Copper Catalysts Supported on CeMnO$_2$ for CO Oxidation in Hydrogen-Rich Gas Streams

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Abstract

The CeMnO$_2$ supports were prepared via co-precipitation method by ammonia as precipitating agent. The CuO/Ce$_2$O$_3$ and CuO/Ce$_{1-x}$Mn$_x$O$_2$ ($x=0.1$, $0.3$ and $0.5$) catalysts were synthesized by wet impregnation method. The physicochemical properties of the prepared CuO/Ce$_{1-x}$Mn$_x$O$_2$ catalysts were characterized by N$_2$ adsorption-desorption, powder X-ray diffraction (XRD) and programmed H$_2$ temperature reduction (H$_2$-TPR). The effects of Cu and Mn loading were investigated on the catalytic performance. The findings illustrated that the 7% CuO/Ce$_{0.9}$Mn$_{0.1}$O$_2$ catalyst shows high activity for CO-PrOx. The high activity of 7% CuO/Ce$_{0.9}$Mn$_{0.1}$O$_2$ catalyst was ascribed to high surface area of the support, synergetic effects of CuO and CeO$_2$ and increases of the mobility of lattice oxygen in ceria by addition of MnO$_2$. The effects of presence of H$_2$O in the reaction feed stream, oxygen to CO ratio ($\lambda$) and gas hourly space velocity (GHSV) on the catalytic activity of 7% CuO/Ce$_{0.9}$Mn$_{0.1}$O$_2$ catalyst was evaluated. It was found that the best performance of 7% CuO/Ce$_{0.9}$Mn$_{0.1}$O$_2$ catalyst was obtained at $\lambda=2$, GHSV=20000 h$^{-1}$ and in addition, the presence of H$_2$O had negative effects on the activity of the catalyst. In the long term stability test, nearly 100% CO conversion was maintained for 50 h at 120°C with 70-80% CO$_2$ selectivity.

Keywords: Cu/CeMnO$_2$ Catalyst; CO oxidation; PrOx; Hydrogen

1. Introduction

Fuel cells are electrochemical devices, which directly convert fuels chemical energy into electrical energy with high efficiency and low environmental effects. Nowadays, fuel cells are among the main candidates in the development of clean and renewable energies [1]. Although there are various methods for hydrogen production, methane steam reforming (MSR) is still the principal method for cost-effective hydrogen and synthesis gas production [2]. The preferential oxidation of CO (PrOx) is one of the critical steps in hydrogen production and purification for Polymer Electrolyte Fuel Cell (PEMFC); since the anode catalyst in PEM is strongly poisoned even by ppm levels of CO in the H$_2$ rich gas [3]. PrOx is used after steam reforming and WGS reactions to remove the trace contaminant CO in the H$_2$ rich gas.

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Among the currently available methods, CO-PrOx is the most cost-effective and efficient approach to reduce CO to the desired level without excessive hydrogen consumption [4]. The main reactions involved in CO-PrOx are as follows:

CO Oxidation: \[ \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \] (1)

H₂ Consumption: \[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \] (2)

Developed catalysts for CO-PrOx are mainly platinum group metals (Pt, Pd, Ru and Rh) catalysts [3-8,33], gold based catalysts [9-11] and transition metal (Co, Cu, and Mn) based catalysts [12-19,34]. Among them, CuO based on CeO₂ catalysts have shown high activity and selectivity for preferential oxidation of CO. Moreover, availability and low cost of ceria supported copper catalyst makes this catalyst a promising candidate to replace the other noble metals and gold. Copper and ceria based catalyst can be synthesized via different methods with a variety of morphologies by using various promoters and with different loading range of metals. Marino et al. synthesized the CuO-CeO₂ catalyst via homogeneous thermal decomposition of urea containing different Cu/Ce ratio [20]. CeCu10 catalyst kept constant nearly 90% CO conversion during 24 h of the reaction. Moretti et al. used a micro-crystalline organized meso-porous γ-alumina prepared by template sol-gel method, resulting in, after impregnation with metal salts and subsequent calcination, active Cu/Ce-based CO-PrOx catalysts with high surface area and a good thermal stability [21]. A Ce20Cu5 catalyst had complete CO conversion at 200°C with 40% CO₂ selectivity. Wu et al. prepared the CuO/CeO₂ by an improved incipient wetness impregnation method using ammonia as chelating agent [4]. The 10% CuO/CeO₂ had high activity and stability for CO-PrOx. In presence of 10% H₂O and 15% CO₂, 100% CO conversion and 75-85% CO₂ selectivity was reported. Pakharukova et al. tested the copper-cerium oxide catalysts supported on monoclinic zirconium oxide and showed that the best performance was obtained for the CuO/CeO₂/ZrO₂ catalysts containing 5-10 wt% copper [22]. Peng et al. synthesized the 7%CuO/Ce₀.₉Mn₀.₁O₂-20%Al₂O₃ catalyst with a T₁₀₀ temperature of 95–100°C [23]. This catalyst was evaluated for 200 h at 140°C in the presence of 15% CO₂ and 10% H₂O which exhibited 60% CO conversion and 95% CO₂ selectivity.

In the present study, the CeO₂ samples were prepared in different conditions of pH, calcination time and temperature and aging time and the optimum condition was achieved for CeO₂ as a support for Cu catalyst. Then the manganese, as a promoter, doped into CeO₂ to obtain the CeMn oxide as a new support for the above-mentioned catalyst. Moreover, Cu/Mn loading ratio was studied. In addition, Cu catalysts supported on CeO₂ and Ce₁₋ₓMnₓO₂ were prepared to investigate their catalytic activity in CO-PrOx reaction. Furthermore, more significant operating conditions such as GHSV, λ ratio
and presence of H2O in feed composition were investigated to explore the best range of operating conditions for these catalysts.

2. Experimental

2-1. Catalyst preparation

0.1 M homogeneous aqueous solution of cerium nitrate was prepared by solving Ce(NO3)3·6H2O [Fluka, 99.5%] powder in deionized water, then ammonia [NH3, Merck, 25%] was added slowly to reach the desired pH (8-10). The resulting suspension was left to settle for 1-12 h. The precipitate was filtered and washed with deionized water several times. Finally, the ceria cake was dried overnight (in various temperature ranging from 80 to 120°C). The dried precipitate was calcined in different time and temperature (Tc=400-600°C and tc=4-6 h). The Ceria which was synthesized in pH of 10, aged for 6 h, dried at 120°C and calcined in 500°C for 6 h had maximum surface area. The surface area of achieved ceria was 74.45 m²/g, with total pore volume of 0.18 m³/g and average pore diameter of about 9.6 nm.

CeMnO2 samples were synthesized with co-precipitation of the manganese nitrate [Mn(NO3)2·4H2O, Merck, 99.5%] and cerium nitrate in the optimum conditions of CeO2, i.e. pH 10, aging time of 6 h, and calcinations temperature of 500°C for 6 h. Three different values (x=0.1, 0.3 and 0.5) of Mn were synthesized.

The CuO/Ce,(1-x)MnxO2 catalysts were prepared by wetness impregnation method using different loadings (5, 7 and 10 wt%) of copper nitrate solution [Cu(NO3)2·3H2O, Merck, 99.5%]. The catalysts were then dried at 120°C for 12 h and calcined at 500°C for 4 h in air.

2-2. Catalyst characterization

The XRD patterns were recorded on an X-ray diffractometer (PAN analytical X’Pert-Pro) using a Cu-Kα monochromatized radiation source and a Ni filter in the range 2θ=20-80°.

The surface areas (BET), mean pore diameter and total pore volume were determined by nitrogen adsorption at -196°C, using an automated gas adsorption analyzer (Gimini, Micromeritics).

Temperature programmed reduction (TPR) analysis was used for evaluating the reduction properties of prepared catalysts. In the TPR measurement, the fresh catalyst (~100 mg) was exposed to a heat treatment (10°C/min up to 800°C) in a gas flow (30 ml/min) containing a mixture of 10 vol% H2 in Argon. Before the TPR experiment, the samples were degassed under an inert atmosphere at 350°C for 3 h.

2-3. Catalytic activity tests

Catalytic activity tests were carried out at 60-200°C temperature range and ambient pressure in a fixed bed quartz reactor (8 mm inner diameter). In addition, 210 mg catalyst with 40-60 mesh was charged in the reactor for each test. Gas feed components are 2% CO, 2% O2 and 96% H2 with the space velocity of 20000 h⁻¹. Before the light-off tests, the catalysts were pretreated at 400°C for 1 h in O2 stream with a flow rate of 20 ml/min. Inlet and outlet gases were analyzed by a Shimadzu-8A chromatograph equipped with a TCD and a Carbosieve column.
The CO and O₂ conversion were calculated based on the carbon monoxide and oxygen consumption in the reactions as follows:

\[ X_{CO} (%) = \frac{[CO_{in}] - [CO_{out}]}{[CO_{in}]} \times 100 \]  

(1)

\[ X_{O_2} (%) = \frac{[O_2_{in}] - [O_2_{out}]}{[O_2_{in}]} \times 100 \]  

(2)

The CO₂ selectivity of CO oxidation reaction in presence of excess hydrogen was calculated from the oxygen mass balance as follows:

\[ S_{CO_2} (%) = 0.5 \times \left( \frac{[CO_{in}] - [CO_{out}]}{[O_2_{in}] - [O_2_{out}]} \right) \times 100 \]  

(3)

The excess of oxygen factor (λ) is defined as:

\[ \lambda = 2 \times \frac{O_2_{in}}{FCO} \]  

(4)

3. Results and discussion
3-1. Catalyst characterization
The XRD patterns of CeO₂, CuO/CeO₂ and CuO/CeMnO₂ catalysts are presented in Fig. 1. The crystalline mean particle sizes of ceria have been determined by the X-ray broadening technique employing the Scherrer equation as:

\[ d_{XRD} = \frac{0.9 \lambda}{FWHM \cos \theta} \]  

(5)

Where λ is the X-ray wavelength (1.5406 Å), FWHM (in Rad) is the full width at half maximum of the characteristic peak (111) of CeO₂ and θ is the diffraction angle for the (111) plane. For ceria, the main characteristic peaks are associated with the Face-Centered Cubic (FCC) fluorite structure. The main peak (2θ=28.8°) corresponds to the (111) reflection of ceria and average calculated crystalline size was 17 nm. The main peaks (2θ=35 and 38°) correspond to the CuO and average calculated crystalline size was 19 nm for 7%CuO/CeO₂ and 7%CuO/Ce₀.₉Mn₀.₁O₂.

Figure 1. XRD patterns of the samples, (a) CeO₂, (b) 7% CuO/CeO₂ and (c) 7% CuO/Ce₀.₉Mn₀.₁O₂.
The TPR patterns for 7% CuO/CeO$_2$ and 7% CuO/Ce$_{0.9}$Mn$_{0.1}$O$_2$ catalysts are presented in Fig. 2. The 7% CuO/CeO$_2$ profile shows three peaks between temperatures of 150-250°C, suggesting that the first two peaks correspond to the reduction of CuO species while the third peak is ascribed to the reduction of the surface lattice oxygen in CeO$_2$ support.

As reported in the previous literature, CuO species identified in CuO/CeO$_2$ catalysts have been summarized in four types: (1) isolated Cu$^{2+}$ ions can strongly interact with the support. (2) Weak magnetic associates consist of several Cu$^{2+}$ ions and these Cu$^{2+}$ ions have close contact with each other. (3) Small two- and three-dimensional clusters have structures so loose that they have no specific and regular lattice arrangement. (4) Large three-dimensional clusters and bulk CuO phase have characters and properties identical to those of pure CuO powder. Accordingly, it is reasonable to ascribe first peak in the H$_2$-TPR profiles to the first two types (1 and 2) of CuO species, which is highly dispersed and strongly interacted with the support. The third peak is ascribed to type (3) CuO species, the small clusters with somehow amorphous properties[4,24-27]. The peak, shown at 500-600°C and 800-900°C, is related to reduction of ceria. In 7% CuO/CeMnO$_2$ pattern, it can be seen that the density of third peak is lower than 7% CuO/CeO$_2$, irrespective of peak due to presence of Mn and decline of ceria amount.

3-2. Catalyst activity
3-2-1. Cu and Mn loading effects
The results of Cu loading variation on CO conversion and CO$_2$ selectivity toward reaction temperature for x% CuO/CeO$_2$ (x=5, 7 and 10 wt%) catalysts are presented in Fig. 3. As can be seen in Fig. 3, 7% CuO/CeO$_2$ catalyst has maximum CO conversion in a wide range, and also CO$_2$ selectivity of this catalyst in lower temperature (<100°C) is more than other catalysts. Therefore, it is obvious that CO oxidation reaction on 7% CuO/CeO$_2$ is the dominant reaction. In the case of copper catalysts supported on ceria, a partial amount of Cu particles has interaction with CeO$_2$ and the remaining is in bulk formation.

![Figure 2. TPR patterns of (a) 7% CuO/CeO$_2$ and (b) 7% CuO/Ce$_{0.9}$Mn$_{0.1}$O$_2$ catalysts.](image-url)
Gamarra et al. reported the CO oxidation on copper oxide species takes place at the interface, while the H₂ oxidation occurs mainly on copper oxide species in the form of nanoparticles, which are not necessarily in contact with the support [28]. Furthermore, an increase in the proportion of CuO species in the bulk form may limit the oxidation of CO because of the decreased number of interfacial sites, while the H₂ oxidation continues to happen on the rest of the supported particles of copper oxide. Thus, the copper species that interact strongly with the support (Cu-O-Ce) are favorable for preferential oxidation of CO [29-31].

Therefore, Cu loading of catalyst for CO-PrOx process has an optimum value to reach more CO conversion with minimum H₂ consumption. Our result showed that 7wt% of Cu is the best content for CuO/CeO₂ catalyst in preferential oxidation process.

The effect of Mn loading as support promoter on activity of 7% CuO supported catalysts is shown in Fig. 4. For Ceₓ₋ₓMnₓO₂ (x=0.1, 0.3 and 0.5) composite, the existence of both Ce⁴⁺-Ce³⁺ and Mn⁴⁺-Mn³⁺ redox couples cause excellent oxygen storage-release capacity, varying with the Ce/Mn ratio [15,32]. It has been seen that increases of Mn content up to 0.1, decreases CO conversion. Mn species enter ceria lattice and increase the mobility of lattice oxygen which leads to their oxygen reacting, but the advantage of manganese oxide is not as much as ceria, so the amount of Mn should not be so much that the effect of ceria decreases and prevents the contact of copper and ceria. For this reason and due to the catalytic activity diagrams, the best amount of Mn is 0.1.

3-2-2. λ Ratio and GHSV effects
The effect of the O₂/CO molar ratio in the feed was analyzed in terms of the oxygen stoichiometric excess (λ). In this work, catalysts were tested in λ≥1. The values of λ lower than 1.0 was not used because the goal of reaching a complete conversion of CO is not possible under such conditions [20]. Fig. 5 shows the CO conversion and CO₂ selectivity as a function of reaction temperature for different λ in the feed composition. As it can be seen in Fig. 5, by increasing λ ratio, the CO conversion increases, but the CO₂ selectivity decreases.
as in higher $\lambda$ ratio, more oxygen is accessible to CO and $H_2$; therefore CO conversion increases and parallel to this the consumption of $H_2$ increases. Therefore, $\lambda$ ratio should be optimized. In this work, among the range of $\lambda$ (1≤ $\lambda$≤4), the results indicate that $\lambda$=2 causes complete conversion of CO in temperature range of 120-200 °C and acceptable CO$_2$ selectivity in CO-PrOx was observed.

GHSV means quantity of feed processing in a specific time over a constant amount of catalyst, so more GHSV values would cause less used catalyst under constant feed processing, which would result in less reactor volume, and finally a more economic process would be obtained. As shown in Fig. 6, the higher GHSV has less time over the catalyst to achieve adsorption, thus leading to a lower CO conversion and higher CO$_2$ selectivity at a specific temperature. At a GHSV of 30000 h$^{-1}$ and 70% CO conversion, the CO$_2$ selectivity is around ~100% which is 10% higher than GHSV of 20000 h$^{-1}$ and 15% higher than GHSV of 10000 h$^{-1}$.

It is obvious that at temperature below 120°C and at higher GHSV, $H_2$ adsorption rate was lower than that of CO, thus the CO$_2$ selectivity was higher. At low GHSV and low temperature, the apparent activation of

Figure 4. Variation of (a) CO conversion and (b) CO$_2$ selectivity for 7% CuO/Ce$_{(1-x)}$Mn$_x$O$_2$ catalysts with different Mn loading. Operating conditions: 96% $H_2$, 2% CO, 2% O$_2$, $\lambda$=2, GHSV=20000 h$^{-1}$.

Figure 5. CO-PrOx performance of 7% Cu/Ce$_{0.9}$Mn$_{0.1}$O$_2$ catalyst in different $\lambda$. Operating conditions: 96% $H_2$, 2% CO, 2% O$_2$, GHSV=20000 h$^{-1}$.
H$_2$ oxidation is lower than that of CO oxidation [33].

Totally, GHSV should not be so high to decrease the CO conversion, and so low to decrease the CO$_2$ selectivity. Our results indicated that GHSV of 20000h$^{-1}$ was appropriate for this catalyst in CO-PrOx.

3-3-3. Effect of H$_2$O

Since the hydrogen rich stream has been produced by WGS, the reaction contains 10-15% H$_2$O. The influence of H$_2$O on the CO-PrOx reaction was investigated. The variation of CO conversion and CO$_2$ selectivity with the reaction temperature over 7%CuO/Ce$_{0.9}$Mn$_{0.1}$O$_2$ catalyst in the presence of 15% H$_2$O in feed composition are shown in Fig. 7. It is obvious that the addition of H$_2$O is not favorable for CO-PrOx. When 15% H$_2$O is present in the stream, the complete removal of CO cannot be achieved at tested temperature range, while in the absence of H$_2$O, ~100% CO conversion is obtained at 120°C with 80% CO$_2$ selectivity. Totally, the negative effect of H$_2$O on the catalytic performance is related to the blockage of the adsorbed molecular water on the active sites [13]. As a result, the water must be removed before PrOx reactor.
3-4. Catalyst stability
The long-term stability of the 7% CuO/Ce$_{0.9}$Mn$_{0.1}$O$_2$ catalyst was evaluated at 120°C during 50 h. Results of CO, O$_2$ conversion and CO$_2$ selectivity are reported in Fig. 8. As shown, during all time of stream and nearly hard condition for reaction, ~100% CO conversion was maintained with 70-80% CO$_2$ selectivity under a GHSV of 20000 h$^{-1}$ and $\lambda=2$. Consequently, it was observed that the 7% CuO/Ce$_{0.9}$Mn$_{0.1}$O$_2$ catalyst has high activity and stability in CO-PrOx conditions.

![Graph showing CO conversion, CO$_2$ selectivity, and O$_2$ conversion over time.](image)

**Figure 8.** Long-term stability test for CO-PrOx on 7% CuO/Ce$_{0.9}$Mn$_{0.1}$O$_2$ catalyst. Operating conditions: 96% H$_2$, 2% CO, 2% O$_2$, $\lambda=2$, GHSV=20000 h$^{-1}$.

4. Conclusions
The performance for CO-PrOx on the CuO/CeO$_2$ catalysts prepared by wetness impregnation method was investigated. The effects of Cu and Mn loading, $\lambda$, GHSV and presence of H$_2$O in feed on the catalytic activity were evaluated. Results indicate that the catalyst with 7% Cu loading and 0.1 Mn loading has been the best performance among the investigated samples. The 7% CuO/Ce$_{0.9}$Mn$_{0.1}$O$_2$ catalyst has high activity and stability for CO-PrOx and in wide range of reaction temperature (120-160°C) nearly 100% conversion of CO with appropriate CO$_2$ selectivity was achieved. The presence of H$_2$O has negative effect on catalyst activity and the best performance was achieved in $\lambda=2$ and GHSV=20000 h$^{-1}$. In the long-term stability test, ~100% CO conversion with 70-80% CO$_2$ selectivity was maintained for 50 h at 120°C.

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