

CuO/CeO₂ supported on SBA-15 for Preferential Oxidation of CO in Hydrogen Rich Environment

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Abstract

Proton exchange membrane fuel cell (PEMFC) is an efficient energy technique due to several advantages, such as high energy density, low emission of pollutants and low operation temperature. However, there are still some challenges needed to overcome. For example, the CO impurity in H₂ fuel may poison the Pt electrode. Copper and cerium mixed oxide has been found as a promising catalyst for PROX due to its high conversion and relatively low cost, in comparison to other catalysts of primarily the precious metals. Various amounts of copper oxide were impregnated onto SBA-15[1]. The catalysts were characterized by XRD, N₂ sorption isotherm, SEM, TEM, XANES, TPR. The activities of the catalysts were tested in PROX reaction under 0.8 % CO, 0.8 % O₂, 50 % H₂, and 48.4 % He with a total flow rate of 100 /min.

Keywords: Mesoporous, SBA-15, PROX, CO oxidation

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1. Introduction

A fuel cell is an electrochemical system that can turn chemical energy into fuel without fuel combustion. Fuel cell was first discovered in 1839 by Sir William R. Grove, a British jurist and physicist, who used platinum as the electrodes and hydrogen as the fuel to generate electricity [2]. Among different types of fuel cells, proton-exchange membrane fuel cell (PEMFC) [3] is considered to be a promising technology due to several reasons, such as high energy density, high energy conversion efficiency and low emission of pollutants.

The most efficient anode catalyst in PEMFC is platinum, which is sensitive to carbon monoxide. In the process of hydrogen production by steam reforming and water-gas shift, there are still 0.25 %~0.5% CO in flowing gas [4], and the tolerance limit of Pt anode in PEMFC toward CO is around 10-100 ppm [5]. Therefore, it is necessary to eliminate 99% of the CO present in the H₂ fuel. Preferential oxidation of CO (PROX) is considered to be an efficient way to remove trace CO in H₂.

CuO-CeO₂ has been reported to be an active catalyst for CO PROX and intensively studied by several groups [6][7]. Mesoporous silica SBA-15 with uniform 2 D hexagonal arrays of pores and high surface area is a promising support to increase CuO/CeO₂ surface area and dispersion. In the present study, CuO-CeO₂ was impregnated onto SBA-15 in order to increase CuO-CeO₂ surface area, and the catalytic activities of the supported mixed oxides in CO PROX were examined.

2. Experiment

2.1 Synthesis of silica supports

The conventional SBA-15 of rod-shape were synthesized following the procedures. 2 g of amphiphilic P123 triblock copolymer (Aldrich, Mn = 5800) were dissolved in 80 ml 0.1M HCl solution. The mixture was stirred in a polypropylene bottle at 35°C overnight, and then added tetraethyl orthosilicate (Acros 98%). After stirring 24 h, the mixture was hydrothermally heated under static condition at 90°C for another 24 h. The molar compositions of the reactants were P123 : TEOS : HCl : H₂O = 0.017 : 1 : 7.94 : 221. The solid products were separated from the synthesis solution by filtering, washing with de-ionized water and drying at 50°C overnight. The

calcined temperature was performed at 500°C for 12 h with a heating rate of 1°C /min in air. Platelet SBA-15 was prepared by adding a small amount of Zr (IV) ions in the conventional SBA-15 synthesis solution [8]. The molar compositions of reactants were TEOS : ZrOCl₂ • 8H₂O : HCl : H₂O = 0.017 : 1: 0.05 : 7.94 : 221 P123 . In order to examine the effect of hydroxy group on the SBA-15 surface, SBA-15 was further calcined at 900°C for 6 h. Amorphous silica was prepared by the same condition only without any template.

2.2 Impregnation of copper-cerium oxide onto SBA-15

0.07594 g Cu(NO₃)₃ • 6H₂O and 0.56772 g Ce(NO₃)₃ • 6H₂O were dissolved in 10 mL ethanol. The solution was added to 0.5 g SBA-15 in powder form, and removed the solvent by a rotary evaporator. The resulting solid was dried at 100°C overnight, followed by calcination at 400°C for 4 h with a heating rate of 100°C/h. The catalysts are denoted as XCuO-YSceO₂/2Silicasupport-900. (X,Y represent the weight ratio of CuO and CeO₂, 900 means the post calcined temperature at 900°C)

2.3 Catalytic activity test

The PROX reaction was carried out in a fixed bed reactor system under atmospheric pressure. The catalyst weight was 200 mg, and the total flow rate of the reaction mixture was 100 cm³ min⁻¹. The feed contained 0.8% CO, 0.8% O₂, 50% H₂, and the balance He. The products were separated and analyzed using a Shimadzu GC-14B gas chromatograph equipped with a thermal conductivity detector. The CO conversion was calculated based on the CO consumption. The selectivity toward CO₂ production was calculated from the oxygen mass balance.

3. Results and discussion

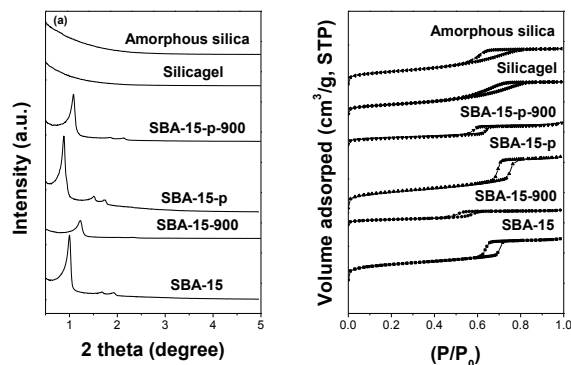


Fig. 1. XRD patterns (a) and N₂ adsorption-desorption isotherms (b) of different silica supports

Fig. 1(a) shows that both SBA-15 and SBA-15-p exhibit (100) (110) (200) diffraction peaks of 2 D hexagonal structure. The materials calcined at 900°C have the diffraction intensity decreased and the peaks shifted to higher angles, implying the shrinkage of lattice. These results were accompanied with the decrease in BET surface area, total pore volume, and pore diameter, as shown in Fig. 1(b) and Table 1.

Table 1. Textural properties of Silica supports

Catalysts	S _{BET} (m ² /g)	D _P (nm)	V _P (cm ³ /g)
SBA-15	780	5.5	1.03
SBA-15-p	851	6.5	1.15
SBA-15-900	272	3.8	0.32
SBA-15-p-900	330	4.6	0.45
Silicagel	508	--	0.73
Amorphous silica	661	5.0	0.80

The intensity of X-ray diffraction peaks of SBA-15 shown in Fig. 2(a) decreases after impregnation of copper-cerium oxide, indicating that the metal oxides were loaded into SBA-15 channels. The broad diffraction peaks of ceria shown in Fig. 2(b), in comparison to unsupported Cu-CeO₂ verify that the high surface area silica support can increase the dispersion.

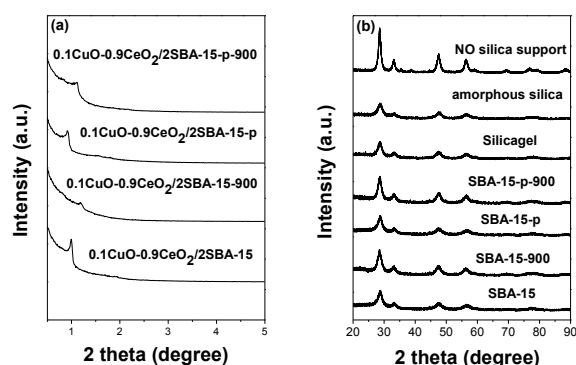


Figure 2: Small (a) and wide angle XRD patterns (b) of impregnate copper and cerium oxide (1:9) into different silica supports.

The CO conversion and selectivity over 0.1CuO-0.9CeO₂ and that supported on various silica materials were shown in Fig. 3(a) and 3(b). The catalyst with SBA-15-p-900 support showed higher conversion than SBA-15-p. It is attributed to that more hydroxy groups on the SBA-15 surface would adsorb water and block the catalytic active sites. The 0.1CuO-0.9CeO₂/2SBA-15-p-900 also showed higher activity than 0.1CuO-0.9CeO₂/2Silicagel even though silica gel provide higher surface area, and it implies that the contribution of highly order porous is more important than surface area.

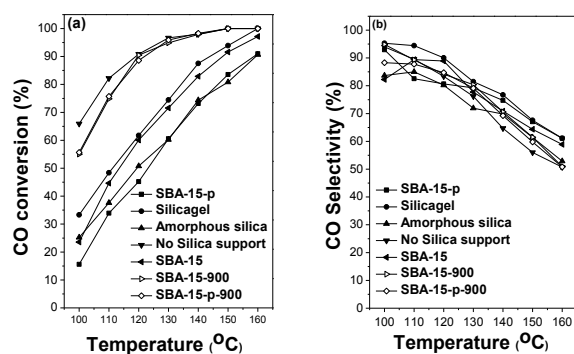


Figure 3: CO conversion (a) and selectivity (b) of copper and cerium oxide on different silica supports. Feed composition 0.8% CO, 0.8% O₂, 50% H₂, and the balance He.

The effect of H₂O and CO₂ in the feeding gas were shown in Fig. 4. The 0.1CuO-0.9CeO₂/2SBA-15-p catalyst was less influenced by CO₂, and it still could reach conversion at

160°C. However, the activity significantly decreased after adding 10% H₂O. This result may be due to the hydrophilic nature of the silica support as mentioned before. The CO activity decreased to 35% when 10% H₂O was present in the feed and to 25% when both 10% H₂O and 15 % CO₂ were present.

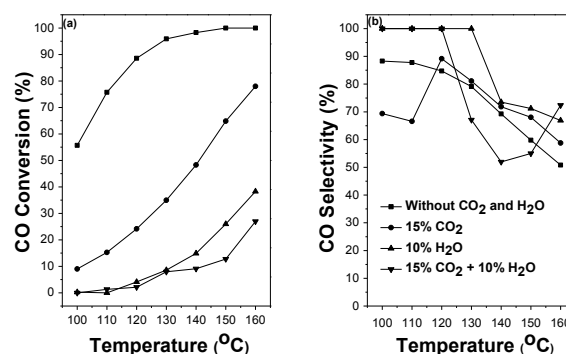


Figure 4: CO conversion (a) and selectivity (b) of copper and cerium oxide on SBA-15-p-900 with different feed compositions.

The effect of adding 10% H₂O on different catalyst were shown in Fig. 5. The catalysts with SBA-15 supports were strongly affected by H₂O. The best catalyst is unsupported 0.1CuO/0.9CeO₂, it can reach 86% conversion and 50% selectivity at 160°C

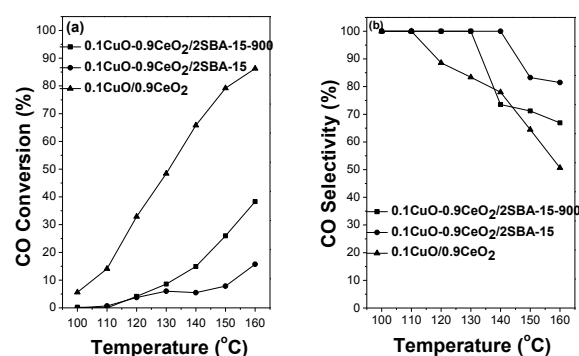


Figure 5: CO conversion (a) and selectivity (b) of copper and cerium oxide on SBA-15 calcined at different temperatures. Feed composition 0.8% CO, 0.8% O₂, 10% H₂O, 50% H₂, and balance He.

4. Conclusions

XRD patterns showed that copper oxide formed small particles and well dispersed when the mixed oxide was supported on SBA-15. CuO-CeO₂ supported on SBA-15

dehydrated at 900°C gave higher catalytic activity than that supported on 500°C calcined SBA-15, probably due to that hydroxyl groups on the surface hinder the PROX reaction. The activities of the catalysts were significantly decreased in the presence of H₂O, especially the silica supported catalysts. This negative effect may be attributed to the hydrophilic surfaces of silica. Among the supported catalysts, 0.1CuO-0.9CeO₂/2SBA-15-p-900 catalyst could reach 100% CO conversion at 140°C with O₂ selectivity around 70%.

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