

CHARACTERIZATION OF CaO-CuO-CeO₂ MIXED OXIDE SYNTHESIZED BY THE IMPREGNATION AND INVESTIGATION OF ITS REUSABILITY

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Received: 1 December 2016; Accepted for publication: 2 July 2017

ABSTRACT

CaO-CuO-CeO₂ 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-CeO₂ mixed oxide were characterized by XRD, SEM, BET, H₂-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 CeO₂, the Ce_{1-x-y}Cu_xCa_yO_{2-δ} 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 m²/g. After three times of use, the catalytic activity of CaO-CuO-CeO₂ mixed oxide was still relatively high and much higher than the mixed oxide CaO-CeO₂ and CuO-CeO₂.

Keywords: CaO-CuO-CeO₂ mixed oxide, phenol oxidation, impregnation method.

1. INTRODUCTION

Recently, several works have shown that CeO₂ 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 CeO₂ is sintered. The sintering process of CeO₂ is greatly reduced when CeO₂ is doped because the doping of other metal ions will form a solid solution with CeO₂. 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 CeO₂ generates oxygen vacancies in the CeO₂ 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 CeO₂ and materials containing CeO₂ [3, 4].

Among the doped CeO₂ materials, CuO-CeO₂ mixed oxide is considered as a very effective catalyst for different reactions such as: the complete oxidation and CO selection in H₂-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 CeO₂ support surface and in the solid solution formed by replacing Ce⁴⁺ with Cu²⁺ in the cubic structure of CeO₂. However, the displacement of Cu²⁺ is limited in a certain range. To further modifying the structure of CeO₂ can be obtained by adding other cations such as Ca²⁺, Mn²⁺, K⁺ etc.[8, 9].

In this paper, CaO-CuO-CeO₂ 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 CuK α wavelength $\lambda = 0.15406$ 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 (H₂-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 % H₂/Ar with a flow rate 50 ml/min.

CeO₂ 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 H₂O₂ under catalytic effect of CuO-CaO-CeO₂

Take 150 ml of phenol of concentration of 536 mg/l and put into a 250 ml conical flask, then add 2 ml of H₂O₂ 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 Cr₂O₇²⁻/Cr³⁺ on Spectroquant NOVA 30, Merck (Germany) at the wavelength of 605 nm [10].

Phenol removal efficiency was calculated using the formula:

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

where: [phenol]_{initial} and [phenol]_{final} are phenol concentrations (mg/l) of phenol solution before and after treatment with H₂O₂ in the presence of CaO-CuO-CeO₂ mixed oxides as the catalyst.

2.3. Materials

2.3.1. Oxides and mixed oxides

CaO-CeO₂ mixed oxide was synthesized by the gel-combustion method from polyvinyl alcohol (PVA), solution of Ce(NO₃)₃ 1M, Ca(NO₃)₂ 1M, and citric acid 2M with the following

condition: mass ratio of PVA/[Ca(NO₃)₂ + Ce(NO₃)₃] = 30 %, ratio molar of citric/(Ca²⁺ + Ce³⁺) = 2/1 and molar ratio of Ca²⁺/(Ca²⁺ + Ce³⁺) = 0.075. When 2/3 of the solution was evaporated with continuous stirring at 80 - 90 °C, the gel was formed. After that, the gel was dried at 160 °C. In 10 - 20 minutes the foam block created a yellowish color and spontaneously combusts. The product was heated at 600 °C for 1 hour and the mixed oxide of CaO-CeO₂ was obtained in the form of fine yellow powder as a support.

CuO, CeO₂ and CuO-CeO₂ mixed oxides were synthesized by this process in the case of CuO-CeO₂ mixed oxides with the molar ratio of Cu²⁺/(Cu²⁺ + Ce³⁺) = 0.015 was applied.

2.3.2. CaO-CuO-CeO₂ mixed oxide

CaO-CuO-CeO₂ mixed oxide was collected by the impregnation method: CaO-CeO₂ support was impregnated with an aqueous solution of 1 M Cu(NO₃)₂ with molar ratio of Cu²⁺/(Ca²⁺ + Cu²⁺ + Ce³⁺) = 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-CeO₂ mixed oxide was obtained as a fine gray powder.

3. RESULTS AND DISCUSSION

3.1. Particle size and surface area of CaO-CuO-CeO₂ 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-CeO₂ mixed oxide.

The nitrogen absorption and desorption isotherms of CaO-CuO-CeO₂ mixed oxides are shown in Figure 2. The BET graph indicates that the surface area is 37.96 m²/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 H₂ flow method was used (H₂-TPR). The H₂-TPR results are shown in Figure 3.

From Figure 3, the three peaks at different temperatures 180.7 °C; 199.2 °C and 204.1 °C, demonstrate three forms of CuO in the mixed oxides, namely amorphous CuO well dispersed on the surface of CeO₂ 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 CeO₂:

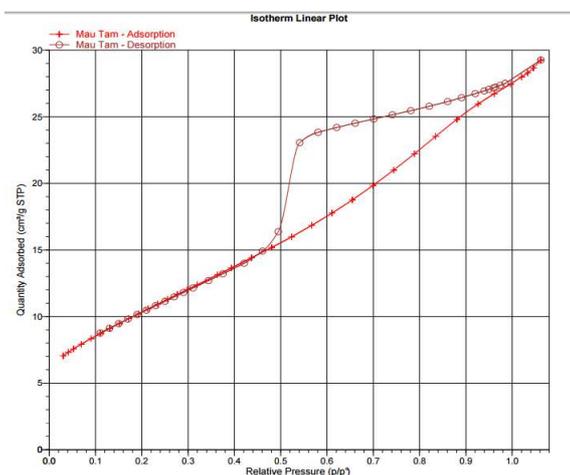


Figure 2. Nitrogen absorption and desorption isotherms of mixed oxides of CaO-CuO-CeO₂

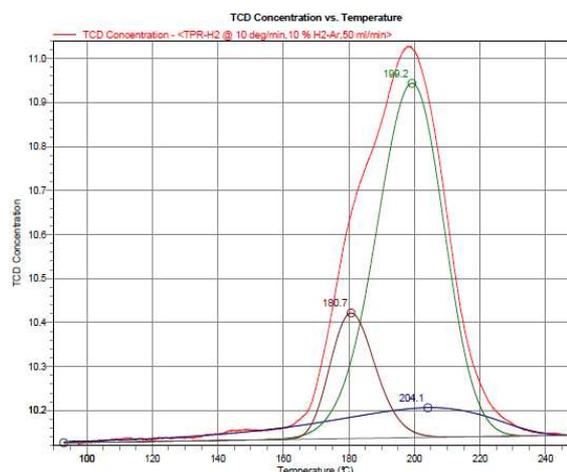


Figure 3. Schematic H₂-TPR of CaO-CuO-CeO₂

The solid solution is formed by replacement of Ce⁴⁺ with Ca²⁺ and Cu²⁺ in the cubic structure of CeO₂ under the equilibrium:



The formation of oxygen vacancies in the structure CeO₂ 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, CeO₂ and mixed oxides for the oxidation of phenol

The results of phenol processing by H₂O₂ 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 CeO₂, the phenol removal performance factor is also low 14.5 % and 11.0 %.

When CaO-CeO₂ 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-CeO₂ mixed oxide increases sharply (reaching 60.1 %). In particular, CaO-CuO-CeO₂ mixed oxide gives highest performance factor (97.4 %).

The results of phenol processing by H₂O₂ with different catalysts confirm that the interaction between CuO with CeO₂ support significantly improves catalytic reactivity of both CuO and CeO₂. At the same time, the doping CeO₂ with CuO-CaO is more effective than doping CeO₂ 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 Ca²⁺ in the catalytic

system increases defects in the CeO₂ structure, thus increases the number of oxygen vacancies in the structure [10].

Table 1. Results of phenol processing by H₂O₂ 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-CeO₂ 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-CeO₂ catalyst for oxidation of phenols is studied.

The experiment with H₂O₂ and mixed CaO-CuO-CeO₂ 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 (%)
1 st time use of catalyst	13.9	97.4
2 nd time use of catalyst	63.8	88.1
3 rd 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-CeO₂ mixed oxide (37.2 %) and CuO-CeO₂ mixed oxide (60.1 %). This result shows that we can use mixed oxide CaO-CuO-CeO₂ 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° , 33° and 47.5° of CeO_2 with cubic structure and the characteristic peaks of CuO with monoclinic structure at $2\theta = 35.7^\circ$ và 38.8° 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..

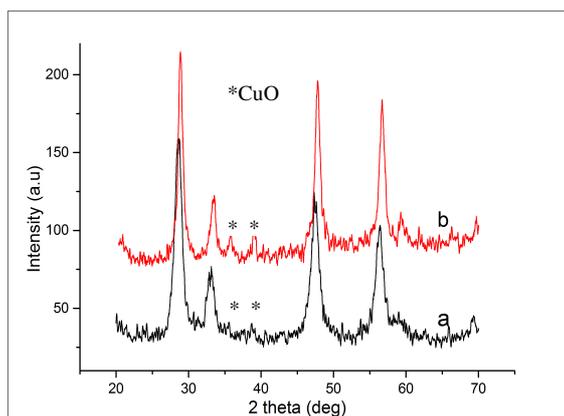


Figure 4. XRD pattern of CaO-CuO-CeO_2 , (a): before using catalyst and (b): after using catalysts for 3 times.

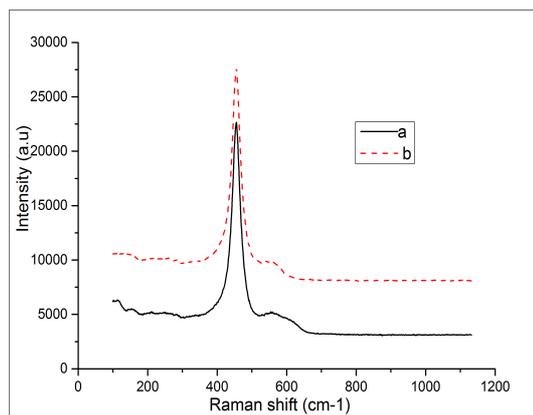


Figure 5. Raman spectra of CaO-CuO-CeO_2 , (a): before using catalyst and (b): after using catalysts for 3 times.

Figure 5 shows that the absorption band with intensity at about $450 - 460 \text{ cm}^{-1}$, corresponding to absorption band of the face-centered cubic structure of CeO_2 , and the broad absorption band with weak intensity at about $500 - 650 \text{ cm}^{-1}$ 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-CeO₂ 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 m²/g. After three times of reuse, the mixed oxide CaO-CuO-CeO₂ remains its relatively high catalytic reactivity, which is much higher than the mixed oxide CaO-CeO₂ and CuO-CeO₂.

Acknowledgement. This work was completed under financial support of QG.14.20 project.

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