Fabrication of CuO-doped catalytic material containing zeolite synthesized from red mud and rice husk ash for CO oxidation

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Abstract
In this study a series of the CuO-doped materials containing zeolite with varying CuO contents were synthesized from red mud (RM) and rice husk ash (RHA). The rice husk ash/red mud with the molar ratio of SiO₂/Al₂O₃, Na₂O/SiO₂ and H₂O/Na₂O being 1.8, 2.5 and 60, respectively, were maintained during the synthetic process of materials. The characteristic structure samples were analyzed by x-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscope (TEM), Brunauer–Emmett–Teller (BET) surface area and H₂ temperature program reduction (H₂-TPR). The catalytic activity of samples was evaluated in CO oxidation reaction in a microflow reactor at temperature range 200 °C–350 °C. The obtained results showed that all synthetic samples there exist the A-type zeolites with the average crystal size of 15–20 nm, the specific surface area of 21.3 – 54.3 m² g⁻¹, and pore volume of 0.073 – 0.130 cm³ g⁻¹. The material synthesized from RM and RHA with the zeolite structure (ZRM, undoped CuO) could also oxidize CO completely at 350 °C, and its activity was increase significantly when doped with CuO. CuO-doped materials with the zeolite structure exhibited excellent catalytic activity in CO oxidation. The ZRM sample loading 5 wt% CuO with particle nanosize about 10–30 nm was the best one for CO oxidation with complete conversion temperature at 275 °C.

Keywords: CuO-doped catalytic material, zeolite, red mud, rice husk ash, CO oxidation

Classification numbers: 2.03, 4.02, 5.06

1. Introduction

Environmental pollution caused by production and human activities is one of the top concerns in the world. Meanwhile, the rapid increasing of global population makes the human impact on the environment more and more serious consequences. Especially, the air pollution problem needs to be given the most attention because of its nature and global scale, and it does not have a specific range because of its dispersion in the air. The waste gas agents such as NOₓ, SO₂, COₓ, volatile organic compounds (VOCs) generated from mobile and immobile resources are the major reasons of human health danger as well as acid rain and greenhouse effect leading to climate change affecting the lives of billion people in the world [1]. That is the reason why the efficient uses of the world’s resources, the treatment, recycling and reusing of wastes are necessary.

The chimney of chemical industry, coal mining and processing, thermo-electricity, blast furnace, etc emit a lot of
toxic gases with high concentration, especially carbon monoxide (CO). Up to now, there are some new methods of treating exhaust gases in which the catalytic method on the basis of noble metal or metal oxide is being investigated by many researchers. Among the catalysts based on noble metals such as Au, Rh, Pt, Pd, etc, catalysts with Pt and Pd exhibited the highest catalytic activity on the deep oxidation CO and/or VOCs [2–6]. In spite of having a high catalytic activity, their disadvantages such as the high cost and limited availability inhibit their large application. The catalysts based on metal oxide and mixed oxides having high activity and thermal stability are good solution to replace these weak points of noble metals in the CO oxidation process [7, 8]. The results of Ferrandon et al. [9] showed that the catalytic activity of CuO supported on γ-Al2O3 was higher than that of Co3O4, NiO, and Fe2O3 in the CO oxidation reaction. Moreover, these catalysts have many advantages such as high activity at high temperature, low cost, stable, and long-time using [10]. SiO2, Al2O3, zeolite, etc. are widely used as a support for these catalysts.

Zeolite material has a good absorbent ability but low catalytic activity for CO oxidation; therefore, doping metal oxides is really necessary to enhance its conversion efficiency. Conventionally, these microporous materials are commonly produced from hydrogel aluminates and sodium silicates. However, the main problem in researches is the availability and cost of raw material specifically the silica source. The preparation of synthetic zeolite from silica and alumina chemical sources is very expensive and cannot be used in large scale [11]. This situation compelled researchers to find alternatives of raw material. Recently, some of cheaper raw materials such as clay minerals, natural zeolite, coal ashes, incineration ashes and industrial wastes are utilized as starting materials for zeolite synthesis [12].

Red mud is the main waste of aluminum processing from bauxite by Bayer technology. It is considered as a hazardous waste because of high alkalinity with large amount. There were many accidents by red mud in the world. In Vietnam, up to 2025, it will be announced that with 15 million tons of aluminum product per annum, and there will be generated about 20 million tons of red mud. The total amount will be increased up to 230 million tons of production of red mud [13]. Both soil and water environments are polluted by red mud due to its remaining chemical component and alkalinity [14]. Therefore, the wasted red mud becomes a serious problem as well as the most important target for bauxite processing. Many studies in recent years were tried to apply red mud into many fields such as pigment, arsenate removing, heavy metal treatment, dye waste adsorption [15]. In gas treatment technology, red mud have been also investigated as a catalyst for CO removal [16], H2S reduction [17], NO reduction [18]. However, these applications do not reused remaining NaOH, so those processes had high price because of a large amount of acid for neutralizing of NaOH. The red mud’s compositions are including many metal oxides such as Fe2O3 (40%–60%), TiO2, and Al2O3. Among these compounds, iron oxide was used as catalyst for CO conversion process to produce C and CO2, even there is no oxygen by using oxygen in iron oxide structure [19]. Mondal et al. [20] proved that the best temperature for the oxidation process is in range of 725 °C–900 °C without oxygen in air. Meanwhile, α-Fe2O3 was synthesized and applied into the CO oxidation process with the conversion of 90% at 300 °C without oxygen [21]. In the other research, red mud activated was employed for CO oxidation in the temperature range of 100 °C–500 °C, and the CO conversion reached higher than 90% at temperature over 400 °C [16].

In this article a new material containing zeolite was synthesized from red mud and rice husk ash without acid to neutralize of NaOH, then CuO was doped in the product to obtain catalyst which has high activity in the CO oxidation reaction. The application of a new material not only brings the high economic efficiency due to low synthesis cost, but also reduces a lot of afore mentioned pollution resources. It can be said that this research way has broken the economic barriers to applying green technology to the gas emission treatment. Besides, the invention of a new catalytic material in treating CO also play a major role to reduce emissions of industrial incinerators, leading positive impacts on the natural habitat, especially in this day and age, when pollution, greenhouse effect and climate change are worse, leaving serious consequences.

2. Experimental

2.1. Materials

Red mud (RM, 12.6 wt% Al2O3) was obtained from Tan Rai Aluminum Factory, Lam Dong province, Vietnam. Rice husk ash (>90 wt% SiO2) was produced at Ho Chi Minh City, Vietnam. Sodium hydroxide (NaOH, >99%) and copper(II) nitrate trihydrate (Cu(NO3)2·3H2O, >99%) were all purchased from Merck. Deionized water was also used in the preparation of catalytic materials.

2.2. Preparation of catalytic materials

CuO-doped catalytic materials were prepared in two steps as follows:

Step 1: Synthesis of the material containing zeolite from red mud and rice husk (ZRM). Firstly, red mud was dried under sunlight until obtained the reasonable humidity, after that it was hand milled and sieved to a specific particle size. Rice husk was heated in muffle furnace at 900 °C for 4h to obtain a white-grey color ash with the content of silica higher 90%wt.

The powder mixture of red mud and rice husk ash was ball milled for 30min to achieve a homogeneous mixture of components. Then, the NaOH solution was gradually added, stirred about 30min, dried at the temperature of 150 °C for 6h and then finely milled. The obtained solution with the SiO2/Al2O3 molar ratio of 1.8 and Na2O/SiO2 molar ratio of 2.5 was calcined in the furnace at 600 °C for 2h. After that, the fused mixture was cooled to room temperature in air. The above mixture was taken into the thermostatic tank under stirred condition, mixed thoroughly with distilled water at the H2O/Na2O molar ratio of 60:1 and carried out at 95 °C for
7h. The mixture was incubated overnight and then extracted by filtration to obtain ZRM product until the pH of filter solution was 10–11. The ZRM product was dried at the temperature of 120 °C for 4h.

Step 2: Synthesis of CuO-based catalysts supported on ZRM (CuO-ZRM). Catalysts CuO-ZRM were obtained by wet impregnation of Cu(NO$_3$)$_2$ solution on ZRM. The loading content of CuO was varied from 0 to 10 wt%. The obtained suspension was standing for overnight before drying in air at 80 °C, 100 °C and 120 °C within 2h at each temperature, and followed by calcination in air at 600 °C for 4h. The obtained CuO-ZRM catalysts were denoted as xCuO-ZRM, where x represented wt% of CuO in catalysts, x = 2.5, 5.0, 7.5, and 10.

2.3. Characteristics analyses

Crystalline phases of prepared catalytic material containing zeolite were investigated by x-ray diffraction (XRD) using Bruker D2 phaser powder diffractometer. Based on the XRD result at the peak with the highest intensity of zeolite, the average crystal size of zeolite was determined following the equation the Scherrer’s equation [22]. The surface area, pore volume, and average pore size of the catalysts were measured by BET nitrogen adsorption at −196 °C on Nova Station B, Quanta chrome Nova Win Instrument. FTIR spectra of synthesized samples were carried out on a Tensor 27-Bruker spectrophotometer operating in the range of 400 – 4000 cm$^{-1}$ at a resolution of 2 cm$^{-1}$. The samples were prepared as KBr pellets. The morphology of catalysts was characterized by scanning electron microscope on FE–SEM JEOL JEM 7401 instrument, and transmission electron microscopy (TEM) using JEOL JEM 1400 instrument. From SEM and TEM images, the nanoparticles size of catalysts was also determined. The hydrogen temperature-programmed reduction (H$_2$-TPR) measurement was performed in a fixed-bed reactor at ambient pressure using 10% H$_2$/N$_2$ reduction gas with the total gas flow rate of 30 ml·min$^{-1}$; the system was kept at 50 °C about 15 min until the baseline was stable; and then the temperature of the reactor was raised linearly from 50 °C to 900 °C at a heating rate of 10 °C·min$^{-1}$. The H$_2$ consumption was monitored online by using a gas chromatograph GOWMAC 69-350 with a thermal conductivity detector (TCD).

2.4. Catalytic activity

The activity of the catalytic materials in CO oxidation was tested in a micro-flow reactor under atmospheric pressure at 200 °C–350 °C after activated in air stream with the flow rate of 121·h$^{-1}$ at 450 °C for 4h. The mass of catalyst sample was 1.0 gram with the size range of 0.25–0.50 mm. The feed flow rate was 121·h$^{-1}$ with the mixture of 0.5 mol% CO and 10.5 mol% O$_2$ in N$_2$. The reaction mixture was analyzed on the Agilent 6890 Plus Gas Chromatograph (HP-USA) using a thermal conductivity detector (TCD) with capillary column HP–PLOT Mole Sieve 5A (30 m length, 0.32 mm outer diameter, 0.25 µm thickness).

3. Results and discussion

3.1. Physicochemical characteristics of materials

X-ray diffraction patterns of ZRM and CuO-ZRM with different CuO-doped contents samples were shown in figure 1. Based on the obtained results, at the synthesized temperature of 600 °C all samples indicated the presence of characteristic peak of A-type zeolite, proving the presence of zeolite in synthetic materials. Obviously, A-type zeolite were observed with the sharp peaks at 2θ = 24.2° and 35.6°. Besides, goethite (α-FeOOH) was observed at 2θ = 33.2°, and the weak peaks at 2θ = 13.9°, 54.1°, 62.5° and 64.2° indicated the presence of the other components in red mud including Fe$_2$O$_3$, Al$_2$O$_3$, SiO$_2$, TiO$_2$, Na$_2$O, CaO [23]. In addition, the intensive and wide peak did not alter significantly when doping CuO on ZRM carrier structure, and also the characteristic peaks at 2θ = 35.4°, 38.8° and 49.8° which can be indexed to the (002), (111) and (200) diffractions for CuO phase respectively were observed in XRD patterns. Based on the XRD peak at 2θ = 35.6°, the average crystal size of A-type zeolite determined following the equation the Scherrer’s equation [22] was 15–20 nm.

FTIR spectra (figure 2) were performed to investigate the possible bond formation between CuO particles and ZRM carrier material. The absorption band observed at 3437 cm$^{-1}$ was assigned to the stretching vibration of –OH in the absorbed water. The weak peak at the wavelength of 1654 cm$^{-1}$ represented the Si–OH vibration of the surface water molecules because of the great hydrophilic property of silica [24]. In addition, the strong absorption band at the wavenumber of 991 cm$^{-1}$ and 436 cm$^{-1}$ on FTIR spectra of all three samples indicated the presence of the asymmetric Si–O stretching vibration and the tetrahedral Si–O bending modes, respectively [25]. Finally, the observed peak at 597 cm$^{-1}$ corresponded to the Fe–O stretching vibration, proving the presence of iron in red mud waste precursor [26].

From H$_2$-TPR diagrams of samples, a broad peak at the temperature range of 500 °C–800 °C and many small peaks
at the temperature from 300 °C to 378 °C were appeared on H2-TPR diagram of ZRM (undoped CuO). According to the component of red mud in our previous work [23], besides of Al2O3, Fe2O3 was the main composition in raw material to synthesize ZRM. So, all small peaks were assigned to the reduction of Fe2O3 to Fe3O4, and a broad peak could be attributed to the reduction of Fe3O4 to FeO then to Fe according to following reaction equations [27, 28]:

\[
\begin{align*}
3\text{Fe}_2\text{O}_3 + \text{H}_2 & \rightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}, \\
\text{Fe}_3\text{O}_4 + \text{H}_2 & \rightarrow 3\text{FeO} + \text{H}_2\text{O}, \\
\text{FeO} + \text{H}_2 & \rightarrow \text{Fe} + \text{H}_2\text{O}.
\end{align*}
\]

In addition, it can be seen from H2-TPR diagrams of CuO-ZRM samples that there is a broad peak at 500 °C–800 °C same to ZRM sample attributed to the reduction of iron oxide (figure 3). Besides, there is a sharp reduction peak at 248 °C on the diagrams of CuO-ZRM catalysts loading 5–10 wt% CuO without that on 2.5CuO-ZRM sample. Meanwhile, H2-TPR diagram of 2.5CuO-ZRM catalyst appeared a reduction peak at 378 °C. According to authors [29–31] both peaks were characteristic of the reduction for CuO via

\[
\begin{align*}
\text{CuO} + \text{H}_2 & \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}, \\
\text{Cu}_2\text{O} + \text{H}_2 & \rightarrow 2\text{Cu} + \text{H}_2\text{O}.
\end{align*}
\]

The peak at 248 °C is assigned to the reduction of small clusters or free CuO, and that at 378 °C attributed to the reduction of copper oxide strongly interacting with supports. So, on CuO-ZRM sample with low CuO content (2.5 wt%), CuO was better dispersed on surface and interacted more strongly with the supports leading to the increase of the temperature reduction of this sample.

Figures 4 and 5 show the SEM and TEM images of ZRM, 5.0CuO-ZRM, and 10CuO-ZRM. Due to the small weight percentage of aluminum oxide (12.6 wt%) and silica (3.77 wt%) compared to other components in the original red mud waste lead to forming the negligible amount of zeolite. That is the reason why crystal sharp zeolite cannot be observed. Besides, the particles of all samples agglomerated together without a defined sharp. However, from the analytic result of the TEM images in figure 5, the particle separation of 5CuO-ZRM sample was better than that of the others. Their particle sizes are about 10–30 nm. So, this synthesis method can produce nanoparticles of catalyst that is very important to increase of catalytic activity.

The results indicated that the ZRM sample had the highest value of specific surface area and pore volume, corresponding to 54.30 m2 g\(^{-1}\) and 0.13 cm3 g\(^{-1}\). Doping CuO led to a reduction of the surface area of CuO-based catalysts supported on ZRM, and the higher the content of CuO the lower the value of surface area and pore volume. When CuO content loading into the zeolite structure of ZRM material increased to 5 wt% and 10 wt%, the surface area of samples decreased sharply from 54.3 down to 35.6 and 21.3 m2 g\(^{-1}\), and porous volume of these samples also decreased significantly from 0.130 down to 0.116 and 0.073 cm3 g\(^{-1}\), respectively. It could be explained that doping CuO from Cu(NO3)\(_2\) precursor resulted in binding a part of CuO molecules to the surface and other part into the porous structure of ZRM zeolite sample. Thus, the denaturation of so much CuO metal oxide will reduce adsorption capacity of ZRM material. Therefore, it is necessary to denature the reasonable amount of CuO into the structure of ZRM to the increase of both adsorption and catalytic activity of CuO-ZRM materials.

3.2. Catalytic activity of materials

Catalytic activities of ZRM and CuO-doped ZRM materials in CO oxidation are presented in figure 6. In these results, the material with the zeolite structure synthesized from RM and RHA (ZRM) without CuO had also the catalytic activity in CO oxidation in range of 200 °C–350 °C and oxidized CO completely at 350 °C. This may due to the facts that ZRM prepared from raw material contained metallic oxides, particularly iron oxides. These metallic oxides were well performed in the CO
Figure 4. SEM images of samples (a) ZRM, (b) 5.0CuO-ZRM, and (c) 10CuO-ZRM.

Figure 5. TEM images of samples: (a) ZRM, (b) 5.0CuO-ZRM, and (c) 10CuO-ZRM.
oxidation. In accordance with these results, it can be found that CO was oxidized to CO$_2$ on activated red mud [16], and it is also noticeable that the range of reaction of catalysts in this research are higher than that of the sample in this study. This could be explained that in this work the sample which was formed with zeolite structure having higher reduction extent and iron oxide content led to increase significantly the activity of this catalytic material.

The activity of samples was grown up significantly when the CuO loading on ZRM is increased from 2.5 to 5.0 wt%. However, it will be reduced sharply when CuO content continuously be increased up to 7.5 and 10 wt%. At the reaction temperature of 275 °C, 5.0CuO-ZRM sample with the CO oxidation efficiency of 100% was the best among the catalyst samples. At the same temperature, the oxidation efficiency of ZRM, 2.5CuO-ZRM, 7.5CuO-ZRM and 10CuO-ZRM samples was 46.6%, 55.1%, 86.7% and 57.6%, respectively. This can be explained that CuO content increased leading to raising density of CuO active sites on the ZRM surface, thus catalytic activity increased significantly. On the other hand, the phenomenon could be interpreted that base on the above characteristic analysis, when CuO loading on ZRM is increased from 2.5 to 5.0 wt%, the specific surface area and pore volume of the catalyst will be decreased, so the catalytic activity will be dropped down, too. So, the suitable CuO content doped ZRM was 5 wt%.

This result was entirely consistent with the physico-chemical characteristics of samples. Compared to the results of CuO loaded on pure supports such as 10 wt.% CuO/Al$_2$O$_3$ and 10 wt% CuO/20 wt% CeO$_2$ + 70 wt% Al$_2$O$_3$ [7], at the same conditions of CO oxidation the activity of 5 wt% CuO/ZRM is lower than that of CuO/Al$_2$O$_3$ + Al$_2$O$_3$ sample. But, it is approximately that of CuO/Al$_2$O$_3$ sample.

4. Conclusion

ZRM material in nano particle size with A-type zeolite structure having a high catalytic activity in CO oxidation were synthesized successfully by using the waste materials from mining industry (red mud) and agricultural production (rice husk ash). The modification of ZRM with CuO led to increase the density of active sites on material surface, so the catalytic activity was significantly improved in spite of the fact that the modification reduced the surface area and porous volume of CuO-based catalysts supported on ZRM. The CuO- loaded catalyst with the suitable content of 5 wt% having particle size about 10–30 nm, the surface area of 35.6 m$^2$ g$^{-1}$ and pore volume of 0.116 cm$^3$ g$^{-1}$ is the best for completely oxidizing CO process at low reaction temperature of 275 °C. This study demonstrated that CuO-doped ZRM material with zeolite structure is a great potential catalyst which could treat completely industrial waste resources of environmental impact as well as could have the economic efficiency in the future.

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