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PREPARATION AND CATALYTIC CO OXIDATION OF CuO/CeO_2__ZrO_2/Al_2O_3.

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ABSTRACT

The effect of preparation methods to catalyst activity was investigated. Mixed oxides of copper, cerium, zirconium, and aluminium were used as a catalyst. There were four different preparation methods studied, i.e., co-precipitation, sol gel, impregnation, and direct mixing of each oxide. The composition of each oxide in mixed oxides was constant, i.e., 8.0%wt copper oxide, 25.6%wt cerium oxide, 6.4%wt zirconium oxide, and 60.0%wt aluminium oxide. Specific surface areas of all catalysts were characterized using Autosorption-1. The results showed that catalyst prepared by co-precipitation method offered the highest specific surface area of 230.5 m^2/g. Specific surface areas of catalysts prepared by sol gel and direct mixing oxides were 177.7 m^2/g and 83.6 m^2/g, respectively, while catalyst prepared by impregnation obtained the least specific surface area of 67.4 m^2/g. The differences in specific surface areas were related with particle/crystalline sizes of each oxide in the samples. XRD results showed that CuO was well dispersed in the catalysts prepared by co-precipitation and sol gel methods. $Ce_2Zr_2O_7$ was formed in catalysts prepared by co-precipitation and sol gel. Particle sizes of $Ce_2Zr_2O_7$ were 5.6 nm and 7.3 nm for co-precipitation and sol gel, respectively. Finally, catalyst prepared by co-precipitation showed the best performance to CO oxidation and catalyst prepared by direct mixing of each oxide showed the worst performance in CO oxidation.

Keywords: Co-precipitation, sol gel, impregnation, CuO, CeO2, ZrO2, CO oxidation.

INTRODUCTION

Poisoning of trace amount of CO in reformed gas to electrode of proton exchange membrane fuel cells has been extensively studied. Many works have been done to remove CO from reformed gas before it enters fuel cells. There are many methods using for removing CO. The most economic one is called selective CO oxidation. This method is simply adding O_2 to the mixed gas under suitable catalysts. The catalysts should selectively burn CO in excess of hydrogen. Many catalysts have been studied for this application such as Pt/Al_2O_3, $Pt\text{-}Pd/CeO_2$, Au/Fe_2O_3, Au/CeO_2, Ru/Al_2O_3, etc. (Manasilp and

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Gulari, 2002; Parinyaswan et al., 2006; Chen et al., 2007; Luengnaruemitchai et al., 2005; Panzera et al., 2004). However, many attempts still carry on obtaining the best catalysts for this application. CuO is a well-known catalyst for oxidation reaction (Yahiro et al., 2007) and has been intensively studied for CO oxidation reaction. It has been reported that mixed oxide of CuO and CeO_2 performed the best selectivity to CO oxidation at low temperatures. However, the activity of this catalyst might be improved by adding other oxides, such as zirconium oxide and aluminium oxide. This may be due to oxygen storage property of cerium oxide (Holmgren et al., 1999), thermal resistance of zirconium oxide, and aluminium oxide (Hori et al., 1998). Moreover, the use of cerium oxide together with zirconium oxide increases the oxygen storage property of cerium oxide (Mattos and Noranha, 2005). Even though CuO together with CeO_2 has been investigated in reforming reaction, its activity of this catalyst cooperated with zirconium and aluminium to selective CO oxidation has not been revealed.

In this work, activities of mixed oxides of copper, cerium, zirconium, and alumina to CO oxidation were investigated. Moreover, the effect of catalyst preparation methods was studied. The obtained results are the preliminary results for the study of activity of this catalyst to selective CO oxidation.

MATERIALS AND METHODS

Preparation of catalysts

Mixed oxides of copper, cerium, zirconium, and aluminium were prepared by different methods, i.e., co-precipitation, sol gel, impregnation, and direct mixing of each oxide. All catalysts contained 8%wt copper oxide, 25.6%wt cerium oxide, 6.4%wt zirconium oxide, and 60%wt aluminium oxide. Chemicals used in co-precipitation method were copper (III) nitrate trihydrate, cerium (III) nitrate hexahydrate, zirconyl nitrate hydrate, and aluminium nitrate nonahydrate. All chemicals were obtained from Aldrich. This method began with the preparation of solution of each metal. All metal nitrate precursors were separately dissolved in deionized water with the concentration of 0.1 M. All solutions were subsequently mixed together. The final solution was continuously stirred, while the solution of a 0.1 M of ammonium hydroxide was slowly added. The precipitate was observed at pH 9. The resulting precipitate in the solution was aged for 3 hours. The precipitate was washed with deionized water several times after aging for removing excess ions. The obtained precipitate was subsequently dried overnight in a conventional oven at 110°C and calcined at 500°C for 5 hours. After calcinations, the obtained solid was ground and sieved to obtain powder for the activity test.

Chemicals used in sol gel method were copper (III) nitrate trihydrate, cerium (III) nitrate hexahydrate, zirconyl nitrate hydrate, and aluminium isopropoxide. This method started with dissolving of known amount of aluminium isopropoxide in hot deionized water. Nitric acid was subsequently added until the solution became clear. The solution was kept stirring to obtain uniformity. Copper (III) nitrate trihydrate was added into the solution, and followed by zirconyl nitrate hydrate and cerium (III) nitrate hexahydrate, respectively. The obtained solution was stirred overnight. The solution was slowly heated to obtain gel. The gel was aged overnight, subsequently dried at 110°C, and followed by calcined at 500°C. The drying process was done according to the procedures mentioned previously for co-precipitation method.

Chemicals used for an incipient wetness impregnation were copper (III) nitrate trihydrate, cerium (III) nitrate hexahydrate, zirconyl nitrate hydrate, and commercial aluminium oxide. The known amount of copper (III) nitrate trihydrate in this method was dissolved in deionized water. The amount of deionized water was important. It should be enough to wet aluminium oxide. The solution was subsequently well mixed with aluminium oxide. The solution of zirconyl nitrate hydrate was well mixed to the solid, which now contained copper and aluminium. Wet solid was dried and calcined at the same condition as the previous method. The wet solid was dried and calcined at the same conditions as mentioned in the previous method. Finally, the solution of cerium (III) nitrate hexahydrate was well mixed with the solid that contained copper, zirconium, and aluminium. The same procedure was carried on for drying and calcining processes.

The last catalyst was directly prepared by mixing all four oxides together. Each oxide was obtained from Aldrich except for copper oxide. Copper oxide was prepared by precipitation method.

Catalyst characterization

The properties of all catalysts were analyzed as follows: specific surface area by autosorption-1 from Quanta chrome, structure of crystal by scanning electron microscopy (SEM) and chemical composition of elements by energy dispersive x-ray fluorescence spectrometer (EDX), and crystalline size and structure by x-ray diffraction (XRD) from Bruker AXS model D8 Discover using nickel-filtered CuKα radiation.

Activity test

All catalysts were tested for their activities to CO oxidation in a micro-reactor. The temperatures inside the reactor were measured by a K-type thermocouple placed on the top of the catalyst bed. Temperature controller controlled the reaction temperatures. The total gas flow-rate was 100 cc./min. Inlet gas was composed of 1%CO, 1%O_2 and balance with He. The outlet and inlet gases were connected to gas chromatography (GC) with TCD. This GC can be used to analyze concentration of CO, O_2, and CO_2 in the gas stream. Before catalysts were tested for their activity to the reaction, they were eliminated water condensing within pore of catalyst by purging them with He at 200°C for 4 hours.

RESULTS AND DISCUSSION

Characterization of catalysts

Specific surface area: All catalysts prepared from different methods were analyzed for their specific surface areas by using autosorption-1 from Quanta chrome and using BET model to predict the specific surface areas. Each sample was evacuated at 573 K for 3 h, and then cooled down to 77 K using liquid N_2. In this work, each catalyst contained 8.0 % wt copper oxide, 25.6 % wt cerium oxide, 6.4 % wt zirconium oxide, and 60.0 % wt aluminium oxide. The results are shown in Table 1.

Table 1. Specific surface area of catalysts prepared by different methods.

Method	Specific surface area, A_s (m^2/g)
Co-precipitation	230.5
Sol-gel	177.7
Impregnation	67.4
Mixing of each oxide	83.6

In Table 1, the differences in preparation methods led to differences in specific surface areas of the final products. The catalyst prepared by co-precipitation offered the highest specific surface area of 230.5 m^2/g, while impregnation gave the lowest specific surface area of 67.4 m^2/g. Specific surface areas of mixed oxides prepared by sol gel and mixing of each oxide were 177.7 m^2/g and 83.6 m^2/g, respectively. Theoretically, sol gel method seemed to be the method offering the highest specific surface area. This was due to the formation of metal oxide during condensation reaction. In this step, when metal hydroxide molecules react to each other to form network structure, this structure traps solvent molecules inside the structure and in turns become soft solid. This is called "gel". When gel is dry, the solvent inside the structure evaporates and leaves empty pores inside the solid structure. This causes the high specific surface area comparing to that of other methods. Therefore, the specific surface area of mixed metal oxides prepared by sol gel was 177.71 m^2/g. However, the specific surface area of this catalyst was 23 % less than that of catalysts prepared by co-precipitation. Further investigation was conducted in order to explain these results.

Next, all catalysts were analyzed for chemical compositions by EDX. The results showed that all catalysts have the same amount of element compositions. Therefore, the differences in specific surface areas were from the preparation techniques but not from the differences in concentrations of each element.

Crystalline sizes of oxides: XRD was used for analyzing structure and crystalline sizes of catalysts. The results are shown in Figures 1 and 2.

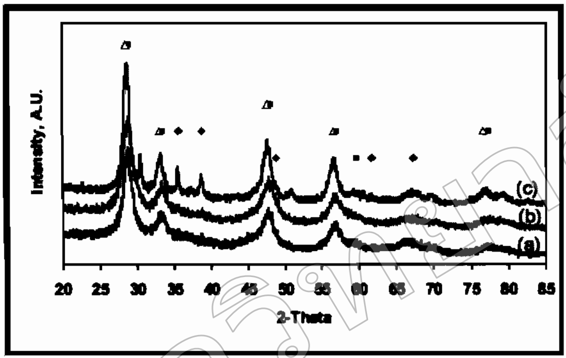

Figure 1. XRD patterns of catalysts prepared by different methods: (a) Sol gel, (b) Co-precipitation, and (c) impregnation. ■ refers to peak positions of reference XRD patterns of $Ce_2Zr_2O_7$, Δ refers to peak positions of reference XRD patterns of CeO_2, and ◆ refers to peak positions of reference XRD patterns of CuO.

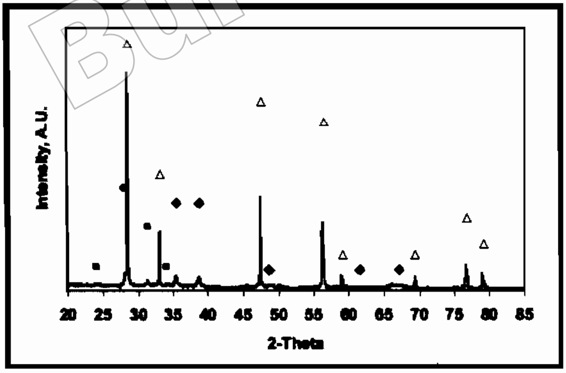

Figure 2. XRD pattern of catalyst prepared by direct mixing of each oxide. Δ refers to peak positions of reference XRD patterns of CeO_2, ● refers to peak positions of reference XRD patterns of ZrO_2, and ◆ refers to peak positions of reference XRD patterns of CuO.

In Figure 1, XRD patterns of catalysts prepared by different methods were reported. Figure 1 (a) was XRD patterns for a catalyst prepared by sol gel method, and Figure 1 (b) was XRD patterns for a catalyst prepared by co-precipitation method. Interestingly, these two patterns looked similar. When these two patterns were compared with XRD patterns of CeO_2 (peak positions defined with "Δ") with peak positions at angles of 28.5°, 32.9°, 47.5°, 56.34°, and 76.5°, there was no matching to the patterns at all. This meant that CeO_2 was not present in the catalysts prepared by these two methods. However, the peaks were matching with standard peak positions of $Ce_2Zr_2O_7$ (peak positions defined with "■") at angles of 28.8°, 33.4°, 47.9°, 56.8°, 59.5°, and 77.2°. Therefore, it was concluded that catalysts prepared by co-precipitation and sol gel obtained the form of $Ce_2Zr_2O_7$ instead. The precipitation process may cause this. The metal precursors were precipitated together and formed the structure that bonded between these three atoms. This also happened to the catalyst prepared by sol gel method. During the condensation, each molecule of cerium precursor and zirconium precursor can react together via condensation reaction and form the bonding of Ce-Zr-O. From Bragg's law, crystalline sizes of $Ce_2Zr_2O_7$ for these two samples were analyzed. It was found that average crystalline size of $Ce_2Zr_2O_7$ in the catalyst prepared by sol gel was 7.3 nm, while that of $Ce_2Zr_2O_7$ in the catalyst prepared by co-precipitation was 5.6 nm. This may lead to the lower of the specific surface area of the catalyst prepared by sol gel. In fact, there were no XRD patterns of CuO observed in these catalysts. It implied that CuO was well dispersed in both catalysts. This result was in agreement with the work done by Antonio Gomez-Cortes et al. (Cortes et al., 2008). They found that the specific surface area of the catalysts was related to crystalline sizes of metal inside the catalysts. They prepared mixed oxides of copper and cerium with two different methods. The crystalline size of metal from the first method was 37.2 nm and this led to specific surface area of 24 m^2/g, while the crystalline size of metal oxide from the second method was 7.6 nm and this led to specific surface area of 145 m^2/g. Therefore, it implied that specific surface area of catalyst depends on crystalline size of oxide. The bigger the crystalline size, the less of specific surface area obtained. Figure 1 (c) was XRD pattern of the catalyst prepared by impregnation. As it can be seen from the co-precipitation, XRD pattern of this catalyst was not in the same positions as the reference XRD patterns of $Ce_2Zr_2O_7$ but matched with the reference XRD patterns of cubic CeO_2 (peak positions defined with "Δ") and monoclinic CuO (peak positions defined with "◆"). No ZrO_2 peak patterns were observed. This could be explained that ZrO_2 was well dispersed in the solid and its average particle size was less than 3 nm. Therefore, it can be concluded that impregnation was a method of physically mixing chemicals. It will not affect the final structure of the solid. Average CeO_2 crystalline size of this catalyst calculated from XRD result was 9.1 nm. Obviously, CuO peaks were found in this sample and its average crystalline size was 24.5 nm. The large sizes of CeO_2 and CuO resulted in the lowest of specific surface area of this catalyst.

In Figure 2, the XRD result of catalyst prepared by direct mixing of copper oxide, cerium oxide, zirconium oxide, and aluminium oxide was shown. The XRD pattern was sharp comparing to others in Figure 1. This means that oxides in the samples were more crystal. The XRD pattern was matched with reference XRD pattern of CeO_2 (peak positions defined with "Δ"), of ZrO_2 (peak positi ons defined with "●"), and of CuO (peak positions defined with "◆"). Average crystalline sizes of CeO_2 and CuO were 45.5 nm and 22.5 nm, respectively.

Activity test

All catalysts prepared by different methods were tested for their activities to CO oxidation. Space velocity was 75,000 cc/g/h. The results are shown in Figure 3.

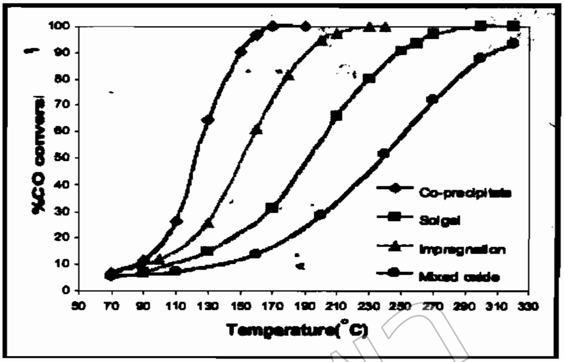

Figure 3. CO oxidation of catalysts prepared by different methods. Gas composition: 1%CO, 1%O_2 and He as balance.

In Figure 3, activities of each catalyst were in the same trend. CO conversion increased with an increase of reaction temperature. As reaction temperatures were less than 90°C, all catalysts were not active to the reaction (CO conversion less than 20%). At temperatures greater than 90°C, catalyst prepared by co-precipitation dramatically increased in its activity to CO oxidation. CO conversion increased to 50% at 120°C and CO conversion reached 100% at 170°C. This catalyst prepared by co-precipitation was the most active catalyst to CO oxidation. Likewise, catalysts prepared by impregnation, sol gel, and direct mixing of each oxide increased their activities with an increase in reaction temperatures. $T_{1/2}$ defined as the temperature at which 50% of reactant concentration is consumed by the reaction. $T_{1/2}$ of each catalyst was 150°C, 190°C and 230°C, respectively. These results implied that preparation method affected to the activities of the catalyst to the reaction. In general, the activity of catalyst to the reaction could be improved by increasing the dispersion of metal in the catalyst or doping with other compounds. In this work, the preparation method may lead to the differences in dispersion of metal. As it can be seen in Table 1, co-precipitation offered the highest value of specific surface area. This was in turn improving the dispersion of copper oxide inside the catalyst. Therefore, no copper oxide peak was observed in the XRD patterns of the sample. This was in agreement with the work done by Park et al. (Park et al., 2004), which reported that the activity of mixed oxides of cerium and copper to selective oxidation reaction depended on the dispersion of copper oxide. The better the dispersion is, the better the activity to the reaction becomes. On the other hand, the catalyst prepared by the sol gel method offered specific surface area of 177.7 m^2/g. This number was quite high comparing to other methods. Again, the results from XRD showed that copper oxide was well dispersed in the catalyst. Therefore, this catalyst should be active to the reaction as that of catalyst prepared by co-precipitation. Unfortunately, the activity test was not in agreement with this idea. This could be because of the differences in surface concentration of copper oxide. It was reported that for sol gel method, metal oxide was trapped inside the solid pore and led to lower of surface concentration of the catalyst (Zheng et al., 2005). This led to the lower of active surface sites for adsorption and reaction. Further investigation needs to be conducted to explain the differences in activities to the reaction. The copper oxide surface concentration can also be used to explain the better performance of the catalyst prepared by impregnation.

Finally, the catalyst prepared by direct mixing of each oxide was not active to CO oxidation. This may be due to the large average particle sizes of cerium oxide and copper oxide. These results were in agreement with other works (Zheng et al., 2005; Liu et al., 2007). It was found that the activity of mixed oxides of copper and cerium to CO oxidation depends on the particle sizes of copper oxide. The good dispersion of copper oxide and cerium oxide leads to the better the activity to CO oxidation. This might happen to the case of mixed oxides of copper, cerium, zirconium, and aluminium.

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