CHARACTERIZATION OF CaO-CuO-CeO$_2$ MIXED OXIDE SYNTHESIZED BY THE IMPREGNATION AND INVESTIGATION OF ITS REUSABILITY

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ABSTRACT

CaO-CuO-CeO$_2$ mixed oxide was prepared by the impregnation method and used as the catalyst for the complete decomposition of phenol in the presence of hydrogen peroxide. The CaO-CuO-CeO$_2$ mixed oxide were characterized by XRD, SEM, BET, H$_2$-TPR and Raman spectroscopy. The results indicated that there were three CuO species in the mixed oxide: the finely dispersed CuO species on the surface of CeO$_2$, the Ce$_{1-x-y}$Cu$_x$Ca$_y$O$_{2-\delta}$ solid solution and the bulk CuO. Most of particles have clear morphology with relatively uniform size in the range of 30 - 50 nm and the BET surface area was 37.96 m^2/g. After three times of use, the catalytic activity of CaO-CuO-CeO$_2$ mixed oxide was still relatively high and much higher than the mixed oxide CaO-CeO$_2$ and CuO-CeO$_2$.

Keywords: CaO-CuO-CeO$_2$ mixed oxide, phenol oxidation, impregnation method.

1. INTRODUCTION

Recently, several works have shown that CeO$_2$ is one of effective catalysts for many oxidation reactions [1, 2]. However, after a certain period (especially in high temperature conditions) its reactivity would decrease as CeO$_2$ is sintered. The sintering process of CeO$_2$ is greatly reduced when CeO$_2$ is doped because the doping of other metal ions will form a solid solution with CeO$_2$. The formation of a solid solution leads to an increase in the heat durability of the system. Moreover, the addition of metal cations with oxidation numbers smaller than +4 on CeO$_2$ generates oxygen vacancies in the CeO$_2$ cubic structure. The oxygen vacancies are considered to be the active centers for oxidation process, thus increasing oxygen vacancies significantly increases the catalytic activity of CeO$_2$ and materials containing CeO$_2$ [3, 4].

Among the doped CeO$_2$ materials, CuO-CeO$_2$ mixed oxide is considered as a very effective catalyst for different reactions such as: the complete oxidation and CO selection in H$_2$-rich gas stream [5], the oxidation of hydrocarbon [6], the oxidation of volatile organic compounds [7], water - gas shift reaction [3]. High reactivity of this catalyst system for the oxidation reaction is

due to the strong interaction between CuO particles in a fine dispersion state on the CeO_2 support surface and in the solid solution formed by replacing Ce^{4+} with Cu^{2+} in the cubic structure of CeO_2. However, the displacement of Cu^{2+} is limited in a certain range. To further modifying the structure of CeO_2 can be obtained by adding other cations such as Ca^{2+}, Mn^{2+}, K^+ etc.[8, 9].

In this paper, $CaO-CuO-CeO_2$ mixed oxide was prepared by the impregnation method, the physico-chemical characteristics of the products as well as their potential reuse as a catalyst will be investigated.

2. EXPERIMENTAL

2.1. Physical Methods

Scanning electron micrograph (SEM) was taken using a HITACHI S-4800 equipment. - Surface area was determined on a V6.07A 3000 Tristar. Oxides mixed composition was determined by X-ray diffraction on a D8 Advance, Bruker (German) using CuKα wavelength λ = 0.15406 nm, and scanning in the 2θ angle range of 25 - 70°.

Formations of CuO in mixed oxides were determined by deoxidization method by hydrogen temperature programmed reduction (H_2-TPR) using an Autochem II V4.01, from room temperature to 300 °C at a heating rate of 10°C/min in gas stream containing 10 % H_2/Ar with a flow rate 50 ml/min.

CeO_2 crystal defects were determined by Raman spectroscopy, on a Labram HR 800 at room temperature and using micro Raman technique with laser wavelength of 632.8 nm.

2.2. Survey of phenol oxidation by H_2O_2 under catalytic effect of $CuO-CaO-CeO_2$

Take 150 ml of phenol of concentration of 536 mg/l and put into a 250 ml conical flask, then add 2 ml of H_2O_2 30% and 0.025 g of the catalyst. The mixture was heated at 70-80°C for a period of 45 minutes with the stirring speed of 300 round/min. Then filter the mixture to remove the catalyst. The filtered solution was used to determine the COD (Chemical Oxygen Demand).

The phenol concentration was determined by measuring the COD according to the standard method $Cr_2O_7^{2-}/Cr^{3+}$ on Spectroquant NOVA 30, Merck (Germany) at the wavelength of 605 nm [10].

Phenol removal efficiency was calculated using the formula:

$$H = \frac{[phenol]_{initial} - [phenol]_{final}}{[phenol]_{initial}} . 100\%$$

where: $[phenol]_{initial}$ and $[phenol]_{final}$ are phenol concentrations (mg/l) of phenol solution before and after treatment with H_2O_2 in the presence of $CaO-CuO-CeO_2$ mixed oxides as the catalyst.

2.3. Materials

2.3.1. Oxides and mixed oxides

$CaO-CeO_2$ mixed oxide was synthesized by the gel-combustion method from polyvinyl alcohol (PVA), solution of $Ce(NO_3)_3$ 1M, $Ca(NO_3)_2$ 1M, and citric acid 2M with the following

condition: mass ratio of PVA/[Ca(NO$_3$)$_2$ + Ce(NO$_3$)$_3$] = 30 %, ratio molar of citric/(Ca^{2+} + Ce^{3+}) = 2/1 and molar ratio of Ca^{2+}/(Ca^{2+} + Ce^{3+}) = 0.075. When 2/3 of the solution was evaporated with continuous stirring at 80 - 90 ^{o}C, the gel was formed. After that, the gel was dried at 160 ^{o}C. In 10 - 20 minutes the foam block created a yellowish color and spontaneously combusts. The product was heated at 600 ^{o}C for 1 hour and the mixed oxide of CaO-CeO$_2$ was obtained in the form of fine yellow powder as a support.

CuO, CeO$_2$ and CuO-CeO$_2$ mixed oxides were synthesized by this process in the case of CuO-CeO$_2$ mixed oxides with the molar ratio of Cu^{2+}/(Cu^{2+} + Ce^{3+}) = 0.015 was applied.

2.3.2. CaO-CuO-CeO$_2$ mixed oxide

CaO-CuO-CeO$_2$ mixed oxide was collected by the impregnation method: CaO-CeO$_2$ support was impregnated with an aqueous solution of 1 M Cu(NO$_3$)$_2$ with molar ratio of Cu^{2+}/(Ca^{2+} + Cu^{2+} + Ce^{3+}) = 0.15. The mixture was soaked in 6 hours, then dried overnight at 80 °C and finally heated at 600 °C for 1 hour, CaO-CuO-CeO$_2$ mixed oxide was obtained as a fine gray powder.

3. RESULTS AND DISCUSSION

3.1. Particle size and surface area of CaO-CuO-CeO$_2$ mixed oxides

SEM image of the mixed oxide is shown in Figure 1. The SEM results reveal that most of particles have clear morphology with relatively uniform size in the range of 30 - 50 nm.
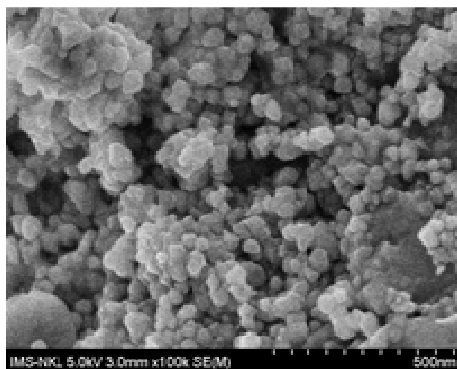

Figure 1. SEM image of CaO-CuO-CeO$_2$ mixed oxide.

The nitrogen absorption and desorption isotherms of CaO-CuO-CeO$_2$ mixed oxides are shown in Figure 2. The BET graph indicates that the surface area is 37.96 m^2/g and absorption and desorption isotherms of mixed oxide are of type 4 (IUPAC classification), and characteristic of inorganic porous oxides.

3.2. Existence forms of CuO in the mixed oxides

To determine forms of CuO in the mixed oxides, the temperature programmed reduction in H$_2$ flow method was used (H$_2$-TPR). The H2-TPR results are shown in Figure 3.

From Figure 3, the three peaks at different temperatures 180.7 ^{o}C; 199.2 ^{o}C and 204.1 ^{o}C, demonstrate three forms of CuO in the mixed oxides, namely amorphous CuO well dispersed on the surface of CeO_2 support, solid solution and CuO crystal [5, 9]. In particular, the amorphous form of CuO has highest reactivity because it causes oxygen vacancies ( ) on surface of CeO_2:
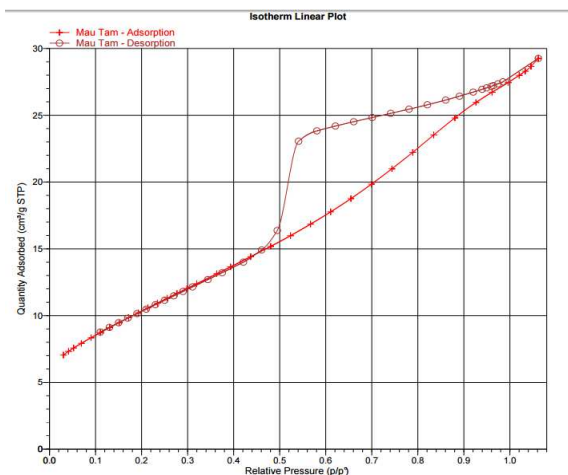
$$Ce^{4+} + Cu^{2+} + O^{2-} \leftrightarrow Ce^{3+} - \quad - Cu^+ + 0{,}5O_2 \uparrow$$

Figure 2. Nitrogen absorption and desorption isotherms of mixed oxides of CaO-CuO-CeO_2.
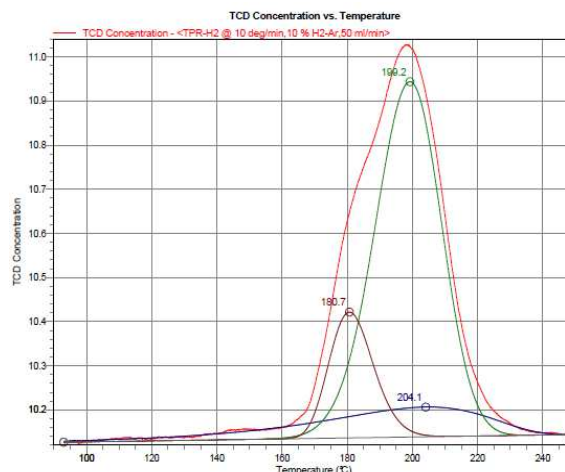
Figure 3. Schematic H_2-TPR of CaO-CuO-CeO_2.

The solid solution is formed by replacement of Ce^{4+} with Ca^{2+} and Cu^{2+} in the cubic structure of CeO_2 under the equilibrium:

$$yCa^{2+} + xCu^{2+} + Ce^{4+} + O^{2-} \leftrightarrow Ca_yCu_xCe_{1-x-y}O_{2-\delta} + (x + y) \quad + 0.5(x + y)O_2$$

The formation of oxygen vacancies in the structure CeO_2 is responsible for the less activity of the product than the amorphous CuO. The CuO crystal possesses the worst response since it is less interactive with the support [5, 7, 9].

3.3. Comparison of the catalytic ability of the oxides CuO, CeO_2 and mixed oxides for the oxidation of phenol

The results of phenol processing by H_2O_2 with catalysts of different types are presented in Table 1.

The results reveal that without catalysts, phenol removal performance factor is very low (4.2 %), with catalysts including oxides CuO or CeO_2, the phenol removal performance factor is also low 14.5 % and 11.0 %.

When CaO-CeO_2 mixed oxide is used as a catalyst, performance factor increases to 37.2 %. But when CaO is replaced by CuO, the phenol removal performance factor of CuO-CeO_2 mixed oxide increases sharply (reaching 60.1 %). In particular, CaO-CuO-CeO_2 mixed oxide gives highest performance factor (97.4 %).

The results of phenol processing by H_2O_2 with different catalysts confirm that the interaction between CuO with CeO_2 support significantly improves catalytic reactivity of both CuO and CeO_2. At the same time, the doping CeO_2 with CuO-CaO is more effective than doping CeO_2 with only CuO or CaO. Phenol removal performance factor has increased by about 1.5 times (from 60.1 to 97.4 %). This result confirms that the addition of Ca^{2+} in the catalytic

system increases defects in the CeO$_2$ structure, thus increases the number of oxygen vacancies in the structure [10].

Table 1. Results of phenol processing by H$_2$O$_2$ with different catalysts.

With catalyst	[Phenol]$_{final}$ mg/l	Performance factor (%)
Without catalysts	513.5	4.2
CuO	458.3	14.5
CeO$_2$	477.0	11.0
CaO-CeO$_2$	336.6	37.2
CuO-CeO$_2$	213.9	60.1
CaO-CuO-CeO$_2$	13.9	97.4

3.4. Ability to reuse the mixed CaO-CuO-CeO$_2$ catalyst for phenol oxidation

The stability of the catalyst after each use is crucial in practice. By this experiment, the ability of reuse of the CaO-CuO-CeO$_2$ catalyst for oxidation of phenols is studied.

The experiment with H$_2$O$_2$ and mixed CaO-CuO-CeO$_2$ oxide as the catalyst was carried out. After conducting the reaction, the product was filtered and then perform photometric measurements to determine the remaining phenol concentration. The catalyst was washed with distilled water several times and then was dried at 100 °C for 3 hours. The experiment with the catalyst used for 1st and 2nd times was repeated to evaluate the possibility of reuse of the catalyst. Results are presented in Table 2.

Table 2. Dependence of the phenol oxidization performance factor on the use times the catalyst.

	[Phenol]$_{final}$	Performance factor (%)
1st time use of catalyst	13.9	97.4
2nd time use of catalyst	63.8	88.1
3rd time use of catalyst	87.9	83.6

From Table 2 it is obvious that after the reuse of the catalysts, the performance factor of phenol oxidization is decreased. However, after using the catalyst for three times, phenol oxidization performance factor is still relatively high (83.6 %) compared with that of CaO-CeO$_2$ mixed oxide (37.2 %) and CuO-CeO$_2$ mixed oxide (60.1 %). This result shows that we can use mixed oxide CaO-CuO-CeO$_2$ as the catalyst for phenol oxidization, a volatile and persistent organic compound.

Oxygen vacancies of the mixed oxide used for the 3rd time as the catalyst is smaller than that of unused catalyst. It indicates that concentration of oxygen vacancies would be decreased after use of the catalyst.

To explain the decrease of catalytic reactivity of the mixed oxides for the phenol oxidation, XRD and Raman spectra of the mixed oxides before and after the re-use of catalysts has been recorded.

XRD diagram (Figure 4) shows that before and after the reuse, the specific peaks at the angle 2θ of 28.5^{o}, 33° and 47.5^{o} of CeO_2 with cubic structure and the characteristic peaks of CuO with monoclinic structure at $2\theta = 35.7^{o}$ và 38.8^{o} with a weak intensity. Meanwhile, the characteristic peaks of CuO in the mixed oxide after 3 times of use of the catalysts have higher intensity than those in unused catalysts. It demonstrates that the CuO crystallite phase content in the catalyst systems after 3-time reuse is higher than that of unused catalyst. This result may be caused after reuse of catalysts, amorphous CuO well dispersed on the support are agglomerated to form the CuO crystallite phase. The decrease of amorphous CuO content and increase of crystal CuO content in catalyst systems lead to the decreasing of concentration of oxygen vacancies, thus cause a decrease in the catalytic activity of the mixed oxides.

The Raman spectra of the mixed oxides before and after 3 times reuse of the catalysts show the decrease of content of oxygen vacancies in catalytic systems..
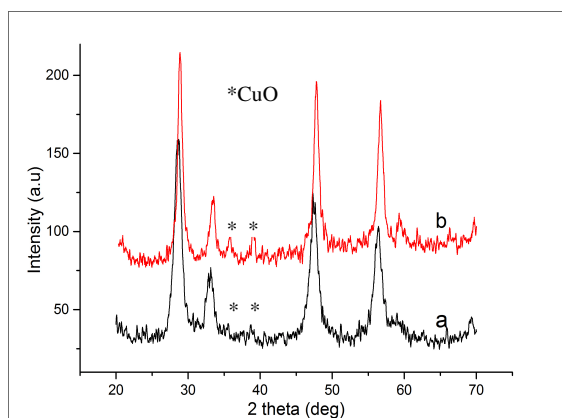

Figure 4. XRD pattern of CaO-CuO-CeO$_2$, (a): before using catalyst and (b): after using catalysts for 3 times.
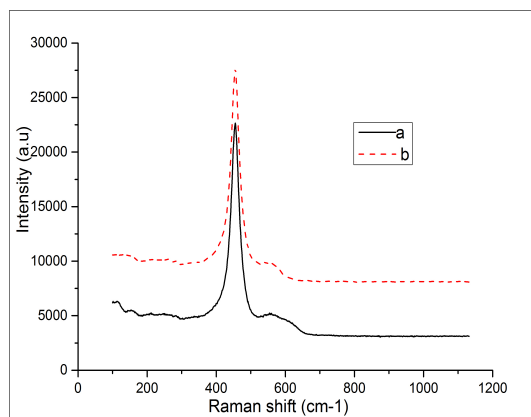
Figure 5. Raman spectra of CaO-CuO-CeO$_2$, (a): before using catalyst and (b): after using catalysts for 3 times.

Figure 5 shows that the absorption band with intensity at about 450 - 460 cm^{-1}, corresponding to absorption band of the face-centered cubic structure of CeO_2, and the broad absorption band with weak intensity at about 500 - 650 cm^{-1} assigned to the defects (or in the presence of oxygen vacancies) in the cubic structure of CeO_2 [9, 10]. The characteristic peaks of CuO and CaO are absent in the Raman spectra due to the negligible content of the compounds and their fine dispersion on the CeO_2 carrier. Moreover, Figures 5a and 5b also show that the area of characteristic absorption bands for concentration of oxygen vacancies of the catalyst systems after 3-time reuse is smaller than that of unused catalyst. That means after reuse, the concentration of the oxygen vacancies of the catalyst systems is decreased.

4. CONCLUSION

The characteristics of mixed oxides CaO-CuO-CeO$_2$ are defined by modern physical methods and the possibility of reuse of the catalyst for phenol oxidation is developed. The results show that the product has nanometer size (30 - 50 nm) with the surface area is 37.96 m^2/g. After three times of reuse, the mixed oxide CaO-CuO-CeO$_2$ remains its relatively high catalytic reactivity, which is much higher than the mixed oxide CaO-CeO$_2$ and CuO-CeO$_2$.

REFERENCES

1. Trovarelli A. - Catalytic science series and Related Materials, Imprerial College Press: London, 2002, pp. 508

2. Mogensen M., Sammes N. M., Tompsett G. A. - Physical, chemical and electrochemical properties of pure and doped ceria, Solid State Ionic*s* **129** (2000) 63-94.

3. Li L., Zhan Y., Zheng Q., Zheng Y., Chen C., She Y., Lin X., Wei K. - Water–Gas Shift Reaction over CuO/CeO$_2$ Catalysts: Effect of the Thermal Stability and Oxygen Vacancies of CeO$_2$ Supports Previously Prepared by Different Methods, Catal Lett. **130** (2009) 532-540.

4. Zou H., Chen Sh., Liu Z., Lin W. - Study on the catalytic performance of CuO-CeO$_2$ catalysts doped with transition metal oxides for selective CO oxidation, Fourth International Conference on Intelligent Computation Technology and Automation **2** (2011) 882-885.

5. Luo M. F., Song Y. P., Wang X. Y., Xie G. Q., Pu Z. Y., Fang P., Xie Y. L. - Preparation and characterization of nanostructured Ce$_{0.9}$Cu$_{0.1}$O$_{2-\delta}$ solid solution with high surface area *and its* application for low temperature CO oxidation, Catalysis Communication **8** (2007) 834-838.

6. Hu C., Zhu Q., Chen L., Wu R. - CuO–CeO$_2$ binary oxide nanoplates: Synthesis, characterization, and catalytic performance for benzene oxidation, Materials Research Bulletin **44** (2009) 2174-2180.

7. Massa P., Ivorra F., Haure P., Fenoglio R. - Catalytic wet peroxide oxidation of phenol solutions over CuO/CeO$_2$ systems, Journal of Hazardous Materials **190** (2011) 1068-1073.

8. Li J., Zhu P., Zuo S., Huang Q., Zhou R. - Influence of Mn doping on the performance of CuO-CeO$_2$ catalysts for selective oxidation of CO in hydrogen-rich streams, Applied Catalysis A: General **381** (2010) 261-266.

9. Qiao D., Lu G., Mao D., Liu X., Li H., Guo Y., Guo Y. - Effect of Ca doping on the catalytic performance of CuO-CeO$_2$ catalysts for methane combustion, Catalysis Communications **11** (2010) 858-861.

10. APHA method 9221: Standard methods for the examination water and wastewater (18th edition), American Public Health Association, Washington D.C., 1993, pp. 9.