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Effects of preparation method on catalytic activities of the CuO/CeO_2-Al_2O_3 catalyst for the selective CO oxidation reaction

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Abstract

CuO/CeO_2-Al_2O_3 were prepared by impregnation, sol gel and coprecipitation. The weight ratio of copper oxide, cerium oxide and alumina was fixed at 40:51:9. N_2 adsorption results showed that specific surface area and pore size varied with changes of preparation method. Catalyst prepared by impregnation has the highest specific surface area of 60.3 m^2/g. X-ray diffraction results revealed the same structure of CuO, CeO_2 and Al_2O_3 in different preparation method. It was found that the catalyst prepared by impregnation showed the best catalytic activity to CO oxidation reaction and selective CO oxidation reaction. Without CO_2 and H_2O in the gas stream, CO conversion reached maximum value of 98.7% at 140-160°C with selectivity of 60-80%. Moreover, the effects of the presence of CO_2 and H_2O in the gas feed were investigated. The results indicated that both CO_2 and H_2O have negative effects to the activity of the catalyst. This was due to the blockage of CO_2 and H_2O molecules over the active sites.

Keywords

Sol-gel; coprecipitation; impregnation; CuO/CeO_2-Al_2O_3; selective CO oxidation

1. Introduction

Fuel cells have been known as an alternative source of power conversion technology. The most promising one for transportation and residential application is proton exchange membrane fuel cell (PEMFC). This is due to fast start-up, high power density, low temperature operation and zero emissions [1]. Steam reforming of methanol [2] or partial oxidation of hydrocarbons [3] followed by water gas shift reaction [4] are commonly used methods to produce H_2-rich gas for PEMFC. The gas composition from these processes contains 40-75% H_2, 15-20% CO_2, ~10% H_2O, 0-25% N_2 and 0.5 to 1% CO depending on operating conditions. CO contained in the gas stream seriously depresses the performance of PEM fuel cell by poisoning the Pt-based anode electrode of PEM fuel cells [5]. Removal CO in the gas stream to 10 ppm or less is necessary for high efficient operation of the fuel cell, with minimum loss of hydrogen. Many methods have been developed for removal of trace CO from H_2 stream such as membrane, methanation and selective CO oxidation [6-8]. Of these method, selective CO oxidation is the most effective and economical approach. By this method, oxygen is added to burn CO via CO oxidation reaction

($CO + 0.5O_2 \rightarrow CO_2$) but not H_2 via H_2 oxidation reaction ($H_2 + 0.5O_2 \rightarrow H_2O$) and this is so called "preferential oxidation or selective CO oxidation". The requirements from a catalyst for this reaction are high CO conversion at low temperature, high selectivity to CO oxidation, wide temperature window at CO conversion greater than 99% and resistance to CO_2 and water vapor in the gas stream. Many researchers have been searching and developing catalysts for this particular reaction [9-10].

Platinum-based catalysts have intensively been studied and shown the promising performance to this application. They are highly resistant to the deactivation due to the presence of CO_2 and water vapor but requires high temperatures (>170°C) and exhibits low selectivity to CO oxidation [11]. On the other hand, CuO- CeO_2 catalysts perform an interesting catalytic activity to this reaction at lower temperatures with high selectivity to CO oxidation but their catalytic performance decreases under the presence of CO_2 and water vapor [12]. CeO_2 is a well-known oxide that is thermally and chemically stable with high capacity to store and release oxygen. Therefore, the catalytic activity to CO oxidation of CuO can be improved by generating oxygen vacancies of CeO_2 which in turns forming interfacial actives between two metals [13]. In general, at low temperature, CO adsorbed on the interface of CuO and CeO_2 directly reacts with surface oxygen of CeO_2 to form CO_2. CO_2 will desorb and leave the surface oxygen vacancy available for O_2 gas to fill in. To enhance this mechanism, high dispersion of CuO and nanocrystals of CeO_2 (<10 nm) are required [14-16]. An increase in dispersion of CeO_2 can be achieved by addition of Al_2O_3. The well dispersed CeO_2 on Al_2O_3 are essential for an increment of oxygen storage capacity [17]. Another strategy to increase metal dispersion is to modify the surface area of the support via preparation methods. The higher the surface area of the support, the better chance to get high dispersion. Huber et.al. [18] prepared Cu-Ce-Zr mixed oxide catalysts by coprecipitation and found that prepared mixed oxide catalyst exhibits high surface area. The preparation conditions such as rate of stirring the solution during precipitation and drying and calcination temperatures affected the pore structure and surface area. Sol gel is of interest for mixed oxide preparation. This is due to an easy control of chemical composition and low temperature synthesis. High surface area of the final product prepared by this method was reported [19]. Impregnation was a widely used method for heterogeneous catalyst preparation. This is because of its simplicity, low cost and limited waste. The solution of active metals is filled into the support pores by capillary forces. Particle size distribution of metal depends on the electrostatic adsorption. The stronger the electrostatic adsorption forces, the better of metal dispersions [20].

In this work, the effect of preparation methods to the catalytic activity of CuO-CeO_2-Al_2O_3 catalysts was studied for CO oxidation and selective CO oxidation. Also the resistance of these catalysts to CO_2 and water vapor was also investigated.

2. Experiment

2.1 Catalyst Preparation

CuO/ CeO_2-Al_2O_3 catalysts with the mass ratio of 40:51:9 were prepared by three different methods: impregnation (IM), sol gel (SG), and coprecipitation (CP). Chemicals used as precursors in catalyst preparation were aluminium isopropoxide, aluminium

nitrate, aluminium oxide, cerium (III) nitrate trihydrate, and copper (II) nitrate trihydrate. All chemicals were purchased from Sigma-Aldrich, Inc.

For an impregnation method, aluminium oxide from Aldrich was used as a support. The desired amounts of copper (II) nitrate tri-hydrate and cerium (III) nitrate tri-hydrate were impregnated into aluminium oxide by incipient wetness impregnation. The obtained solid was dried at 110 °C for 10 hr. and then calcined at 500 °C for 5 hr.

For a sol gel method, a 100 ml of deionized water was heated to 80 °C and controlled to this temperature. The desired amount of aluminium isopropoxide was added into the hot water and the solution was stirred for 30 min. Then, a nitric acid was added and the solution turned from opaque to clear solution. The solution was kept stirring for another 30 min. After that, the solution was cool to room temperature. The known amount of cerium nitrate was added into the solution and the solution was stirred at room temperature for 30 min and then the desired amount of copper nitrate was added. The solution was kept stirring for 24 hr. This solution is called "sol". To make gel, sol was placed into a beaker controlled temperature to 50 °C. Sol was gradually changed its viscosity and then turn into gel. After gel formed, the beaker was cool to room temperature and the gel was aged for 24 hr. Then, the gel was dry at 110 °C for 10 hr. and followed by calcined at 500 °C for 5 hr.

For a coprecipitation method, the desire amounts of copper (II) nitrate trihydrate, cerium (III) nitrate tri-hydrate and aluminium nitrate were dissolved in deionized water to obtain the concentration of 0.1 M. The solution was rigorously stirred while 0.1 M of Na_2CO_3 solution was slowly added into the solution. When the pH of the solution reached 9, stopped adding Na_2CO_3. At this point, the precipitate was observed, and the solution became cloudy. The solution was kept continuously stirring for 12 hr. After that, the precipitate was filtered and cleaned several times with deionized water. Then, the precipitate was dried at 110 °C for 10 hr., followed by calcined at 500 °C for 5 hr.[21]

The above synthesized samples were denoted as 40Cu/Ce-Al(IM), 40Cu/Ce-Al(SG) and 40Cu/Ce-Al(CP), respectively.

2.2 Catalyst Characterization

The crystal structure of catalysts was analyzed by X-Ray diffraction measurements (XRD) using Cu Kα radiation (0.154 nm) from 20 to 80°, voltage of 40 kV, current of 30 mA and the step size of 0.02°. The mean crystallite size of oxides was calculated by Scherrer's equation according to the X-ray line broadening of the (111) diffraction peak [22].

Nitrogen adsorption-desorption analyses were performed on an Autosorption-1C (Quantachrome, Inc.), using ultra high purify nitrogen gas at -196°C. Prior to the analysis all catalysts were degassed under vacuum at 300 °C for 3 hr. Using the nitrogen adsorption-desorption isotherms, the specific surface areas of the catalysts were calculated by the Brunauer-Emmett-Teller (BET) method and the average pore sizes of the catalysts were calculated by Barrett-Joyner-Halenda (BJH) method [23].

2.3 Catalytic Activity Test

All catalysts prepared were tested for their activity to CO oxidation reaction and preferential CO oxidation. The experiment was carried out in a tubular flow microreactor with an internal diameter of 6.0 mm under the atmospheric pressure. The amount of catalyst was 80 mg and the total gas flow rate was 100 $mlmin^{-1}$. The reaction temperature was

controlled by temperature controller with K-type thermocouple attached on the surface of catalyst bed. For CO oxidation reaction, the gas stream consisted of 1% CO, 1% O_2 and 98% He as balance. For preferential CO oxidation reaction, the gas feed consisted of 1% CO, 1% O_2, 50% H_2 and He as balance. CO, O_2 and CO_2 in the inlet and outlet gas streams were periodically analyzed online with a gas chromatograph (GC) equipped with a column packed with molecular sieve (Carbosphere from Agilent) and a thermal conductivity detector (TCD). Before, the outlet gas entered GC, H_2O was trapped from the gas stream. For preferential CO oxidation reaction, selectivity to CO oxidation was defined as the fraction of O_2 consumption for the CO oxidation to CO_2 over the total O_2 consumption by the reactions. CO conversion and selectivity to CO oxidation were calculated using equation (1) and (2), respectively. Be noted that there is no methane observed in this study.

$$CO\,conversion, \% = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100 \qquad (1)$$

$$Selectivity\,to\,CO = \frac{0.5\left([CO]_{in} - [CO]_{out}\right)}{[O_2]_{in} - [O_2]_{out}} \times 100 \qquad (2)$$

Where $[CO]_{in}$ is the inlet concentration of CO

$[CO]_{out}$ is the outlet concentration of CO

$[O_2]_{in}$ is the inlet concentration of O_2

$[O_2]_{out}$ is the outlet concentration of O_2

3. Results and Discussion

In this section, catalyst characterization and catalytic activities to CO oxidation and selective CO oxidation reactions were conducted. The results were shown as follows:

3.1 Catalyst Characterization

N_2 adsorption-desorption isotherms of prepared catalysts are shown in Figure 1. The isotherms of all prepared catalysts corresponded to a type IV isotherm with a hysteresis loop specified a H4, indicating narrow slit-like pores with irregular shape and broad size distribution [24]. This is typically found in complex material containing both micropores and mesopores. Specific surface area and average pore size of catalysts are reported in Table 2. Specific surface area of 40Cu/Ce-Al(IM) was 60.3 m^2/g while others were 29.0 and 53.9 m^2/g for 40Cu/Ce-Al(CP) and 40Cu/Ce-Al(SG), respectively. The highest specific surface of 40Cu/Ce-Al(IM) resulted from the commercial aluminium oxide (A_{sp}= 150 m^2/g). A decrease of specific surface area when Cu and Ce impregnated in aluminium oxide may result from pore blocking [25]. For 40Cu/Ce-Al(SG), its specific surface area was comparable to that of 40Cu/Ce-Al(IM). This was due to the fabrication of porous material by sol gel method. Gel is a semi-solid that contains liquid trapped inside network of oxide. In drying process, heat was slowly applied to gel in order to increase the connectivity within the gel network. Under controllable conditions, the liquid in the gel was removed and a highly porous and low density oxide were obtained [26]. The lowest specific surface area of 40Cu/Ce-Al(CP) resulted from the differences of activity coefficients of each ion in the solution which resulted to a wide size distribution of the final product.

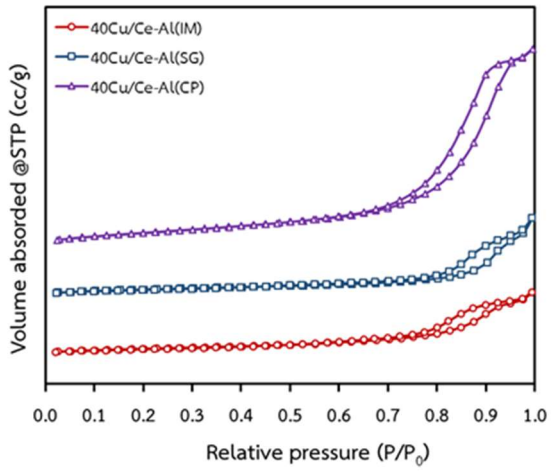

Figure 1 N_2 adsorption- desorption isotherms of prepared catalysts.

Table 1 Specific surface area and average pore size

Preparation method	Specific surface area (m^2/g)	Average pore size (nm)
Impregnation	60.3	10.9
Co-precipitation	29.0	11.1
Sol gel	53.9	6.0

Figure 2 shows the comparison of diffraction patterns between catalysts prepared by different methods. As can be seen, all XRD patterns have same peak positions but different intensity. The strongest peak of CuO appeared at 2-theta of 35.5° and 38.7° while the strongest peak of CeO_2 appeared at 2-theta of 28.7°. These peak patterns are corresponding to the presence of CuO in a monoclinic structure and of CeO_2 in faced center cubic structure. The XRD peak at 28.7° of 40Cu/Ce-Al(IM) was sharper than that of 40Cu/Ce-Al(SG) and 40Cu/Ce-Al(CP). This led to the biggest crystallite size of CeO_2 in 40Cu/Ce-Al(IM). On the other hand, XRD peaks at 35.5° (strongest line for CuO) for all catalysts have comparable width. Therefore, they have quite similar crystallite sizes of CuO. Using Scherrer's Equation, average crystallite sizes of oxides were determined and shown in Table 2. The average crystallite size of CuO was approximately 21.0 nm while those of CeO_2 were 4.2 nm for 40CuO/Ce-Al(CP), 6.3 nm for 40CuO/Ce-Al(SG) and 13.0 nm for 40CuO/Ce-Al(IM).

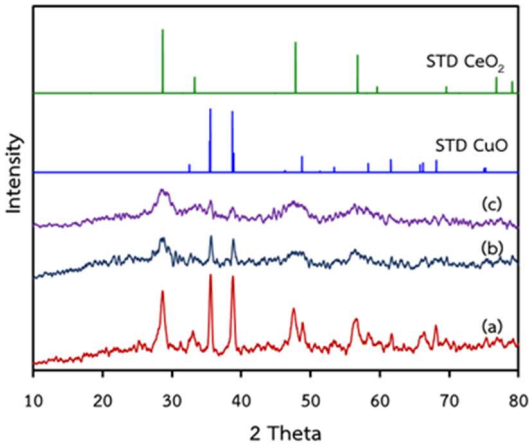

Figure 2 XRD patterns of prepared catalysts: (a) 40Cu/Ce-Al(IM), (b) 40Cu/Ce-Al(SG) and (c) 40Cu/Ce-Al(CP).

Table 2 Average crystallite sizes of metal oxides.

Preparation method	Crystallite size (nm)	
	CeO_2	CuO
Impregnation	12.4	20.5
Co-precipitation	4.0	19.2
Sol gel single step	6.0	22.4

3.2 Catalytic Activity Tests

3.2.1 CO Oxidation Reaction

The catalytic activities of catalysts were investigated in the temperature range of 70–190°C. As seen in Figure 3, CO conversion increased when varying the reaction temperature from 70°C to 190°C. Among these catalysts, 40Cu/Ce-Al(CP) exhibits the lowest activity and T_{50} (the temperature of CO

conversion at 50%) is 120 °C, whereas the T_{50} for 40Cu/Ce-Al(IM), and 40Cu/Ce-Al(SG) catalysts are 80 and 105 °C, respectively. At 100% CO conversion (T_{100}), 40Cu/Ce-Al(IM) exhibits the highest activity with T_{100} at 150 °C, whereas the T_{100} of 40Cu/Ce-Al(SG) and 40Cu/Ce-Al(CP) increased to 170°C. The results of catalytic performance were comparable to that of 40%CuO/CeO_2 (Zhang's group) synthesized by a facile hydrothermal method and performed activity test for CO oxidation reaction. T_{50} of the catalyst was 88°C which is in the same range of temperature of our work [27]. Also, this result indicated that the preparation method affected to the catalytic activity of the catalyst. The better performance of this catalyst towards CO oxidation reaction may be attributed to high specific surface area of the catalyst and this results to the enhancement of interfacial sites where CO oxidation is occurred [28].

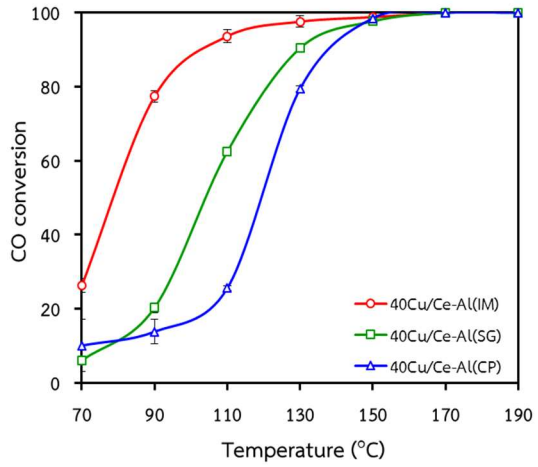

Figure. 3 CO conversion as a function of temperature for CO oxidation reaction.

3.3.2 Selective CO Oxidation Reaction

The catalytic activities of catalysts under H_2-rich stream were investigated in the temperature range of 110–210 °C. The gas stream consisted of 1% CO, 1% O_2, 55% H_2 and He as balance. As can be seen in Figure 4, catalysts prepared by different methods performed different catalytic activities. Since the inlet gas contained both trace CO and excess H_2, the competition between CO oxidation and H_2 oxidation reaction was observed. Figure 4 demonstrated 3 different plots: (a) is a plot of CO conversion, (b) is a plot of O_2 consumption and (c) is a plot of selectivity to CO oxidation reaction. The candidate catalyst for this application should highly active to CO oxidation reaction and less active to H_2 oxidation reaction. Therefore, high CO coversion and selectivity are needed. In Figure 4 (a), CO conversion increased with an increase in reaction temperature until the temperature at 170 °C for 40Cu/Ce-Al(IM), 190 °C for 40Cu/Ce-Al(SG) and 40Cu/Ce-Al(CP), further increasing in reaction temperature decreased CO conversion. This result implied that H_2 oxidation reaction is dominant at high temperature. Comparing the CO conversion of three catalyst, 40Cu/Ce-Al(IM) was more active to the reaction than others and also active at lower temerature while catalytic activities of both 40Cu/Ce-Al(SG) and 40Cu/Ce-Al(CP) were comparable. Considering Figure 4(c) selectivity to CO oxidation, at maximum CO conversion of each catalsyt, selectivities were 70% for 40Cu/Ce-Al(IM), 45% for 40Cu/Ce-Al(SG) and 40Cu/Ce-Al(CP). It is obviously indicated that 40Cu/Ce-Al(IM) performed the best catalytic activity to selective CO oxidation. A decrease of selectivity to CO oxidation occurred from the competition between CO oxidation and H_2 oxidation reaction. At high temperature, H_2 oxidation reaction is preferrred. The better catalytic activities of 40Cu/Ce-Al(IM) may relate to the high specific surface area. The mechanism of the reaction is Mars and van Krevelen mechanism. It involves the reduction and oxidation of active oxygen sites. CO oxidation occurs on the Cu^+ site and oxygen lattice of CeO_2 while H_2

oxidation occurs via dissociative adsorption steps [29]. The more the availability of Cu^{+} active sites adjacent to oxyen lattice vacancy of CeO_2, the better the catalytic activity.

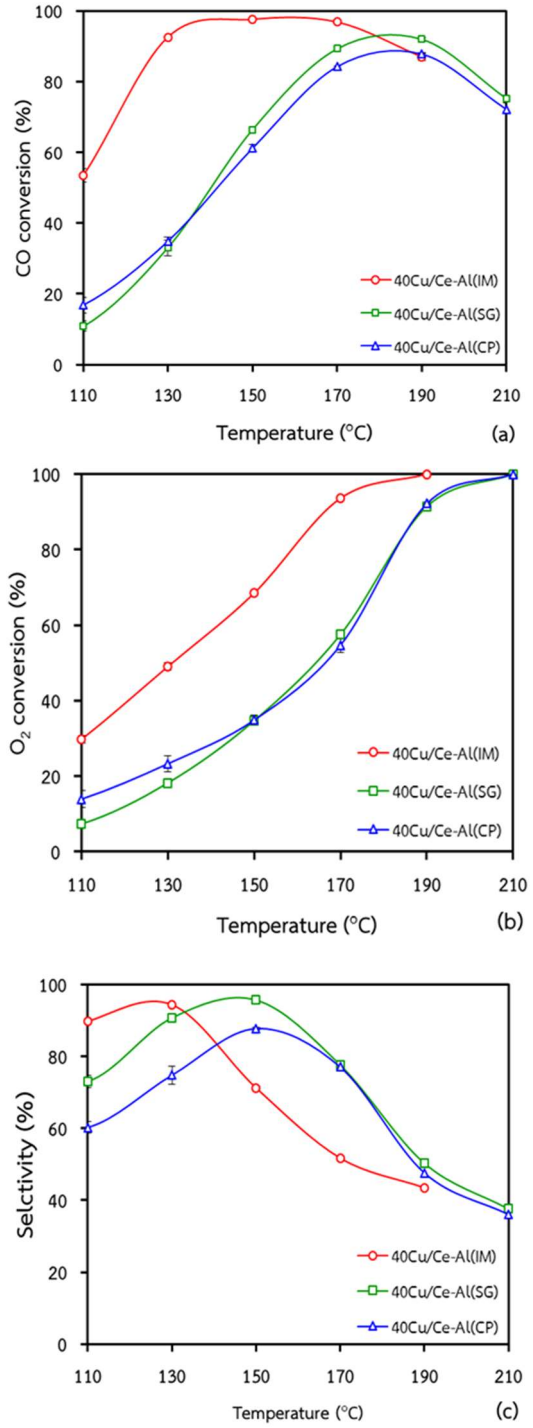

Figure 4 Selective to CO oxidation in the presence of excess H_2; (a) CO conversion, (b) O_2 consumption and (c) selectivity

3.3.3 Effect of CO_2 on Selective CO Oxidation

The reformed gas contains 50-55% H_2 as a main gas. It also contains 15-20% CO_2. Consequently, the effect of CO_2 on selective CO oxidation needs to be investigated over these catalysts. In this section, the simulated gas contains 1%CO, 1%O_2, 50%H_2, 20%CO_2 and He as balance and the results are shown in Figure 5.

The presence of CO_2 in the gas stream has a negative effect to the catalytic activity of the catalysts. Maximum CO conversion reduced to 95% for 40Cu/Ce-Al(IM), 70% for 40Cu/Ce-Al(SG) and 65% for40Cu/Ce-Al(CP). Also selectivity to CO oxiation decreased with an increase in temperature. This is due to (i) at low temperature range, CO_2 physically adsorbed on the active sites of the catalysts in the form of carbonate or carbonyl [30] and this in turn blocking the process of lattice oxygen in cerium oxide reacting with adsorbed CO on CuO, and (ii) at high temperature, adsorbed CO_2 reacted with H_2 via reverse water gas shift reaction to produce CO and water ($CO_2 + H_2 \rightarrow H_2O + CO$). 40Cu/Ce-Al(IM) was tested activity to reverse water gas shift reaction. The inlet gas contains 20%CO_2, 50%H_2 and He as balance. 90 ppm of CO was produced at 170°C. An increase in reaction temperature increases CO concentration to 243 ppm at 190°C and 780 ppm at 210°C. The formation of CO from this reaction at temperature above 170°C led to a reduction of selectivity to CO oxidation. The better the resistance of 40Cu/Ce-Al(IM) to CO_2 may result from catalyst structure. The details of catalyst structure will be conducted as a future work.

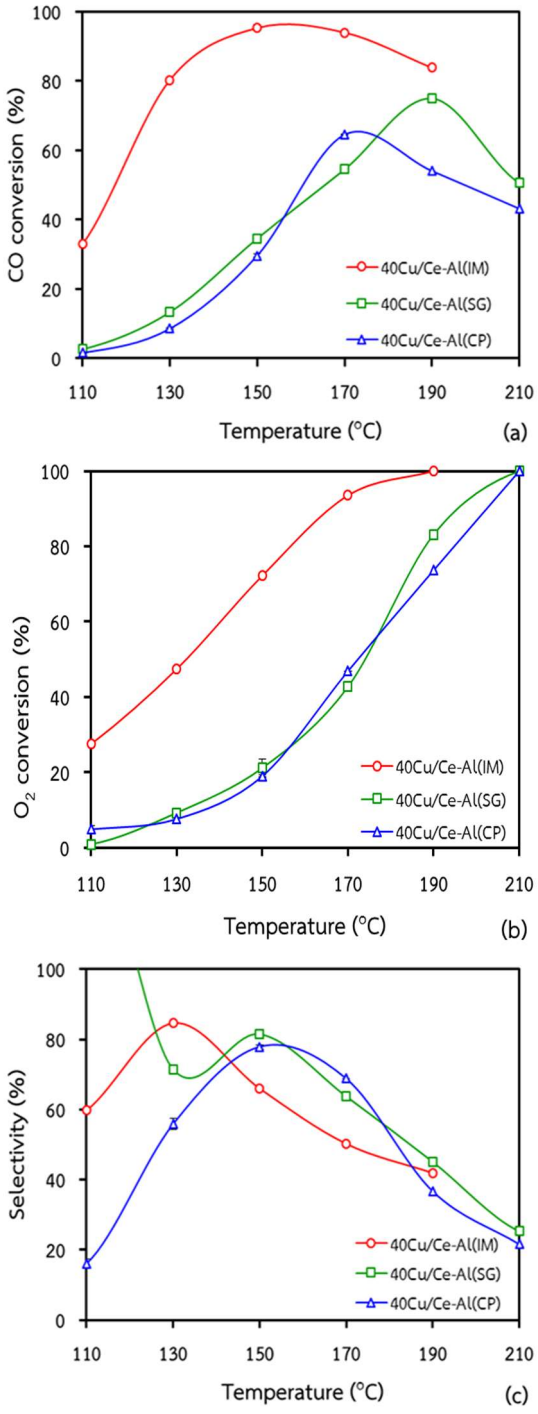

Figure 5 Effect of CO_2 to catalytic activity as a function of temperature; (a) CO oxidation, (b) O_2 consumption and (c) Selective CO oxidation

3.3.4 Effect of H_2O on Selective CO Oxidation

Again water also exists in a reformed gas. In this section, 15%H_2O was added into the gas stream. The effect of H_2O to catalytic activity of the catalyst is shown in Figure 6. The inlet gas contains 1% CO, 1% O_2, 50% H_2, 15% H_2O and He as balance.

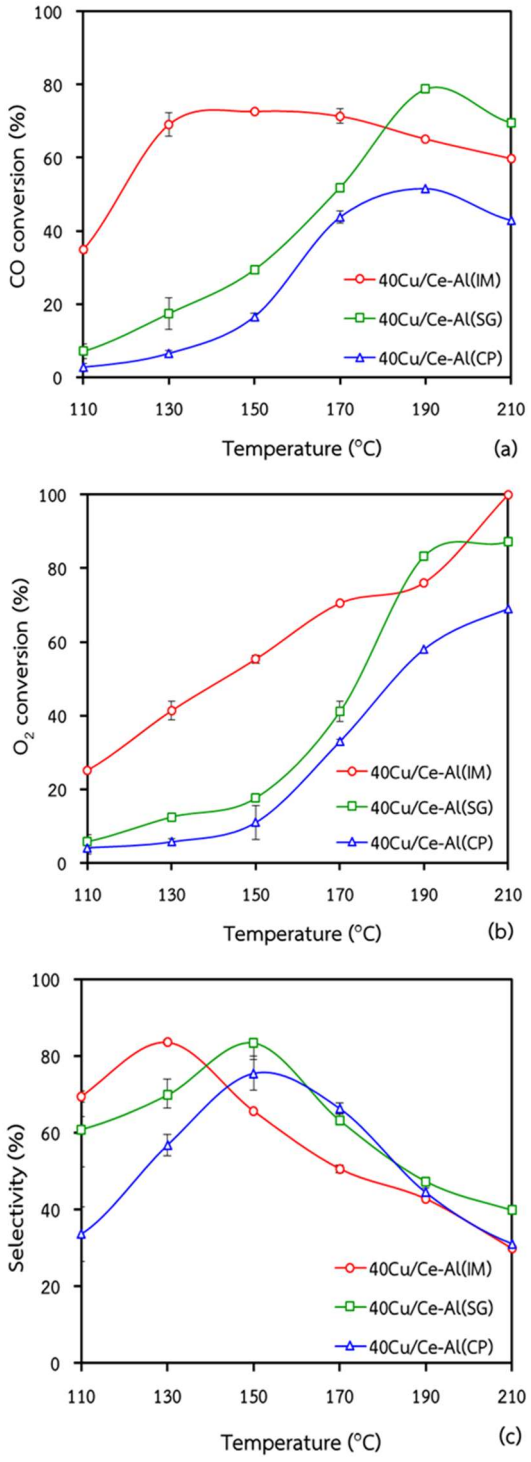

Figure 6 Effect of H_2O to catalytic activity as a function of temperature; (a) CO oxidation, (b) O2 consumption and (c) Selective CO oxidation

The presence of H_2O in the feed stream is strongly negative to CO oxidation reaction for all catalysts. Maximum CO conversion drops to 70% for 40Cu/Ce-Al(IM), 75% for 40Cu/Ce_Al(SG) and 50% for 40Cu/Ce-Al(CP). Likewise, selectivity to CO oxidation is high at low temperature and goes down to below 50% at temperature above 170°C. The reduction of CO conversion may result from the adsorption of water on the surface and porous of the catalyst blocking the active sites for O_2 molecules to adsorb. Noticed that the O_2 consumption sluggishly increased at the low temperature in the presence of CO_2 and H_2O.

The catalytic activity of the catalysts is fully recovery when CO_2 and H_2O is taken out from the gas stream. This means the deterioration of catalyst from CO_2 and H_2O is a reversible process. Also, deactivation test of the catayst was conducted under 1% CO, 1% O_2, 50% H_2 balance with He for 36 hr. There was no deactivation observed. This was due to high thermal and chemical stability of the catalysts.

The best catalyst for CO oxidation and selective CO oxidation in this work is 40Cu/Ce-Al(IM). It was due to high surface area of the catalyst.

4. Conclusions

In this work, CuO/CeO_2-Al_2O_3 catalysts were prepared by incipient wetness impregnation, sol gel and coprecipitation methods. N_2 physical adsorption-desorption technique and X-ray diffraction were used for catalyst characterization. Specific surface area varied by preparation method. Catalyst prepared by impregnation has the highest surface area of 60.3 m^2/g while that prepared by coprecipitation has the lowest surface area of 29.0 m^2/g. Crystallite size of CuO was ~20 nm (estimated from Scherrer equation). The catalytic activity were found to be influenced by preparation method. The catalyst prepared by impregnation showed the best catalytic activity: CO conversion nearly 100% , high selectivity to CO oxidation and wide temperature window at CO conversion greater than 99%. It is resulted from high specific surface area which increses the active sites for CO oxidation reaction to occur. Among these three preparation methods, impreganation is the suitable one for preparation of CuO/CeO_2-Al_2O_3 used as a catalyst for selective CO oxidation reaction.

Acknowledgements

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