International Journal of Engineering & Technology, 7 (4) (2018) 4260-4265

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET
doi: 10.14419/ijet. v7i4.15888
Research paper

CuO and CeO_2 co-doped catalytic nanomaterial synthesized from red mud and rice husk ash for the deep oxidation of benzene, toluene and xylene

Nguyen ThanhTinh [1], Nguyen ThiThuy Van [2], Nguyen PhungAnh [2], Huynh Ky Phuong Ha [1], Nguyen Tri [2] *

[1] University of Technology – VNU-HCM, 268 Ly ThuongKiet Str., Ho Chi Minh City, Vietnam
[2] Institute of Chemical Technology - VAST, 01 Mac Dinh Chi Str., Ho Chi Minh City, Vietnam
**Corresponding author E-mail: ntri@ict.vast.vn*

Abstract

CuO-CeO_2 catalysts with fixed content supported on material (ZRM) synthesized from red mud and rice husk ash were prepared by wetness co-impregnation and conbustion method. The effects of calcination conditions on physic-chemical properties and catalytic performance of CuCe/ZRM catalysts were emphasized. Several techniques, including Brunauer-Emmett-Teller nitrogen physisorption measurements (BET), X-ray powder diffraction (XRD), hydrogen temperature programmed reduction (H_2-TPR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to investigate the properties of catalysts. It was obvious that the modification CuO-doped ZRM materials by CeO_2 resulted in better surface morphology and more homogenous particles. The results evidenced that calcination conditions strongly affected the particle size, morphology and reduction of CuCe/ZRM catalysts. CuCe/ZRM sample calcined at 500 for 3 hours with higher porous and smaller nanoparticles with higher reduction was the best in terms of activity in deep oxidation of p-xylene at temperature of 275 − 400°C, achieving a 90% p-xylene conversion at 350 °C with WHSV of 12,000 $mL.h^{-1}.g^{-1}$. The catalytic activity of the most prominent catalyst (CuCe/ZRM-500-3) sample increased in the following order: benzene < toluene < p-xylene. The presence of water vapor had a negative effect on catalytic activity due to the competition of water molecules with VOCs molecules for adsorption on surface active sites.

Keywords:*CuO; CeO_2; Catalytic Material; Red Mud; Rice Husk Ash; Deep Oxidation.*

1. Introduction

The emission of volatile organic compounds (VOCs) established by industrial manufacturing caused many seriously environmental problems, such as offensive odors, toxic emissions, ozone formation and petrochemical smog [1]. Benzene, toluene and xylene (BTX) are volatile organic compounds (VOCs) used as common solvents as well as raw materials in the production of other chemicals [2, 3]. All three substances, especially p-xylene, are known to be toxic and have mutagenic or carcinogenic properties and distinctive unpleasant odour [4]. Therefore, emissions of these pollutants require strict monitoring. The deep oxidation is one of the most important approaches for the abatement of VOCs at low concentrations [5, 6]. It can be operated at a lower temperature (200–400 °C) than thermal oxidation (700 °C) and does not require additional fuel and reducing energy consumption [7].

Although noble metal catalysts (Pt and Pd) have high catalyst activity, but they are quite expensive, can easily be poisoned, and limited using in industrial level [7]. Transition metal oxide catalysts, particularly CuO, have high thermal resistance and not expensive or be easily poisoned, although their catalyst activity is lower than precious metal catalyst [8-10]. In recent years, supported CuO catalysts have been described as promising catalysts for the treatment of VOCs. CeO_2 has also been investigated intensively in the field of catalysis for the past several years [11]. The broad range applications of ceria are mostly due to its remarkable oxygen storage capacities. Ceria has very good redox properties due to the very quick reduction of Ce^{4+} to Ce^{3+} associated with the creation of oxygen vacancies. It has the ability of releasing oxygen under reducing atmosphere and storing oxygen under oxidizing environment by filling oxygen vacancies [12]. It is well known that the CuO–CeO_2 composite oxide is one of the most important heterogeneous catalysts, widely used in deep oxidations [13-16]. Indeed, the authors observed that CuO-CeO_2 catalysts exhibited great catalytic performance in the deep oxidation of benzene, toluene and xylene [17]. In addition to, CuO–CeO_2 catalysts are very effective in the deep oxidation of CO at low temperatures [18-20], to an extent comparable to platinum catalysts. Their high activity is attributed to the high oxygen storage capacity of ceria, the facile Ce^{4+}/Ce^{3+} redox cycle, and the synergistic effect between CuO and CeO_2 [19].

Many kinds of support materials such as SiO_2, Al_2O_3, MgO, Fe_2O_3, TiO_2, NiO_x, CoO_x,... have been widely used for preparation of supported CuO catalysts [21]. Many supports have been demonstrated to be beneficial for deep oxidation, but the exploitation of new catalyst support with much low cost and rich porous structure is still a challenge. Currently, the exploitation of catalyst based on waste materials has sparked interest, because it is an environmental friendly process which can not only reduce costs but also save raw materials.

Red mud (RM) is the residual solid waste after bauxite leaching by alkali in the aluminum industry [22, 23]. Furthermore, RM cannot be easily treated due to its high alkalinity (pH = 10−13), so this waste residue can cause serious impacts to the environment. Thus, RM needs proper handling to minimize its negative effects on the environment. The main components of RM are Fe_2O_3, Al_2O_3, SiO_2, CaO and Na_2O [24]. Compared with the structure of natural ore, there are a lot of hydrated and carbonate minerals in RM. Such minerals can be easily decomposed in the calcination process, which may contribute to form the material with fine particles, internal porous structure and large surface area [25]. On the other hand, RM is a great material because of its small particle size, high thermal stability, sintering resistance and resistance to poisoning [26]. Nowadays, there has been a great deal of effort to utilize RM as a coagulant, adsorbent as well as catalyst for environmentally benign processes [27, 28]. Utilization of industrial solids like RM for other processes can help reduce the solid waste in landfills and produce environmental benefits. However, the large-scale catalysis application of RM is limited because of its alkalinity [29], mainly originating from Na and Ca, and their oxides can cause poisoning in the catalyst and reduce the catalytic activity [30].

Rice husk ash (RHA) released from the rice husk combustion process to provide energy is available in rice producing countries as a waste, mainly for recycling low value applications. RHA is mainly composed by SiO_2, about 95%, and other trace elements like potassium, calcium, magnesium, iron, copper, manganese, zinc, etc[31]. This composition of RHA makes it a candidate in industrial applications, with the advantage of its low cost. An attempt was made to investigate the synthesis of material with partial zeolite structure from RHA and RM at high pH so the alkalinity is unnecessary to be neutralized or acidified, so the cost of this synthesis process will be cheaper than ever.

In our previous work [32, 33], catalytic material in nano particle size with zeolite structure (ZRM) was synthesized successfully by using the waste materials from RM and RHA. CuO-CeO_2 catalysts supported on ZRM (CuO-CeO_2/ZRM) were prepared by the co-impregnation method. The modification of CuO/ZRM catalyst by CeO_2 had reduced the size as well as increased the dispersive performance and the synchronism of catalysts' nanoparticles led to improve significantly the catalytic activity in p-xylene deep oxidation at temperature range 275–400 ^oC. The sample 5 wt.% CuO/ZRM modified with 3 wt.% CeO_2 was the best for p-xylene deep oxidation. Beside, 5 wt.% CuO/ZRM catalysts were synthesized with combustion method and effect of the molar ratio urea/nitrate on properties and activity in p-xylene deep oxidation was investigated. It proved that by urea–nitrate combustion method, active sites - copper and iron oxides - had better dispersion on material surface with smaller particle size, leading to increase the oxidation activity of catalyst. The 5 wt.% CuO/ZRM synthesized with the urea/nitrate molar ratio of 2 was the best in terms of activity in deep oxidation of p-xylene.

The calcination conditions (temperature and time) had a significant effect on the physico-chemical properties of the catalyst, such as crystallite size, catalyst surface area, reducibility of the catalyst, formation of metal support complex and acidity/basicity of the catalyst surface [34, 35]. Changes in these physicochemical properties can affect the activity and stability of catalyst by increasing or decreasing the metal support interaction and formation of non-reactive complex species over the catalyst surface. Various studies have shown that catalyst having larger particle size exhibit lower metal support interaction while smaller particle size results in strong metal support interaction [36]. The high calcination temperature with a long time also resulted in a decrease in support surface area and metal dispersion as well as the catalyst activity. Studies have shown that the ambience of the catalyst during calcination can also influence its physico-chemical properties which in turn affected the activity and stability of the catalyst [37].

In this work, 5 wt.% CuO/ZRM material modified with 3 wt.% CeO_2 was synthesized by combustion method with the molar ratio urea/nitrate of 2. The effects of calcination conditions on performance of the material in the BTX (benzene, toluene and p-xylene) oxidation were investigated.

2. Experimental

2.1. Materials

The material with apart zeolite structure (ZRM) was synthesized from red mud and rice husk arcording to process as detailed in the work [32], $Cu(NO_3)_2.3H_2O$ (Xilong, >99%), $Ce(NO_3)_3.6H_2O$ (Merck, >99%), urea (Xilong, >99%) and deionized water.

2.2. Preparation of catalytic materials

The material with partial zeolite structure (ZRM) was synthesized from red mud and rice husk according to the process as detailed in the work [33]. Catalysts were obtained by wet impregnation of the mixture solution of Cu $(NO_3)_2$, $Ce(NO_3)_3$ and urea on ZRM. The loading content of CuO and CeO_2 was fixed at 5 wt.% and 3 wt.%, respectively, and the urea/nitrate molar ratio of 2. The obtained suspension was dried in air at 80, 100 and 120 ^oC within 2 hours at each temperature. Finally, the sample was calcined in air at the desired temperatures and time. These samples were denoted as CuCe(U)-x-y catalyst, where x represented the final calcination temperature, x = 450, 500, 550 and 600 ^oC; and y represented the calcination time, y = 2, 3 and 4 hours. For example, the CuCe(U)-500-3 refers to the sample calcined at 500 ^oC for 3 hours.

2.3. Characteristic analyses

Crystalline phases of prepared catalytic material with zeolite structure were investigated by X–ray diffraction using Bruker D2 Phaser powder diffractometer. The surface area, pore volume, and average pore size of the catalysts were measured by BET nitrogen adsorption at −196 ^oC on Nova Station B, Quanta chrome Nova Win Instrument. FT-IR spectra of synthesized samples were carried out on a Tensor 27-Bruker spectrophotometer operating in the range of 400–4,000 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 7401 instrument, and transmission electron microscopy (TEM) using JEOL JEM 1400 instrument. The hydrogen temperature-programmed reduction (H_2-TPR) measurement was performed in a fixed-bed reactor at ambient pressure using 10% H_2/N_2reduction gas with the total gas flow rate of 30 mL/min; the system was kept at 50 ^oC about 15 minutes until the baseline was stable; and then the temperature of the reactor was raised linearly from 50 to 900 ^oC at a heating rate of 10 ^oC/min. 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

Before the activity is tested, the samples were activated at 450 ^oC for 4 hoursin air flow with the velocity of 200 $mL.min^{-1}$. The catalytic measurement of the samples in deep oxidation of BTX (benzene, toluene and p-xylene) was carried out in a micro-flow reactor under atmospheric pressure at temperature range of 275–400 ^oC. The concentrations of BTX and O_2 in the stream were 0.34 and 10.5 mol%, respectively. The weight hourly space velocity (WHSV) was 12,000 $mL.h^{-1}.g^{-1}$, and the mass of catalyst was 1.0 g with the size range of 0.25–0.50 mm.

Gas mixtures in the input and output flow of the reactor were analysed on a gas chromatograph of Agilent Technologies 6890 Plus usinga FID detector, capillary column DB 624 (30 m length; 0.32 mm outer diameter; 0.25 μm thickness). The tests were undertaken in triplicate to ensure accuracy of the results.

3. Results and discussion

3.1. Physicochemical characteristics of materials

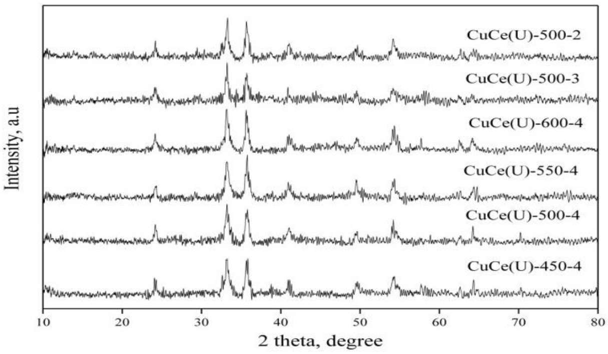
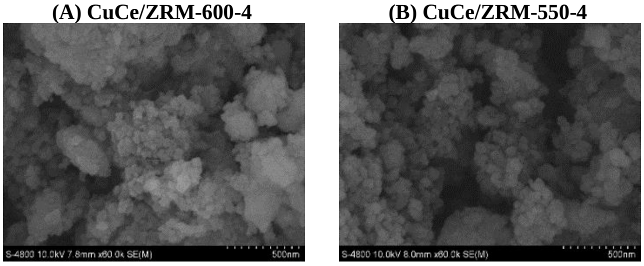


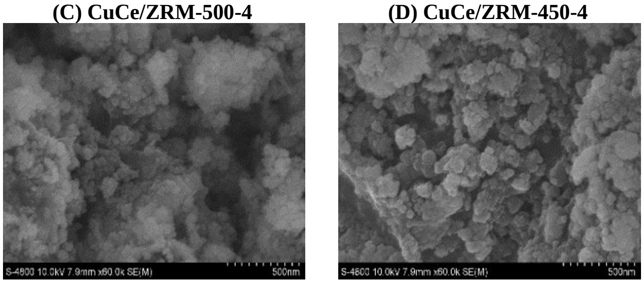
Fig. 1: XRD Patterns of Samples Calcined at Various Calcination Conditions.

X-ray diffractions (XRD) of the samples calcined at various calcination conditions were displayed in Fig.1. It can saw the main components of red mud and rice husk ash; the typical reflections of hematite (Fe_2O_3) can be observed at 2θ = 24.4, 29.8, 34.5, 36.1, 41.3, 54.4, 63.5 and 64.5°; the reflections may also indicated the presence of rulite (TiO_2) at 2θ = 34.5°, calcite ($CaCO_3$) at 2θ = 34.5° and Quartz (SiO_2) at 2θ = 24.4° [38]. Acording to Huang et al. [39], the peaks of A–type zeolite can be observed at 2θ = 24.4, 29.8 and 36.1°. Besides, acording to Volanti et al. [40], the typical reflections of CuO can be exhibited at 2θ = 36.1, 41.3, 49.9 and 54.4° in the XRD patterns. Therefore, it demonstrated that XRD patterns of the samples appeared simultaneously of the main components of red mud and rice husk ash, A–type zeolite and CuO crystals, with the strongest intensity at 2θ = 34.5 and 36.1°. The CeO_2 species can hardly be detected by means of XRD technique, suggesting that CeO_2 is well dispersed. The intensity of peaks of the samples was similar, it demonstrated thatthe main components of the materials reached crystalline at 450 °C.

(A) CuCe/ZRM-600-4 **(B) CuCe/ZRM-550-4**



(C) CuCe/ZRM-500-4 **(D) CuCe/ZRM-450-4**



(E) CuCe/ZRM-500-3 **(F) CuCe/ZRM-500-2**

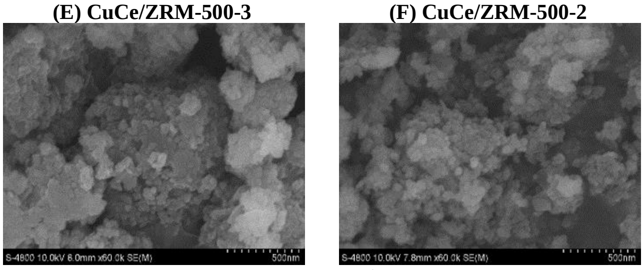
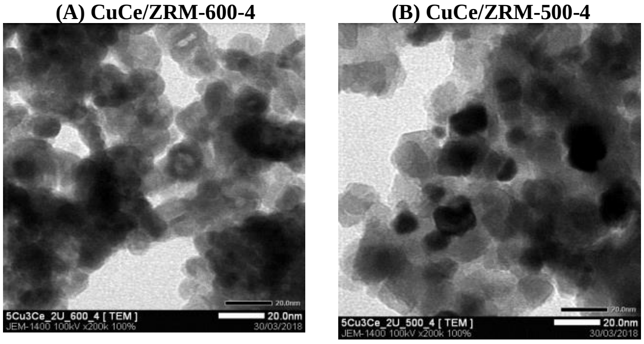


Fig. 2: SEM Images of Catalysts.

SEM of the samples calcined at various showed that the nanoparticles have been formed (Fig.2). The catalysts reached highly porous with small nanoparticle size. It was obvious that the modification CuO-doped ZRM materials by CeO_2 resulted in better surface morphology and more homogenous particles. In which, the structure of CuCe/ZRM-500-3 sample seem to be more porous and smaller than others. Based on the TEM images of samples, one can deduce that the CuO component with support of CeO_2 promoters showed high dispersion (seen in Fig.3). The CuO element was found to be homogeneously distributed throughout the ZRM material. The nanoparticles had the size range of 20–30 nm on CuCe/ZRM catalysts. In which, the CuCe/ZRM-500-3 sample exhibited the highest CuOdispersibility. The BET specific surface area, average pore diameter, pore volume of CuCe/ZRM calcined at various calcination conditions were shown in Tab.1. The samples reached medium BET surface and porosity.

(A) CuCe/ZRM-600-4 **(B) CuCe/ZRM-500-4**



(C) CuCe/ZRM-500-3

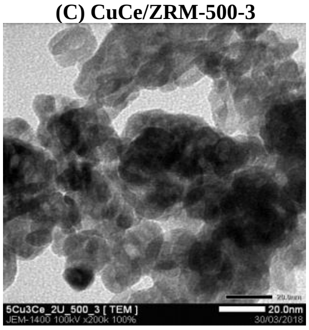


Fig. 3: TEM Images of Catalysts.

Table.1: The BET Surface (S_{BET}), Average Pore Diameter (D_{pore}), and Pore Volume (V_{pore}) of Catalysts

Catalysts	S_{BET} (m^2/g)	d_{pore} (Å)	V_{pore} (cm^3/g)
CuCe/ZRM-600-4	44.3	19.6	0.030
CuCe/ZRM-500-4	38.9	19.4	0.026
CuCe/ZRM-500-3	40.0	19.6	0.027

H_2-TPR patterns of samples calcined at different temperature and time was depicted in Fig.4. It can be found that the H_2-TPR of CuCe/ZRM sample appeared three reduction peaks. The first peak at 200 – 300 °C with T_{max} = 250 °C was created due to the reduction of the bulk-like CuO phases [41], the second peak at the range of 380 to 530 °C was attributed characteristic for CuO bound to CeO_2, and the third broad one at 450–850 °C with T_{max} = 700 °C could be ascribed to the reduction process from Fe_3O_4 to FeO or Fe [25].Compared with previous studies, CuCe/ZRM materials synthesized by combustion method shifted to the lower temperature range, therefore this catalyst was reduced more easily. On sample calcined at 500 °C for 3 hours, the peak was narrower than another. This proved that CuO, CeO_2 and Fe_2O_3 have better dispersion with smaller particle size on this sample. The results evidenced that calcination conditions strongly affected the particle size, morphology and reduction of the CuCe/ZRM catalysts. In which, CuCe/ZRM-500-3 sample showed higher porous and smaller nanoparticles with higher reduction, which could lead to a better catalytic performance.

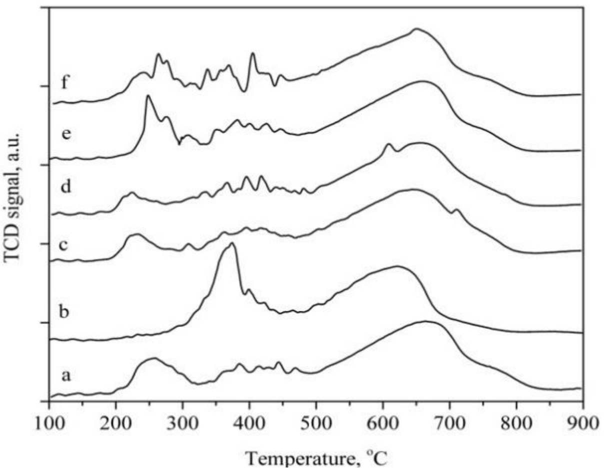
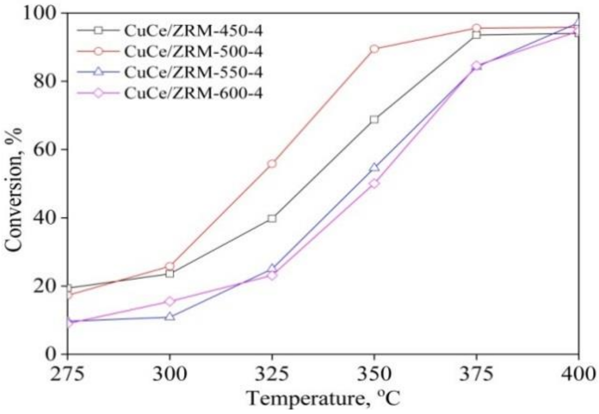


Fig. 4: TPR Profiles of CuCe(U)/ZRM Catalysts Calcined at Different Conditions; a) 450 °C – 4 Hrs; b) 500 °C – 4 Hrs; c) 550 °C – 4 Hrs; d) 600 °C – 4 Hrs; e) 500 °C – 3 Hrs; and e) 500 °C – 2 Hrs

3.2. Catalytic activity of materials

The catalytic activity of CuCe/ZRM materials calcined at different conditions towards p-xylene oxidation was shown in Figure 5.

(A) Catalysts Calcined at Different Temperature for 4 Hours



B) Catalysts Calcined at 500 °C for Different Duration

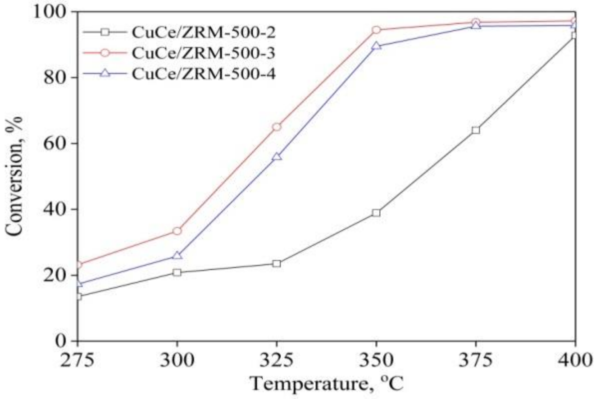


Fig. 5: The Catalytic Activity in p-Xylene Oxidation of 5Cu3Ce/ZRM Catalysts Calcined at Different Conditions

All catalysts exhibited a low activity at the reaction temperatures below 300 °C. With further increasing reaction temperature, the catalysts become highly active performances, and the complete conversion of p-xylene over all materials obtained at the reaction temperature of 400 °C. The catalyst activity had a strong dependence on the calcination temperature (seen in Fig.5a). The catalyst calcined at temperature of 500 was the most active, and achieved 90% conversion of p-xylene at 350 °C whereas the catalyst calcined at 600 °C only showed p-xylene conversion of approximately 40% under the same conditions. It has been revealed that the highest p-xylene conversion was obtained by the sample calcined at 500 °C for 3 hours (CuCe/ZRM-500-3) (Fig. 5b). As shown in Fig. 5b, the CuCe/ZRM-500-2 sample just exhibited 40% p-xylene conversion at reaction temperature of 350 °C. With prolonged calcination time (3 – 4 hours), the catalytic activity of materials was improved appreciably. The most interesting result is that by extending calcination time of catalyst to 3 hours, it exhibited superior catalytic performance with 95% p-xylene conversion at 350 °C. However, excessive calcination time as shown by CuCe/ZRM-500-2 sample led to the decreased catalytic performance with 90% p-xylene conversion under same conditions. So, the suitable calcination condition was 500 °C for 3 hours.

Another interesting phenomenon in Fig. 6 showed that the activity of Cu/ZRM was much lower than that of CuCe/ZRM with the same CuO content. The results implied that the existence of CeO_2 could be improved the activity of Cu/ZRM. The effect of CeO_2 could be ascribed that CeO_2 in contact with Cu^{2+} facilitates the formation of Cu^{+} due to its redox process of Ce^{4+}/Ce^{3+} which could transfer electrons to Cu^{2+} resulting in formation of Cu^{+}, thus enhancing the adsorption of p-xylene. The formation of CuO-CeO_2 interfacial sites produced the synergistic redox properties. Besides, CeO_2 serves also as an oxygen supplier through either the formation of superoxide species (O^{2-}) by gas phase oxygen reacting with oxygen vacancies on its surface or the direct involvement of lattice oxygen. Furthermore, the oxygen vacancies are easily formed in the CeO_2 support due to its high oxygen mobility to favor catalyst activity. Therefore, oxygen vacancies play an important role in the reaction since they provide sites for oxygen activation to form superoxide (O^{2-}), which was considered as the intermediate species in the oxidative reactions occurring on the catalyst surface. Furthermore, the modification of CuO/ZRM catalyst by CeO_2 promoter had better dispersion, higher reduction with smaller particle size. This was demonstrated by the TEM and H_2-TPR of the catalysts. Thus, the catalytic activity in p-xylene deep oxidation was significantly improved.

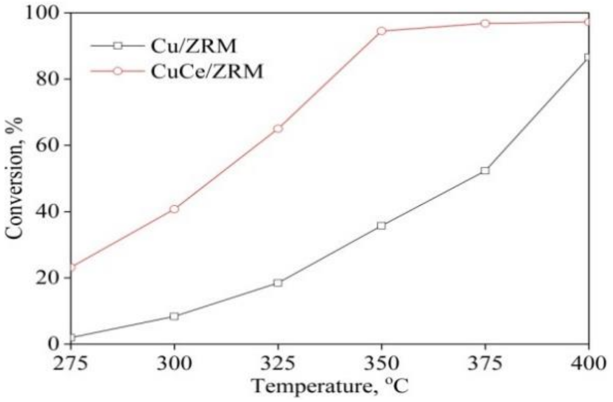


Fig. 6: The Comparison of the Catalytic Activity of ZRM Doped CuO and Codoped CuO and CeO_2 in p-Xylene Oxidation.

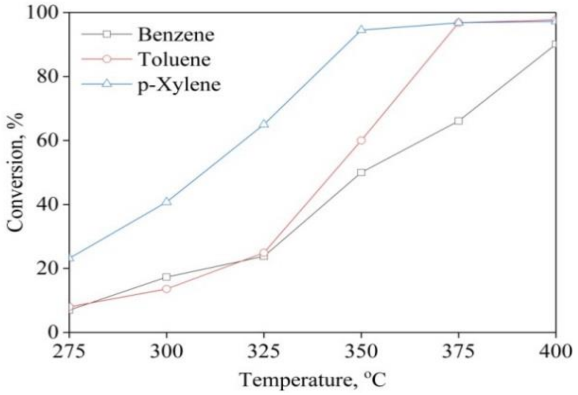


Fig. 7: The Catalytic Activity of 5Cu3Ce/ZRM Catalyst in Benzene, Toluene and p-Xylene Oxidation.

The most prominent catalyst (CuCe/ZRM-500-3) was also investigated in other VOCs oxidation (Benzene and Toluene). The conversion of p-xylene was higher than that of both benzene and toluene. Evidently, the catalytic activity of CuCe/ZRM-500-3 sample increased in the following order: benzene < toluene < p-xylene (Fig.7). The thermal effects could be important since the oxidation of BTX is very exothermic. Therefore, the higher conversion of p-xylene may be due to the fact that the reaction is heat transfer controlled, leading to a higher temperature at the catalyst surface than that measured because of the much higher concentration of p-xylene compared with that of benzene and toluene. This result indicates that the catalytic activity of aromatic compounds is highly dependent on the relative adsorption strength of the model compounds, the ionization potential of the methyl derivatives and the strength of the weakest C\H bond in the structure.

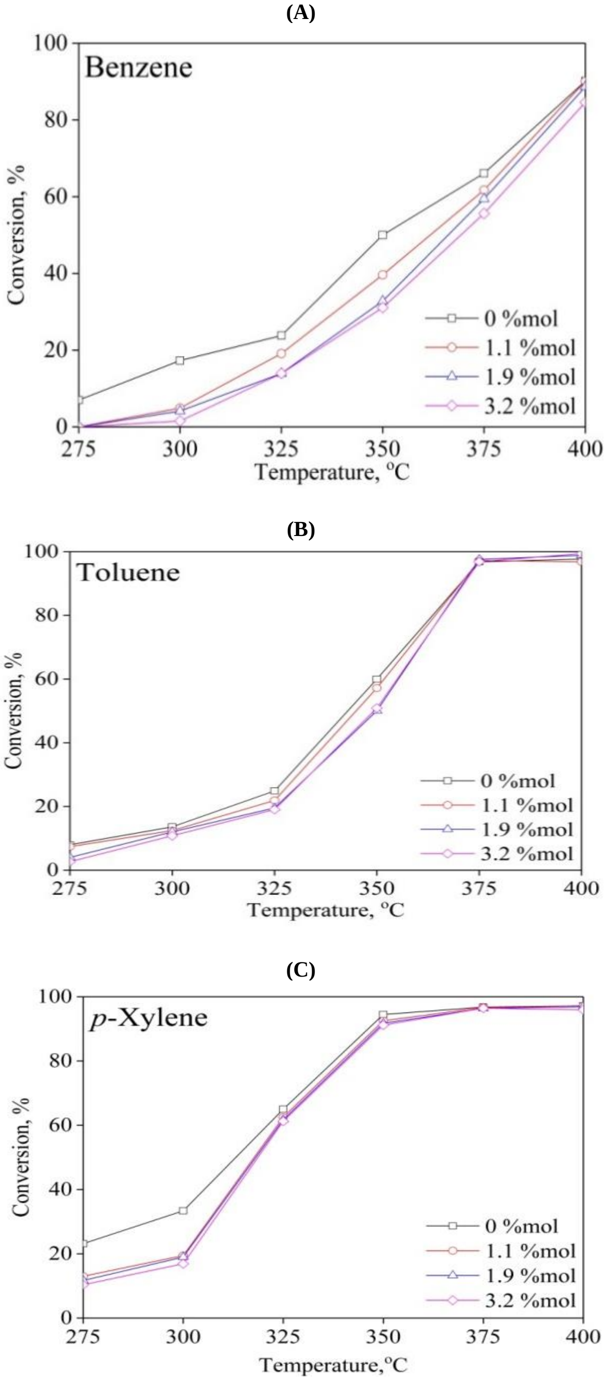


Fig. 8: Effect of Water Vapor with Various Contents on Catalytic Activity of 5Cu3Ce/ZRM Catalyst in Benzene, Toluene and p-Xylene Oxidation.

In the process of the catalytic oxidation, water is always present, because of either gas humidity or as a combustion product, which would affect the reaction kinetics, resulting in an serious inhibition of the oxidation reactions. The presence of vapor in the VOCs oxidation could speed up a degradation of the catalysts. It can be seen from Fig.8 that all of the BTX conversion profiles shift slightly to higher temperatures with an increase in water vapor concentration. It suggested that the presence of water vapor had a negative effect on the catalytic activity in the VOCs oxidation. It was mainly attributed to the competition of water molecules with BTX molecules for adsorption on the active sites. The higher coverage of the active sites by the water vapor led to a reduction in the number of active sites available for the reaction of BTX, and thus resulted in the reduction of catalytic activity of catalyst. On the other hand, it was noticed that the effects of water vapor on the conversion of BTX over CuCe/ZRM catalyst were somewhat different. The degree of BTX degradation by water vapor followed the order: benzene < toluene < p-xylene. It was mainly ascribed to difference in competitive adsorption ability of these three reactants toward water vapor.

4. Conclusion

CuCe/ZRM catalysts were prepared by wetness impregnation and conbustion method followed by calcination at various temperatures and time and their catalytic activities towards VOCs oxidation were evaluated. The materials showed the small nanoparticle size, the high dispersion of copper and ceria species and strong support metal interaction, which presented more Ce^{4+}/Ce^{3+} and Cu^{2+}/Cu^{+} redox couples so as to possess high redox ability. The calcination conditions also had a great influence on the dispersion and the local structure of CuO and CeO_2 species on the ZRM carrier surface. The results nicely demonstrated the effect of calcination conditions on the structure and catalytic performance towards VOCs oxidation of CuCe/ZRM catalysts and highlight the important role of CuO-CeO_2 on on ZRM surface. It was interesting to found that CuCe/ZRM material calcined at 500 ºC four 4 hours exhibited the best catalytic performance towards VOC oxidation, achieving a 90% p-xylene conversion at 350 ºC. The conversion of p-xylene over the most prominent catalyst (CuCe/ZRM-500-3) was higher than that of both benzene and toluene. This result indicated that the catalytic activity in the aromatic compounds oxidation is highly dependent on the strength of the weakes C\H bond in the structure of each BTX. The presence of water vapor had a negative effect on the catalytic activity in the VOCs oxidation. It was mainly attributed to the competition of water molecules with BTX molecules for adsorption on the active sites.

Acknowledgement

The study was supported by Science and Technology Incubator Youth Program, managed by the Center for Science and Technology Development, Ho Chi Minh Communist Youth Union, the contract number is "09/2018/HĐ-KHCN-VƯ ".

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