than 423 K for 10CuO and 40CuO. It means that H<sub>2</sub> oxidation does not happen until this temperature. At the increase temperature the selectivity tends

to decrease, indicating that the H<sub>2</sub> oxidation occurs over the catalysts. It can be suggested that the adsorption and catalytic take place at low temperature. When the temperature increases H<sub>2</sub> molecules can be adsorbed and reaction[8]. In addition, a decrease in the amount of CeO<sub>2</sub> in catalyst may result in a decrease in selectivity at high temperature due to the reduction of oxygen storage [12]. The selectivity of catalysts at the max CO conversion is 85% for 5CuO, 50% for 10CuO, 70% for 20CuO, 65% for 30CuO and 52% for 40CuO catalysts.

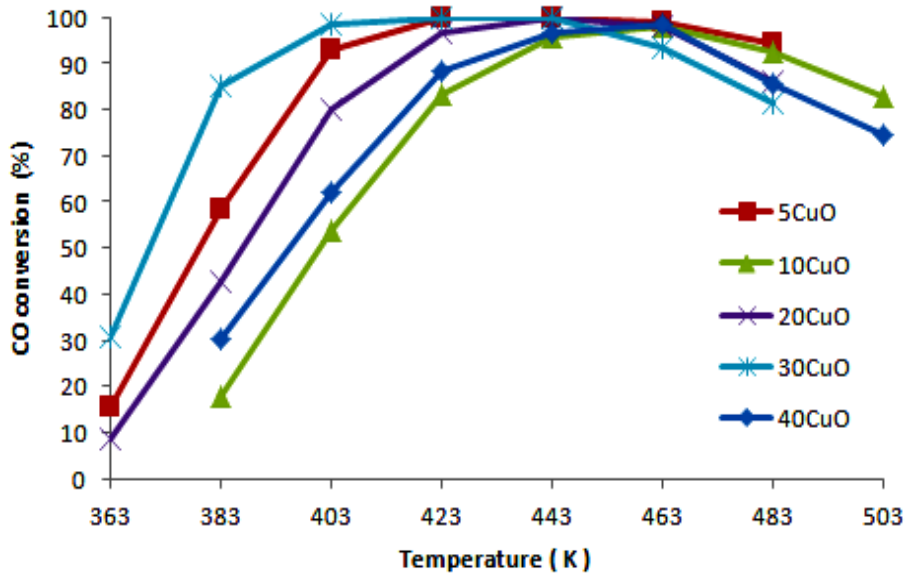


Figure 3. The CO conversion of catalysts as a function of temperature.

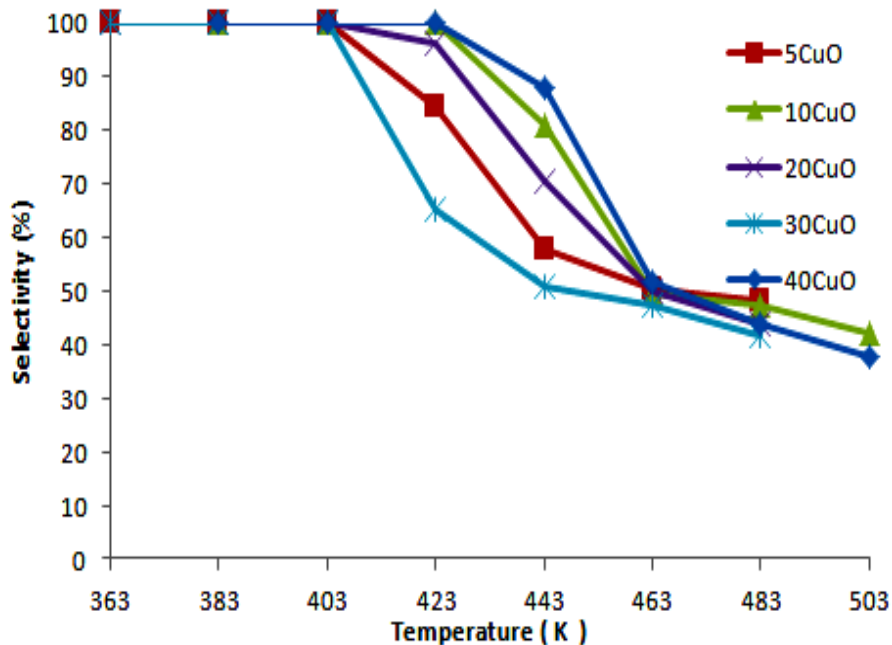


Figure 4. The selectivity of catalysts as a function of temperature.

It can also be concluded that, the wt% Cu loading has an effect on selective CO oxidation. Adding more CuO increases activity and CO removal at low temperature. For CO oxidation, the catalysts activity in presence of excess hydrogen is as follows,  $30\text{CuO} > 20\text{CuO} > 40\text{CuO} > 10\text{CuO}$ . In contrast, when comparing the selectivity at the maximum CO conversion, the activity of catalyst is as follows;  $20\text{CuO} > 30\text{CuO} > 40\text{CuO} > 10\text{CuO}$ .

The 5CuO catalyst show the highest activity with 100% CO conversion and 85% selectivity for removal CO in  $\text{H}_2$ -rich gas. A good dispersion of CuO in catalyst made to easily adsorb CO and activity with  $\text{O}_2$  rapidly. Including the appropriate amount of cobalt oxide to promote efficient catalysis of CuO and high specific surface area.

#### 4. Conclusions

The  $\text{CuO/CeO}_2\text{-Co}_3\text{O}_4$  catalysts were prepared by coprecipitation method and characterized by the XRD and BET techniques. XRD measurements show that the catalysts are composed of monoclinic CuO and cubic fluorite  $\text{CeO}_2$ . BET shows the large surface area and small average pore size diameter. The performance of catalyst suggest the 5CuO shows the best activity at low temperature and shows high selective CO oxidation when the CO conversion reach to 100%. The performance of catalysts verifies that complete in the CO-PROX system.

#### 5. Acknowledgements

This research was supported by Burapha University (NRCT 2555) under the contract # 48/2555.

#### REFERENCES

- [1] O. Bicakova and P. Straka, "Production of Hydrogen from Renewable Resource and its Effectiveness," *International Journal of Hydrogen Energy*, Vol. 33, 2008, pp. 1335-1344.
- [2] Z. Nada and L. Xianguo, "Transient of Carbon Monoxide Poisoning and Oxygen Bleeding in a PEM Fuel Cell Anode Catalyst Layer," *International Journal of Hydrogen Energy*, Vol. 33, 2008, pp. 1335-1344.
- [3] A. Mishra and R. Prasad, "A Review on Preferential Oxidation of Carbon Monoxide in Hydrogen Rich Gas," *Bulletin of Chemical Reaction Engineering & Catalysis*, Vol. 6, No. 1, 2011, pp. 1-14.
- [4] G. Avgouropoulos, T. Ioannides, C. Papadopoulou, J. Batista, S. Hocevar and H. K. Matralis, "A Comparative Study of  $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ ,  $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$  and  $\text{CuO-CeO}_2$  Catalysts for the Selective Oxidation of Carbon Monoxide in Excess Hydrogen," *Catalysis Today*, Vol. 75, 2002, pp. 157-167.  
[doi:10.1016/S0920-5861\(02\)00058-5](https://doi.org/10.1016/S0920-5861(02)00058-5)
- [5] S. Salvatore, C. Carmelo, P. M. Riccobene, P. Giacomo and P. Alessandro, "Selective Oxidation of CO in  $\text{H}_2$ -rich Stream over  $\text{Au/CeO}_2$  and  $\text{Cu/CeO}_2$  Catalysts: An Insight on the Effect of Preparationmethod and Catalyst Pretreatment," *Applied Catalysis A: General*, Vol. 417-418, 2012, pp. 66-75.
- [6] M. Kang, M. W. song and C. H. Lee, "Catalytic Carbon Monoxide Oxidation over  $\text{CoO}_x/\text{CeO}_2$  Composite Catalysts," *Applied Catalysis A: General*, Vol. 255, 2003, pp. 143-156.  
[doi:10.1016/S0926-860X\(03\)00324-7](https://doi.org/10.1016/S0926-860X(03)00324-7)
- [7] Z. Liu, R. Zhou and X. Zheng, "Influence of Preparation Methods on  $\text{CuO-CeO}_2$  Catalysts in the Preferential Oxidation of CO in Excess Hydrogen," *Journal of National Gas Chemistry*, Vol. 17, 2008, pp. 125-129.
- [8] J. L. Ayastuy, E. Fernandez-Puertas, M. P. Gonzalez-Marcos and M. A. Guitierrez-Ortiz, "Transition metal Promoters in  $\text{CuO/CeO}_2$  Catalysts for CO Removal from Hydrogenstreams," *International Journal of Hydrogen Energy*, Vol. 37, 2012, pp. 7385-7397.  
[doi:10.1016/j.ijhydene.2012.02.007](https://doi.org/10.1016/j.ijhydene.2012.02.007)
- [9] S. Christopher, H. Nair and D. Chelsey, "Study of Active Sites and Mechanism Responsible for Highly Selective CO Oxidation in  $\text{H}_2$  Rich Atmospheres on a Mixed Cu and Ce Oxide Catalyst," *Journal of Catalysis*, Vol. 266, 2009, pp. 308-319.  
[doi:10.1016/j.jcat.2009.06.021](https://doi.org/10.1016/j.jcat.2009.06.021)
- [10] M. Meng, Y. Liu, W. L. Z. Sun, L. Zhang and X. Wang, "Synthesis of Highly-dispersed  $\text{CuO-CeO}_2$  Catalyst Through a Chemisorption-hydrolysis Route for CO Preferential Oxidation in  $\text{H}_2$ -rich Stream," *International Journal of Hydrogen Energy*, Vol. 37, 2012, pp. 14133-14142.  
[doi:10.1016/j.ijhydene.2012.07.075](https://doi.org/10.1016/j.ijhydene.2012.07.075)
- [11] J. W. Park, J. H. Joeng, W. L. Yoon, C. S. Kim, D. K. Lee, Y. K. park and Y. W. Rhee, "Selective Oxidation of CO in Hydrogen-rich Stream over Cu-Ce Catalyst Promoted with Transition Metal," *International Journal of Hydrogen Energy*, Vol. 30, 2005, pp. 209-220.  
[doi:10.1016/j.ijhydene.2004.04.016](https://doi.org/10.1016/j.ijhydene.2004.04.016)
- [12] S. Chang, M. Li, Q. Hua, L. Zhang, Y. Ma, B. Ye and W. Huang, "Shape-dependent Interplay between Oxygen Vacancies and  $\text{Ag-CeO}_2$  Interaction in  $\text{Ag/CeO}_2$  Catalysts and Their Influence on the Catalytic Activity," *Journal of Catalysis*, Vol. 293, Vol. 30, 2012, pp. 195-200.