

Catalytic oxidation of airborne toluene by using copper oxide supported on a modified natural diatomite

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ABSTRACT

The catalytic oxidation of toluene over copper oxide supported on natural diatomite was investigated. The catalyst was prepared by the wet impregnation method and characterized by using the Brunauer Emmett Teller (BET), field emission Scanning Electron Microscopy (FESEM), X-ray diffraction (XRD), X-ray fluorescence (XRF) and Temperature-programmed reduction (TPR) analysis. The highest catalytic performance for airborne toluene oxidation was obtained at 14 wt% Cu loading. The toluene conversion at 270°C and 380°C, were 50% and 90%, respectively. According to the results of GC/MS and formation the CO₂ in effluent gas, no intermediates such as CO or other hydrocarbons were detected and the selectivity towards CO₂ was almost 100%.

Keywords: Diatomite, CuO, Toluene, Catalytic oxidation.

1. Introduction

Volatile organic compounds (VOCs) are the most important group of air contaminants which are emitted from various sources such as industrial and commercial process. The VOCs are harmful to human health and environment. They contain more than 300 compounds such as oxygenated hydrocarbons, aromatic hydrocarbons and halogenated hydrocarbons. Benzene, toluene, ethyl benzene, toluene (BTEX) compounds are the most important. They find abundantly in cities and industrial areas and have classified as toxic priority pollutants. Their major problem in the atmosphere is the risk of cancer and production of "Air Toxic". Toluene is highly used in oils, paints, resins, and detergents, preparation of chemical agents, rubber, printing ink, adhesives, polishes, leather tanning and disinfectants. It has engaged as an octane improvement of gasoline in internal combustion engines, petrol and other aviation fuels to raise the octane number. Due to economic aspects, toluene has been added to amount of vehicle fuel as a "fuel additive" in some countries [1].

Different methods have been used to remove toluene from polluted air stream such as adsorption, thermal and catalytic oxidation and advanced oxidation processes.

Among these methods, catalytic oxidation has been the most effective and economically viable way for reducing the emissions of VOCs in a wide range of concentrations and gas flow rates. The catalytic oxidation can be classified into two main categories: supported noble metals which possess high activity, but are expensive, and transition metal oxides (bulk or supported forms) which are cheaper but less active. Nevertheless, the metal oxide catalysts have demonstrated the catalytic performance as high as the supported noble metal catalysts [2-7].

Diatomite (DE), also known as diatomaceous earth or bio-silica, is an inexpensive source of amorphous hydrated silica with the cristobalite, quartz and feldspar crystalline phase and consists of 79–89% silicon dioxide (SiO₂) along with quantities of alumina (Al₂O₃) and iron oxide (Fe₂O₃). Diatomite is abundant in many areas of the world and has favorable characteristics, such as high porosity, small particle size, low thermal conductivity, appropriate specific

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surface area from 16 to 70 m² g⁻¹ and high adsorption capacity. With regard to these features, diatomite can be as a suitable support for impregnation with catalytic active components [8-12].

In this work, toluene was favored as a good representation of VOCs for the catalytic tests; copper oxide was chosen as a catalyst due to its high catalytic oxidation activity and diatomite was selected as an inert support because of its availability, special properties and low cost. To our knowledge, there are no reported investigations on the toluene removal from the air stream by using copper oxide-modified diatomite. Therefore, the aim of the present work was to study the catalytic oxidation of airborne toluene over natural diatomite modified by copper oxide.

2. Experimental

2.1. Catalyst preparation

The natural diatomite was obtained from the mines of South Khorasan (Birjand), Iran. Prior to modification with a copper nitrate solution, the raw diatomite was ground to the size of 2-2.38 mm (8-10 mesh), washed several times with deionized water and drying at 110°C for 18 h (named DE-H₂O). Afterward, it was treated with 3M H₂SO₄ solution (Pro-analysis 95–97% sulfuric acid GR for analysis, from Merck) at 100°C for 4 hours in reflux system and after cooling at room temperature, the slurry was filtered, washing with hot deionized water and drying at 110°C for 18 hours. It was named DE-H₂SO₄. More details about this method have been described elsewhere [11].

Diatomite-copper oxide catalyst was prepared by impregnation method of Cu (NO₃)₂·3H₂O (Merck) on natural diatomite treated with sulfuric acid (DE-H₂SO₄). The diatomite was mixed with the copper nitrate solution (1 M) in a solid (g)/liquid (ml) ratio of 1:2.5 (10g diatomite/25ml copper nitrate) and agitated in a shaker incubator at 200 rpm at room temperature for 6 h. The samples were filtered, washed with deionized water several times, dried at 110°C for 3 h. Finally, they were heated at 400°C for 2h in a programmable furnace (muffle stove). A temperature ramp of 5°C min⁻¹ was used for heating diatomite-copper oxide from room temperature to 400°C. The obtained catalyst was nominated DE-CuO.

2.2. Catalyst characterization techniques

The structure and crystalline phases of the diatomite samples were characterized with X-ray diffraction analysis (XRD) using Philips X'Pert equipment with a cobalt tube anode diffractometer ($\lambda = 0.178901$ nm, step size: 0.02°/s) operated at 40 kV and 40 mA in a

continuous scan mode, by scanning range of 10–100 (2 θ degree). In addition, the chemical compositions were identified with Philips PW-2404 X-ray fluorescence (XRF) spectrometer. Their morphology was considered by using a field emission scanning electron microscopy (FESEM, VEGA\\TESCAN) equipped with an energy dispersive X-ray spectroscopy (EDS). The nitrogen gas adsorption method with Quanta Chrome Nova 2200, high speed gas sorption analyzer was used for determining the specific surface area (BET method) and pore volume distribution (BJH method) of the samples. Temperature-programmed reduction (TPR) analysis was carried out by using the BELCAT-A BEL apparatus equipped with a thermal conductivity detector (TCD). The gaseous mixture (5% H₂/Ar) was passed over 200 mg sample at a rate of 50 ml/min while the temperature increased from room temperature to 900°C at a rate of 10°C /min [5-7].

2.3. The Catalytic test

The catalytic performance of the diatomite-copper oxide for oxidation of toluene was investigated in a fixed-bed steel tubular reactor with 2.54 cm inner diameter and 30 cm length in the temperature range of 150–500°C. An experimental setup used for generating continuously the known concentration of toluene. The schematic design of this setup is illustrated in Fig. 1.

Toluene concentration at the inlet and outlet of the reactor were measured using an Ion Science™ Phocheck Tiger with a photo ionization detector (PID) while toluene concentration was maintained at 200 ppm ± 5 in the reactor inlet. However, the PID system response of Ion Science™ Phocheck Tiger tool for determining the toluene concentration was evaluated using a gas chromatograph equipped with a flame ionization detector (GC-FID, Agilent 7890A). The details have been reported elsewhere [1].

3 g of DE-CuO with the particle size of 2-2.38 mm was used for catalytic activity measurement. Catalysts were sandwiched between two pieces of glass wool and empty spaces of the reactor were filled with ceramic balls (an inert product with 2-2.5 mm in size, from Gahar Ceram Co) for establishing the heat gradient and the air flow steady state. Catalytic activity was measured at a toluene concentration of 200 ppm. The total flow rate of reactant at the inlet of the reactor was 1000 ml/min corresponding to gas hourly space velocity (GHSV) 8600 h⁻¹. The temperature of catalyst bed was monitored and controlled by a temperature controller linked to a K-type thermocouple placed which was just near the catalyst bed. Prior to catalytic test, the catalysts were pretreated under flowing of ambient air (1000ml/min) at 400°C for 1h.

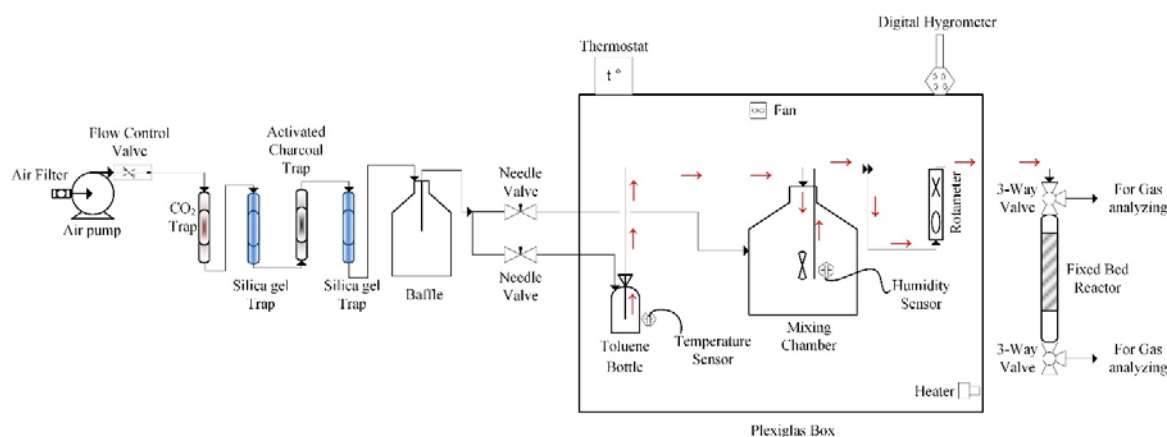


Fig. 1. The schematic diagram of the experimental setup for generating the known concentration of toluene. The red arrows show the path of toluene vapor to the reactor.

Thereafter, the temperature was declined to 150°C to prevent the toluene adsorption in the initial stages of the test, and then the temperature was raised from 150°C stepwise, 50°C each time to 500°C. The heating rate was 10°C/min. At each step, the temperature was held at 20 min and the effluent gases were analyzed after the steady state was attained.

The extent of toluene oxidation was evaluated by continuously monitoring CO₂ formation with a non-dispersive infrared sensor (NDIR, AQ110 Kimo). A portable CO sensor (NDIR, DELTA 1600S-IV) was also used to obtain information about the possible formation of carbon monoxide. The toluene conversion and yield CO₂ were calculated by following:

$$X_{\text{toluene}} (\%) = \frac{[\text{toluene}]_{\text{inlet}} - [\text{toluene}]_{\text{outlet}}}{[\text{toluene}]_{\text{inlet}}} \times 100 \quad (1)$$

$$X_{\text{CO}_2} (\%) = \frac{[\text{CO}_2]_{\text{outlet}}}{7[\text{toluene}]_{\text{inlet}}} \times 100 \quad (2)$$

3. Results and Discussion

3.1. Characterization of samples

Fig. 2 shows the XRD patterns of the diatomite samples. The X-ray diffraction spectra displayed that silica was the major component. The cristobalite, quartz and feldspar noteworthy were revealed in the range of $25 < 2\theta < 33$ in the X-ray diffraction spectra, respectively. The diffraction peaks of CuO were observed at 2θ of 41.5° and 45.3°, which were monoclinic, from the crystallography perspective. These phases were reported by references [13-16]. Table 1 shows elemental analysis of the samples that were obtained by XRF technique. The results showed that the Birjand natural diatomite had a high silica content (>82 wt %). The main chemical compositions were the oxides of Si and Al. The other important components were the metal oxides of Fe, Ca, K, Na, and Mg. Approximately, 14 wt % Cu was determined for the diatomite-copper oxide catalyst.

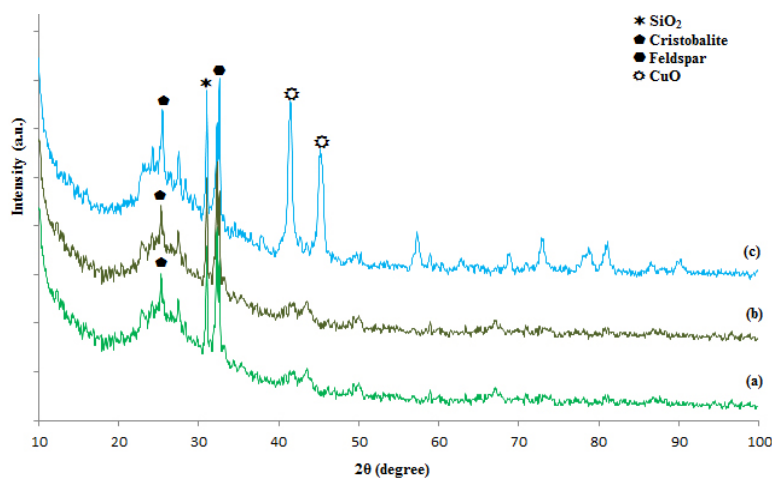


Fig. 2. XRD patterns of the diatomite samples: (a) treated diatomite with sulfuric acid (DE-H₂SO₄), (b) modified diatomite with copper nitrate (DE-CuO).

Table 1. The chemical characterization of the diatomite samples.

Chemical components	DE-H ₂ O (Wt %)	DE-H ₂ SO ₄ (Wt %)	DE-CuO (Wt %)
SiO ₂	82.27	89.98	72.10
Al ₂ O ₃	4.97	2.58	4.86
Fe ₂ O ₃	1.81	0.39	1.80
CaO	1.47	0.72	1.00
MgO	1.29	0.24	1.22
Cu	----	----	13.76
K ₂ O	0.90	0.53	0.41
Na ₂ O	0.54	0.42	1.20
TiO ₂	0.23	0.09	0.22
P ₂ O ₅	0.17	0.02	0.08
L.O.I.	6.27	4.90	3.17
Other	0.08	0.13	0.18

In our study, according to the X-ray diffraction data, the crystallite size of CuO at 2θ of 41.5° and 45.3° were 32.6 and 27.2 nanometres, respectively. The SEM micrograph structure and the EDS analysis of the diatomite samples are given in Fig. 3. The SEM images of DE-H₂SO₄ and DE-CuO showed that there was a

difference between their surface textures and pores. The EDS elemental analysis of diatomite-copper oxide revealed clearly that silica was the main component and Cu content was nearly 14wt %. The elemental mapping showed that CuO was uniformly dispersed on the surface of the diatomite (Fig. 4).

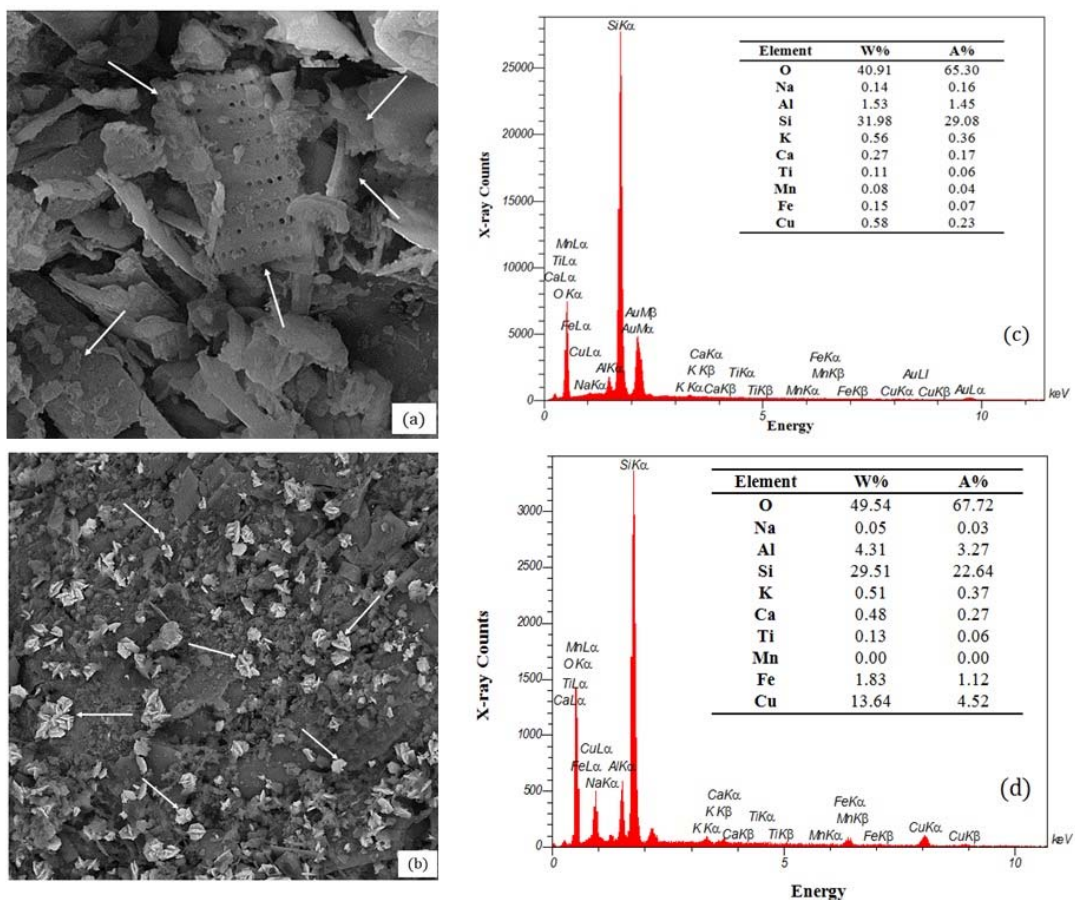


Fig. 3. SEM images and EDS analysis of the diatomite samples: (a) DE-H₂SO₄, the arrows show the pores (b) DE-CuO, the arrows show the CuO and EDS of (c) DE-H₂SO₄ (d) DE-CuO.

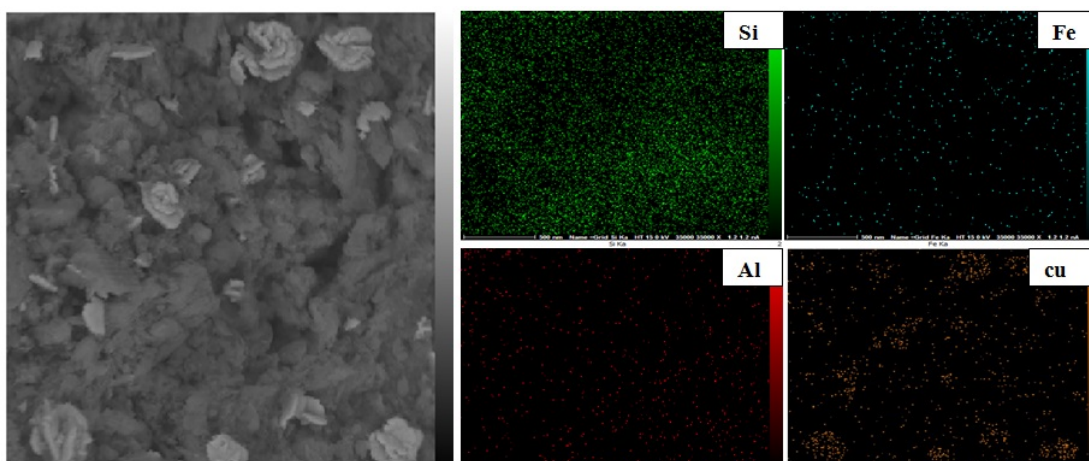


Fig. 4. Elemental mapping of the diatomite modified with copper oxide (DE-CuO).

The natural diatomite treated with sulphuric acid showed an increase in the BET surface area, total pore volume and average pore radius that were $43.31 \text{ m}^2 \text{ g}^{-1}$, $0.07403 \text{ cm}^3 \text{ g}^{-1}$ and 34.19 \AA , respectively. The BET specific surface area, total pore volume and average pore radius of diatomite-copper oxide were determined $34.84 \text{ m}^2 \text{ g}^{-1}$, $0.07119 \text{ cm}^3 \text{ g}^{-1}$ and 40.31 \AA , respectively. This modification on diatomite resulted in a decrease in BET specific surface area and total pore volume, but an increase in average pore radius which related to enlarging the pore size in the mesopores.

TPR curve of DE-CuO (Fig. 5) shows a single strong peak of maximum hydrogen consumption at 301°C , which is in agreement with the previous reports [6,17,18]. The reduction of the sample occurred in one step, which probably corresponds to the reduction of CuO to Cu. It is known that with higher Cu loading, segregation of CuO appears. Reduction of CuO at 301°C can be ascribed to the reduction of bulk-like CuO phases that include large clusters and bulk CuO, which also corresponded to the XRD and FESEM analyses (Fig. 2 and Fig. 3b).

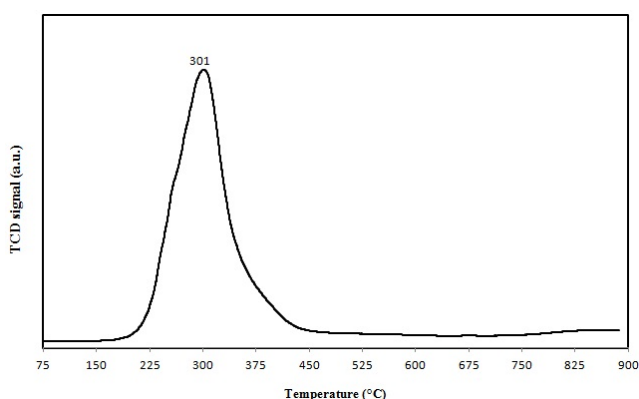


Fig. 5. TPR pattern of diatomite-copper oxide catalyst.

On a large CuO aggregate, H_2 first reduces the surface, generating a skin of metallic copper on the top of CuO. This may in turn reduce the H_2 -diffusion rate in the bulk CuO [7-9].

3.2. The Catalytic test

Fig. 6 shows that there is no catalytic activity at temperatures below 150°C and the oxidation reaction starts at 200°C . The catalyst content of 14 wt% Cu was able to convert 50% (T_{50}) and 90% of toluene (T_{90}) at 270°C and 380°C , respectively. The higher activity of the catalyst supported on diatomite was obtained at 14 wt% Cu. The conversion of toluene and formation the CO_2 in 24 wt% Cu catalyst was slightly less active than the 14 wt% Cu catalyst. The highest toluene conversion (98.85 %) was obtained at 500°C for 14 wt % Cu catalyst and the removal efficiency of toluene (higher than 90%) was stable at 400°C for 480 min. At 90% conversion of toluene (T_{90}), the diatomite copper oxide catalysts containing 4 wt% and 1 wt% copper, showed a lower performance than diatomite-CuO catalysts with 14 wt% and 24 wt% Cu. The bare support (blank) was shown to be inactive for this oxidation reaction. Saqer *et al.* found that the conversion of toluene on $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ (15 wt% CuO) was 90% at 360°C [5]. Pozan *et al.*, reported that $\text{CuO}/\text{Clinoptilolite}$ -type zeolite (9.5 wt% CuO) showed a high catalytic activity, as the toluene conversion was up to 90% at a temperature of 401°C [7].

According to relevant literature [19,20], the formation of intermediates and by products was checked by GC-Mass spectrometry. The effluent gas was analyzed with a GC/MS Varian Saturn 2200, capillary column VF-5 MS, 5% phenyl, 95% dimethyl polysiloxane, fused silica 30m, ID: 0.25mm, film thickness: $0.25\mu\text{m}$ equipped with the ion trap mass analyzer.

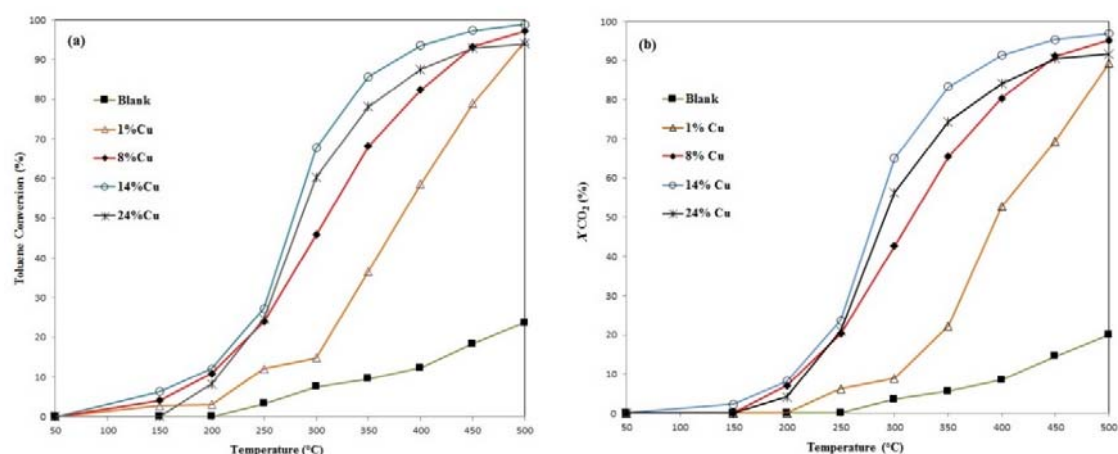


Fig. 6. (a) Toluene conversion and (b) CO₂ yield vs. reaction temperature over the CuO/diatomite.

The injector was maintained at 200°C and the oven temperature programming was 35°C (5 min) to 220°C (10 min) rate 4°C/min. The flow rate of helium carrier gas was 1 ml/min. Fig. 7 shows the chromatogram of GC/MS analysis for identifying of toluene degradation products. At 500 °C and 98.85% toluene conversion, there was only a toluene peak (2.7 ppm) and indicated that toluene was degraded to CO₂ by the DE-CuO catalyst during the oxidation reaction. Therefore, the selectivity towards CO₂ was almost 100% and no intermediates, such as CO or other hydrocarbons, were detected.

According to the results of GC/MS and CO₂ being in effluent gas, the catalytic oxidation of toluene over diatomite-CuO catalyst takes place via Mars-Van Krevelen mechanism. In this mechanism, the toluene molecules are oxidized by the lattice oxygen of CuO. Then, the catalyst being re-oxidized by gas phase oxygen in the feed gas. Hence, the reducibility of diatomite-CuO catalyst at 301°C (from TPR pattern) and oxygen removal activity appear to be two critical parameters determining its catalytic performance for toluene oxidation. In addition, adsorbed oxygen species are also active in toluene oxidation catalysis [21-24].

4. Conclusion

In this study, the catalytic oxidation of toluene over copper oxide supported on a natural diatomite was investigated. The conversion of toluene is affected by the temperature and the amount of copper in the catalyst. The order of the toluene conversion and CO₂ yield of the four catalysts were as follows:

14%Cu/DE > 24%Cu/DE > 8%Cu/DE > 1%Cu/DE

The conversion of toluene and CO₂ yield in 24 wt% Cu catalyst was slightly less active than the 14 wt% Cu

catalyst. The 14wt % Cu loading on diatomite showed a higher performance as the toluene conversion of 90% was obtained at 380°C. The toluene conversion (higher than 90%) was stable at 400°C for 480 minutes. The selectivity towards CO₂ was almost 100% and no intermediates, such as CO or other hydrocarbons, were detected. The XRD pattern of the DE-CuO catalyst (14 wt % Cu) showed the presence of CuO at two peaks. The crystallite size of CuO on diatomite was less than 33 nanometers. The TPR curve of DE-CuO showed the reduction of CuO to Cu at 301°C with a single strong peak.

The FESEM elemental mapping showed that CuO was uniformly dispersed on the surface of the diatomite. The natural diatomite treated with 3M H₂SO₄ created a suitable specific surface area (BET) and an increase in total pore volume. Therefore, the diatomite introduced as a proper solid matter for impregnating and an inert support that had appropriate features for catalytic active components. Diatomite is an inexpensive source of amorphous hydrated silica with the cristobalite, quartz and feldspar crystalline phase. Its major chemical components are SiO₂, Al₂O₃ and Fe₂O₃. The presence of these compounds can improve the diatomite mechanical strength.

It has been found that copper oxide (CuO) supported on diatomite exhibited a good catalytic activity. Therefore, the natural diatomite was introduced as a proper solid matter for impregnating and an inert support that had appropriate features for catalytic active components.

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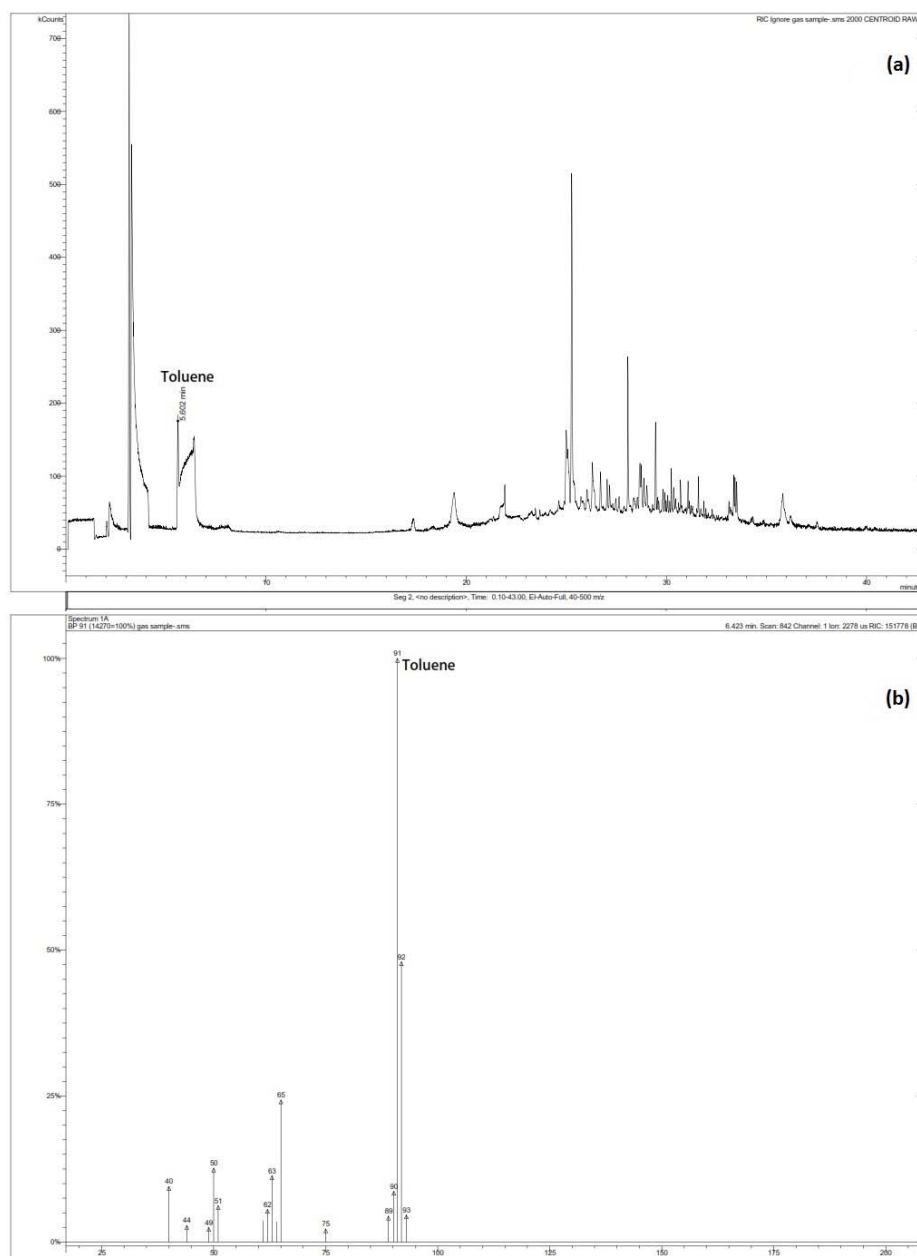


Fig. 7. GC/MS analysis for identifying of Toluene degradation products: (a) Chromatogram plot and (b) Spectrum plot.

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