

The beneficial use of HCl-activated natural zeolite in ultrasound assisted synthesis of Cu/clinoptilolite–CeO₂ nanocatalyst used for catalytic oxidation of diluted toluene in air at low temperature

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Abstract

BACKGROUND: To remove toluene (a representative volatile organic compound (VOC)) from a waste gas stream, catalytic oxidation was utilized over Cu/Clinoptilolite–CeO₂ nanocatalyst. The nanocatalyst with different loadings of Cu (5, 10, 15 wt%) was sonochemically synthesized and its performance in catalytic oxidation of toluene was studied. Characterization by XRD, FESEM, BET, EDX and FTIR were applied.

RESULTS: XRD results indicated well-dispersed small copper particles even at high loadings of copper. Non-sonicated Cu/Clinoptilolite–CeO₂ catalyst showed agglomerated, non-uniform morphology, while small particles with uniform shape and size with different degrees of agglomeration were observed in sonicated Cu/Clinoptilolite–CeO₂ catalyst. A narrow particle size distribution with average size 21 nm was observed in the sonicated sample. BET analysis demonstrated considerable effects of HCl treatment in increasing the specific surface area of clinoptilolite. It also showed the strong influence of CeO₂ addition as a promoter that sharply enhanced the surface area to 71.7 m² g^{−1}.

CONCLUSION: Catalytic performance tests revealed that Cu(15%)/Clinoptilolite–CeO₂ synthesized with ultrasound had the best performance of about 98% toluene abatement even at high concentrations of toluene (3000 ppm). A stability test of the synthesized nanocatalyst confirmed its constant activity for 1440 min, making it a promising catalyst for removal of VOCs.

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Keywords: natural zeolite; clinoptilolite; Cu/Clinoptilolite–CeO₂; toluene; total oxidation

INTRODUCTION

Owing to the worldwide growth of industry, controlling harmful emissions from these is of global concern. Among these harmful emissions, volatile organic compounds (VOCs) are the main source of air pollution^{1,2} and due to their toxicity and adverse effects on the human body, it is crucial to consider some effective measures to control their emissions. Among the VOCs, toluene is one of the most hazardous materials both for the environment and the human body.³

There are numerous methods that have been used and developed to decrease the amount of VOCs discharged from industrial plants such as adsorption, absorption, ozonation, and etc. Among these techniques, catalytic oxidation is considered to be more effective for its high destructive efficiency at lower ranges of temperature in comparison with other thermal methods.^{4,5} The desired reaction is the complete oxidation of toxic organic pollutants to CO₂ and H₂O.^{6–8} There are various types of catalysts that can be utilized in catalytic oxidation, including supported noble metals,^{9,10} metal oxides,^{11,12} and mixture of these two.^{13,14} Selection of an appropriate catalyst relies on such parameters as

nature of pollutants, cost, and stability of catalyst. Although noble metals are more active than metal oxides, from an economics point of view they are not suitable because of their high cost. In addition, they are less resistant to poisoning, thus they have a shorter life-time and must be regenerated regularly. The performance of catalysts depends strongly on the catalyst preparation method and promoters used to determine the activity, dispersion, and durability of the catalyst.^{15–17} In this regard, clinoptilolite was used as a natural zeolite supporter, CeO₂ was applied as a promising promoter, and innovative treatments such as acid leaching and sonochemical processes have been employed. Recent literatures

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has demonstrated the ability of natural zeolite for the removal of pollutants.^{18,19} Clinoptilolite is one of the most abundant zeolite resources in Iran^{20,21} and its chemical composition, surface characteristics, and ion exchange properties have been well studied.^{22–24}

Acid treatment of natural zeolites can help to improve their adsorption capacity and porosity,¹⁸ and to remove impurities that block the pores of clinoptilolite and dealuminate natural zeolite.^{25,26} Along with clinoptilolite, CeO₂ is an attractive compound for mixed oxide catalysts because of its special feature of storing and releasing oxygen. The main outcome of this unique property is oxygen vacancies which help the supports to have high thermal resistance and fine dispersion of supported metals.^{27–33} Abbasi et al.³⁴ synthesized CeO₂ and found that the reduction ability of CeO₂ from Ce⁴⁺ to Ce³⁺ leads to oxygen vacancies that make CeO₂ active enough for catalytic applications. Furthermore, combination of clinoptilolite supports with CeO₂ has been found to improve catalytic support activity in VOC total oxidation.^{35,36}

Among the different techniques for synthesizing catalysts, sonochemical methods based on the principle of acoustic cavitation due to high local temperature (5000–25 000 K) and pressure (180 MPa) generation are considered to be more effective than conventional methods.³⁷ Since ultrasonic cavitation occurs in less than a nanosecond,³⁸ very high cooling rates ($>10^9$ K s⁻¹) and less agglomeration of particles are obtained.^{39,40} Despite various technologies applied for total oxidation of VOCs, the effects of the sonochemical method have not been fully understood, particularly with transition metal oxides as an active phase. Therefore, the main purpose of our current research was to investigate the toluene oxidation from waste gas stream with the nanocatalyst of Cu/Clinoptilolite–CeO₂ and comparison of ultrasonic with impregnation synthesis. Also, the effects of different loadings of Cu together with various concentrations of toluene on nanocatalyst activity were studied. Our samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), surface area measurements (Brunauer–Emmett–Teller method (BET)), energy dispersive X-ray (EDX), and the Fourier-transformed infrared (FTIR).

MATERIALS AND METHODS

Materials

In this study the materials used included natural zeolite of clinoptilolite from Mianeh mine (East Azerbaijan, Iran), which was received in powder form and was treated with HCl (37%). NH₃, Ce(NO₃)₃·6H₂O and Cu(NO₃)₂·3H₂O were used as precipitant and precursor of CeO₂ and CuO, respectively. A major air pollutant (representative of VOCs) used for the investigation of catalyst activity in this research was toluene. All the materials were supplied by Merck company.

Nanocatalyst preparation and procedures

Figure 1 illustrates the procedures for synthesizing Cu/Clinoptilolite–CeO₂ catalyst. In the first step the natural zeolite of clinoptilolite was treated with 12 mol L⁻¹ HCl for 8 h at 80 °C under stirring in order to change the Si/Al ratio and the morphology of clinoptilolite. After the treatment, clinoptilolite was dried at 110 °C then calcined at 500 °C. Both drying and calcination were performed for 24 h under air flow. At the second step, Clinoptilolite–CeO₂ (30 wt%) was synthesized via precipitation of cerium nitrate over clinoptilolite. 0.1 mol L⁻¹ aqueous solution of cerium nitrate and 1 mol L⁻¹ aqueous solution of NH₃ were added

drop wise to an aqueous slurry of treated clinoptilolite for 30 min at constant pH of 9. After 1 h mixing, the sample was dried for 12 h at 110 °C, then calcined at 500 °C for 5 h.

Finally, Cu of different loadings (5%, 10% and 15 wt%) was used to impregnate the Clinoptilolite–CeO₂ composite support by means of ultrasonic waves. A SONOPLUS HD 3200 was applied to provide sonication waves. The slurry was irradiated under a high-intensity ultrasonic waves, employing a direct immersion titanium horn of 1 cm² (20 kHz, power output 90 W cm⁻²) which was inserted 1 cm below the solution surface for 30 min. Drying and calcination were performed at 110 and 500 °C for 14 and 5 h, respectively, under air flow.

Nanocatalyst characterization techniques

In this study the synthesized nanocatalysts were characterized through several different techniques. X-ray diffraction (XRD) was applied to verify the phase structures of the samples. It was carried out on a Siemens diffractometer D5000 with Cu-K α radiation source and operating conditions 40 kV and 30 mA over a 2θ scanning range of 10–90°. The morphology and structures of the nanocatalysts were investigated using a field emission scanning electron microscopy (FESEM) analyzer (Hitachi S-109 4160). For elemental analysis, energy dispersive X-ray analysis (EDX) was performed with a Vega\\Tescan, BSE Detector. Also, the specific surface areas of the samples were studied in a Quantachrome ChemBET-3000 unit applying the standard Brunauer, Emmett and Teller (BET) method. For detecting surface functional groups, Fourier transform infrared spectroscopy (FTIR, Unicam 4600) was employed in the wave number range 400–4000 cm⁻¹ using the KBr pellet method.

Experimental setup for catalytic performance test

The experimental set up used for activity evaluation of the Cu/Clinoptilolite–CeO₂ is shown in Fig. 2. Catalytic oxidation runs for the abatement of toluene were performed in a U-shape Pyrex microreactor (6 mm i.d.) at atmospheric pressure. A saturator was used to produce the gas stream containing toluene. The saturator container has an inlet pathway for carrier gas (air). Pure air enters the saturator and diffuses through the liquid toluene. Then it carries toluene vapour and exits from an outlet pathway. In order to control the temperature of the saturator an ice-water bath was utilized. The other air flow was mixed with the polluted stream to stabilize the concentration of the toluene-containing stream. In order to ensure precise control of flow rates, flow meters with needle valves were utilized.

The microreactor (6 mm i.d.) has an air condenser to cool down the exhaust gas stream to analysers. To provide the required temperature for catalytic oxidation the microreactor was placed in an electrical furnace. About 0.5 g of nanocatalyst was placed in the reactor for each run. Catalysts were placed between Pyrex balls. The catalytic experiments were evaluated in the temperature range 150–350 °C. The samples were pre-treated before each run at 120 °C to prevent overestimation of toluene removal caused by adsorption, since toluene may be removed mostly by adsorption rather than oxidation due to the low temperature at the beginning of the tests. The concentrations of the inlet and outlet gas streams were analysed by a gas chromatograph (GC Chrom, Teif Gostar Faraz, Iran) equipped with two electrical controlled six-port switching valves, a 1 mL sample loop and a flame ionization detector (FID). For activity tests of catalysts, the total flow rate was set at 70 mL min⁻¹, the concentration of the pollutant was 1000 ppm and

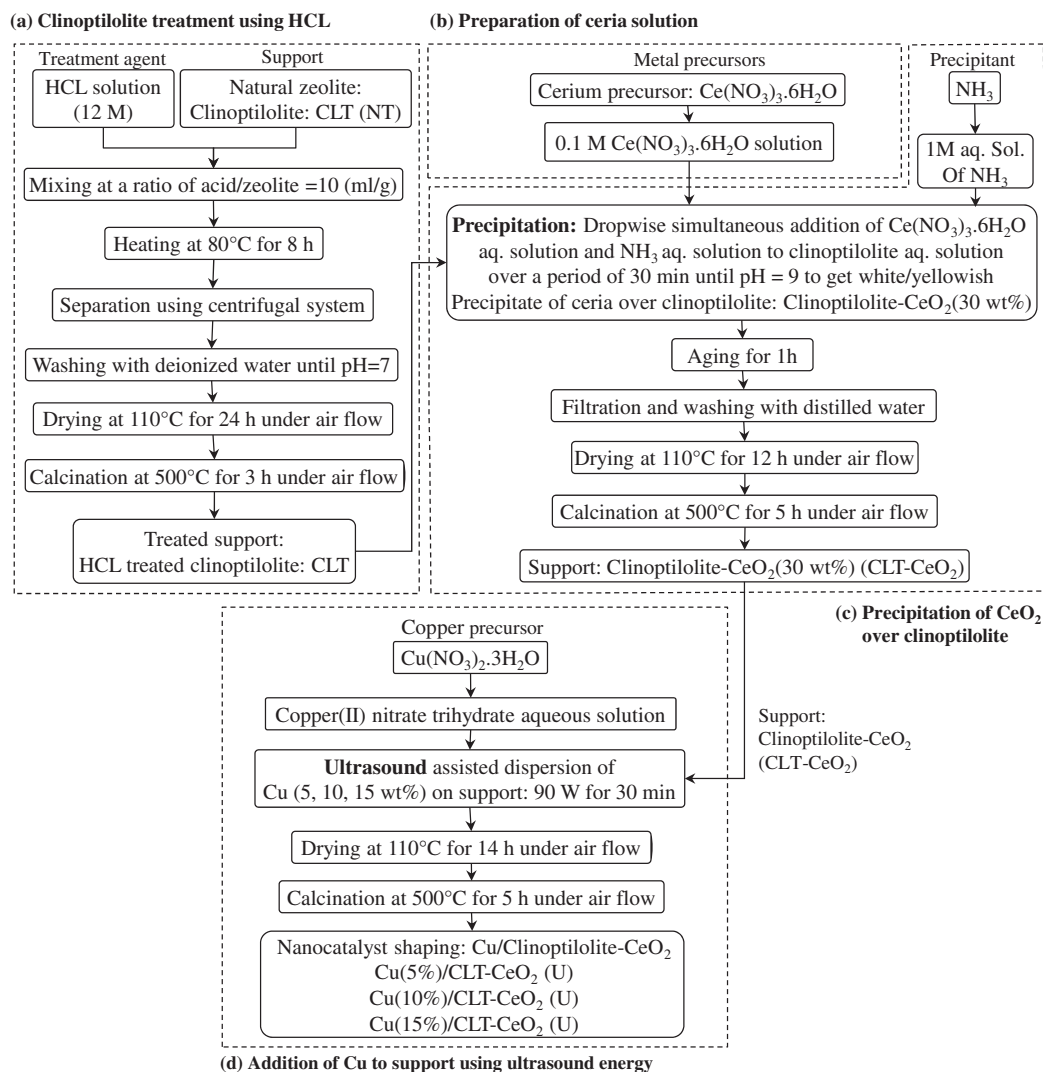


Figure 1. Preparation steps of Cu/Clinoptilolite–CeO₂ nanocatalyst via HCl treatment, CeO₂ precipitation and ultrasound assisted dispersion of Cu over support.

GHSV = 6000 h⁻¹. For tests to assess the effect of pollutant concentration, the toluene concentration was varied from 1000 to 2000 and 3000 ppm. Stability tests of the catalyst were carried out at a toluene concentration of 1000 ppm in GHSV = 6000 h⁻¹.

RESULTS AND DISCUSSION

Nanocatalysts characterization

Chemical analysis of Clinoptilolite

In Fig. 3, the difference in chemical analysis of clinoptilolite before and after HCl treatment is clearly illustrated. The significant modification due to this treatment is the change of Si/Al ratio, which has a value of 4.86 before treatment and 21.13 after treatment. Moreover, the percentages of different metals in the natural zeolite reduce dramatically in accordance with the work of Ates *et al.* and Ackley *et al.*^{25,26}

XRD analysis

The XRD patterns of non-treated clinoptilolite, clinoptilolite treated with HCl, synthesized CeO₂–clinoptilolite, and Cu/

Clinoptilolite–CeO₂ nanostructured catalyst are shown in Fig. 4. The first pattern proves that the sample has a natural zeolite of clinoptilolite structure according to JCPDS 00-025-1349 and other literature.⁴¹ Although comparison of patterns (a) and (b) shows no shift in the position of peak points of non-treated clinoptilolite and HCl treated clinoptilolite, dramatic changes in the intensity of the peak points of the treated sample can be detected. This indicates destruction of crystal phase structures of natural zeolite and formation of some amorphous structures as a result of acid treatment.⁴² Introduction of CeO₂ to the sample can be detected in the pattern (c) with broad and weak peaks of CeO₂ (JCPDS 01-075-0076). This means those crystal phases corresponding with the peaks of CeO₂ are relatively small, with a low degree of crystallinity or amorphous structures. There are no characteristic peaks attributed to CuO or other Cu compounds when adding various loadings of Cu even at high concentrations. This shows that amorphous structures of Cu were dispersed finely over clinoptilolite by the sonochemical method. As mentioned earlier, due to extreme local heating of the bubble collapse and its short lifetime of less than a nanosecond³⁸ and its subsequent enormous cooling rates (>10⁹ K s⁻¹), amorphous structures of metal powder

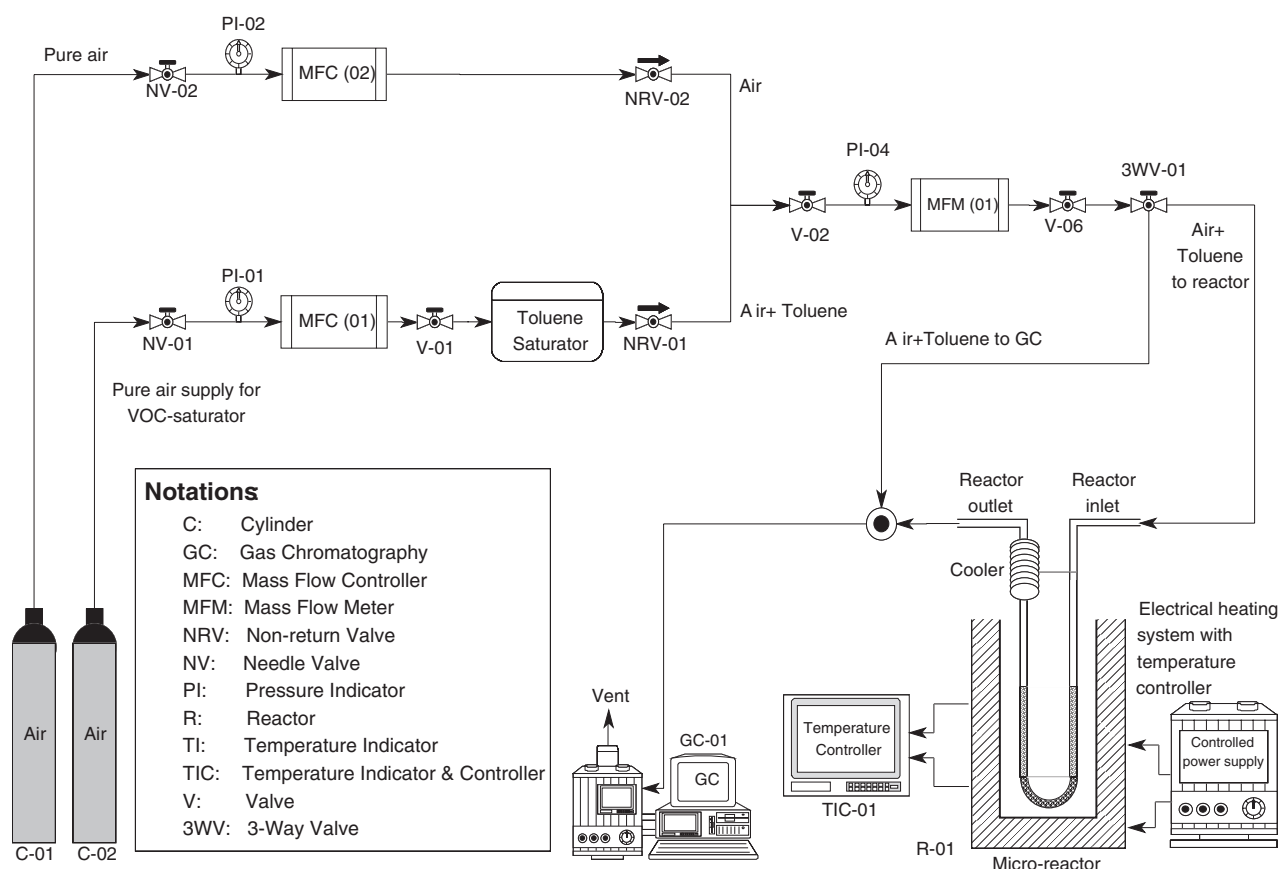


Figure 2. Experimental setup for the catalytic evaluation of Cu/Clinoptilolite–CeO₂ nanocatalyst for toluene abatement from waste gas stream at low temperature.

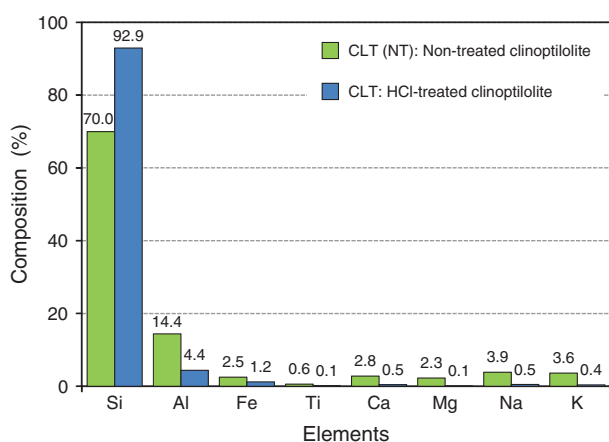


Figure 3. Chemical analysis of non-treated clinoptilolite and HCl-treated clinoptilolite.

were formed by the sonochemical decomposition of volatile organometallics. These amorphous structures are highly useful because of their high surface area.⁴³

FESEM analysis

The surface morphology of raw clinoptilolite, HCl treated clinoptilolite, synthesized CeO₂–clinoptilolite, and Cu/Clinoptilolite–CeO₂ nanocatalysts were studied by FESEM and the corresponding images are presented in Fig. 5. As shown in

Fig. 5(a), raw clinoptilolite has a dense structure. Acid treatment, besides some modifications in crystal phase of raw clinoptilolite (according to XRD), changed the morphology of natural zeolite as indicated in Fig. 5(b). Figure 5(c) shows some changes in the structure of treated clinoptilolite due to the introduction of CeO₂. Nanoparticles of CeO₂ provide more active phase and reducible sites that yields higher catalytic performance.³⁴ By the addition of different loadings of Cu to the samples obvious changes in the morphology of catalyst were observed as shown in Fig. 5(d)–(g). In Fig. 5(d) and (e) a distinct difference in the morphology of synthesized nanocatalyst via ultrasound and impregnation was observed. By comparing these two figures, it can be seen that the ultrasound method has a greater influence on the morphology of the nanocatalyst and provides more uniform and smaller catalyst particle size. Figure 5(d) shows the adverse effects of impregnation: the formation of more agglomerates in the structure of the catalyst. With 5%Cu loading, tiny particles together with the formation of aggregates were noticed. With a loading of 10%Cu to the sample a uniform morphology was noticed. In the 15%Cu loaded material more agglomerates can be seen. It is worth noting that in sonicated samples particle surfaces are rough, while they are smooth in other samples.

The insets of Fig. 6 show a particle size distribution histogram at Cu(5%) over treated Clinoptilolite–CeO₂ synthesized by ultrasound. It is identified that the distribution of Cu(5%)/CLT–CeO₂ was mostly in a nanosized structure and in the range 9.7–43.7 nm with an average size of 21 nm. Most of the particles (28.1%) are in the range 15–20 nm.

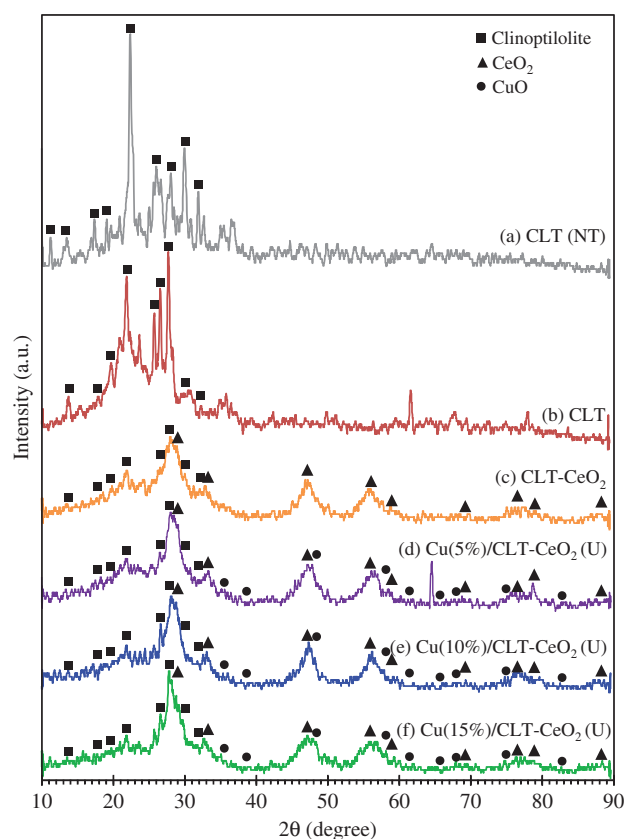


Figure 4. XRD patterns of support: (a) non-treated clinoptilolite, (b) HCl-treated clinoptilolite, (c) CeO₂-doped clinoptilolite; and ultrasound assisted synthesized Cu/Clinoptilolite–CeO₂ nanocatalyst with various Cu loadings: (d) 5 wt%, (e) 10 wt% and (f) 15 wt%.

EDX dot-mapping analysis

EDX dot-mapping is the best way to confirm the presence of different components in the structures of our samples and also the distribution of Cu as a main and desirable element of the toluene abatement. Figure 8 indicates results of EDX dot mapping analysis of Cu(5%) over CLT–CeO₂ synthesized via ultrasound and impregnation. Outcomes of elemental analysis of the samples coated with gold demonstrate a fine distribution of Cu as a desirable element over treated clinoptilolite. Comparing Fig. 7(a) and (b) confirms the positive effects of ultrasound in the dispersion of Cu over the support rather than impregnation. As can be observed in specific areas, there are more detected particles of Cu on the support dispersed via ultrasound than that using the impregnation method. The fine dispersion of Cu using ultrasound could be as a result of the acoustic cavitation that occurs.

BET analysis

Table 1 illustrates specific surface area (BET) results of the synthesized samples. Raw clinoptilolite has a specific surface area of 13.1 m² g^{−1}, which is increased sharply by acid treatment to 23.7 m² g^{−1}. This phenomenon could be the result of acid leaching that opens pores during modification of the zeolite.⁴² As mentioned before, acid treatment of natural clinoptilolite may remove impurities that block pores; therefore it enhances the porosity and catalytic activity of the support. As indicated in the table, by adding CeO₂ to the sample, the specific surface area was increased enormously to 71.7 m² g^{−1}. This sharp change in specific surface area

provides enough space for Cu loading. In this study, Cu loading was performed by two methods, ultrasound and impregnation. Each of these methods has a special influence on the specific surface area of the samples. As shown in the table, 5% loading of Cu in the sample by means of ultrasound provides 76.1 m² g^{−1} surface area, whereas using impregnation the surface area reached 54.2 m² g^{−1}. This means ultrasound has a greater positive influence on the surface area due to the fine dispersal of Cu over the support. Furthermore, Cu loading provides a specific area in the range 76.1–85.1 m² g^{−1} giving a considerable area for adsorption sites for toluene oxidation.

FTIR analysis

Figure 8 shows FTIR patterns of natural clinoptilolite, HCl treated clinoptilolite, CeO₂–clinoptilolite and Cu(5%–10%–15%)/Clinoptilolite–CeO₂. A comparison between FTIR spectra of these samples reveals no dramatic differences. However, stretching vibrations for structural –OH and adsorbed water at the wave numbers of 3450 and 1640 cm^{−1} were noticed for all samples.^{44,45} These vibrations refer to physically adsorbed water in all samples after catalyst heat treatment.^{46,47} The main characteristic bands of clinoptilolite⁴⁸ were found at the wave numbers of 460, 600, 725, and 1075 cm^{−1}. Figure 8(b) shows the specific bands of zeolite for the bending vibrations of SiO₄/AlO₄ internal tetrahedral, the double-ring vibration of zeolite, and the asymmetric valence vibrations in tetrahedral SiO₄ by the bands at 400–1080 cm^{−1}. Bands with the range of wave numbers at 760–840 and 830–1000 cm^{−1} are attributed to aluminates and silicates, respectively.^{48,49} Figure 8 indicates Ce–O bonding and an oxygen band around 800 and 500 cm^{−1}, respectively.^{34,50} Introduction of different loadings of Cu to our samples does not show any characteristic bonds referring to Cu compounds such as Cu(OH)₂ and CuO or Cu₂O. This could be due to overlapping of clinoptilolite peaks in these regions.

Catalytic performance study toward toluene abatement from polluted air

Effect of ultrasound irradiation

The curves of catalytic oxidation of toluene over Cu(5%)/Clinoptilolite–CeO₂ nanocatalyst produced via ultrasound and impregnation methods are demonstrated in Fig. 9. As indicated, toluene oxidation mostly depends on the preparation method of the synthesized nanocatalyst. The oxidation of toluene samples in this research using the catalyst prepared by the ultrasound method in the temperature range of 150–350 °C gives much better results than those of the impregnation method. For instance, at 275 °C the toluene oxidation of the nanocatalyst synthesized by ultrasound method is around 60%. However, the result for the catalyst prepared by the impregnation method is only 40% for the same sample. This could be due to the more efficient synthesis of nanocatalyst by ultrasound. Ultrasound produces nanocatalysts with high loadings of dispersed active sites (as confirmed by XRD, FESEM and EDX) in comparison to other preparation methods such as impregnation.⁴⁴ The good results of the activity tests are due to the smaller and more homogeneous particle size, greater dispersion and increased number of adsorption sites.³

Effect of Cu-loading

The effect of Cu loading on the activity of synthesized clinoptilolite, clinoptilolite–CeO₂, and Cu(5%–10%–15%)/Clinoptilolite–CeO₂, was investigated over the temperature range of 150–350 °C

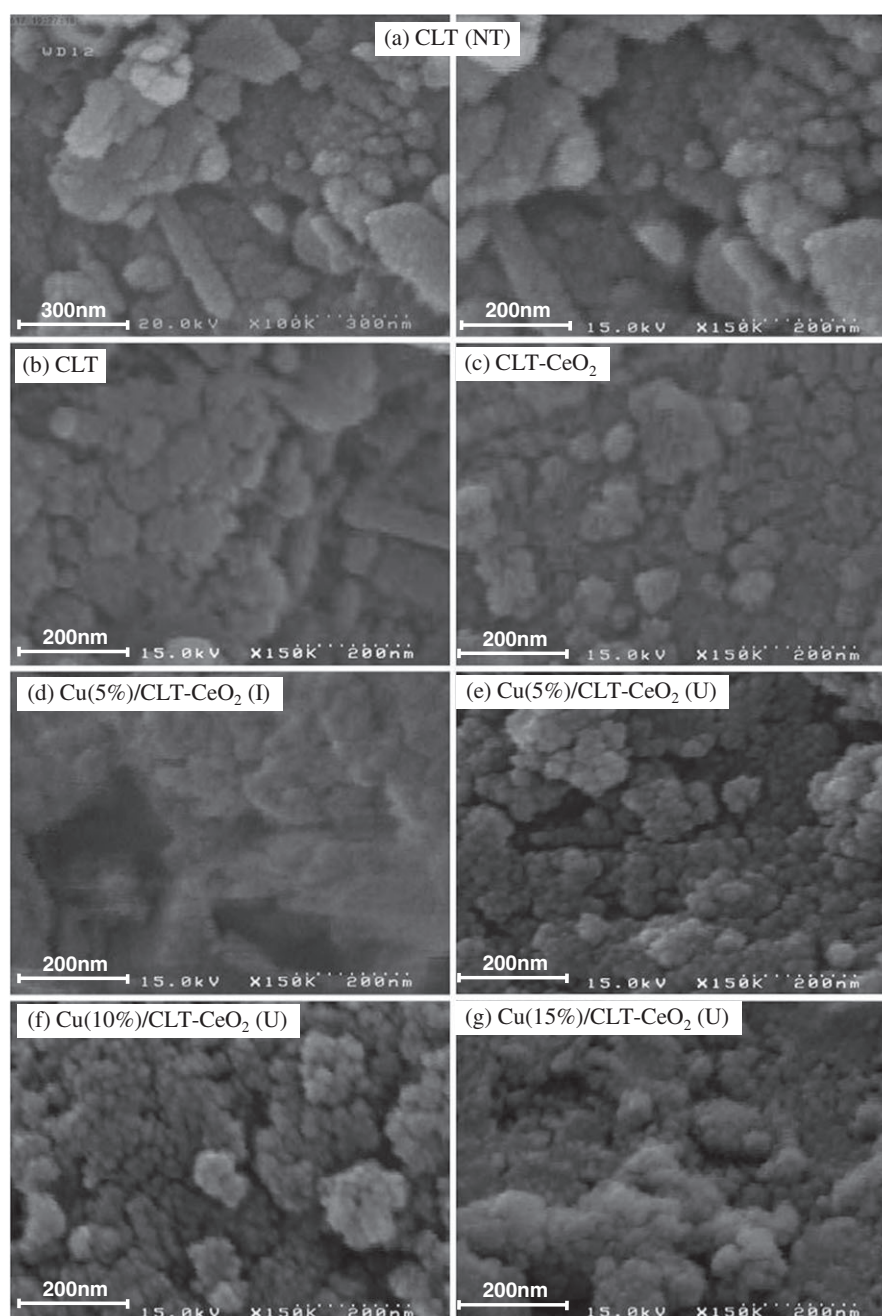


Figure 5. FESEM images of support: (a) non-treated clinoptilolite, (b) HCl-treated clinoptilolite, (c) CeO_2 -doped clinoptilolite; and Cu/Clinoptilolite– CeO_2 nanocatalyst with various Cu loadings: (d) 5 wt% (imp.), (e) 5 wt% (Ult.), (f) 10 wt% (Ult.) and (g) 15 wt% (Ult.).

as shown in Fig.10. The figure demonstrates the parallel relation of temperature with toluene oxidation so that by increasing the temperature toluene oxidation is enhanced sharply. As expected, it is observed that toluene oxidation depends strongly on Cu loading while the trend in activity is: $\text{Cu}(15\%)/\text{Clinoptilolite}-\text{CeO}_2 > \text{Cu}(10\%)/\text{Clinoptilolite}-\text{CeO}_2 > \text{Cu}(5\%)/\text{Clinoptilolite}-\text{CeO}_2 > \text{Clinoptilolite}-\text{CeO}_2 > \text{Clinoptilolite}$. As can be seen in the figure, toluene oxidation of all samples in the temperature region below 225°C gradually increases with increasing temperature, while toluene oxidation in the region above 225°C increases sharply, reaching a maximum at 350°C . Therefore, the best toluene oxidation and the highest nanocatalyst activity is achievable at the reaction temperature of 350°C

together with the loading of Cu(15%) on the Clinoptilolite– CeO_2 support. Clinoptilolite shows some activity in the removal of toluene at high temperatures which can be related to thermal decomposition of the pollutant.

Effect of toluene concentration

The performance of Cu(15%)/Clinoptilolite– CeO_2 nanocatalyst with different toluene concentrations was studied and results are shown in Fig. 11. The figure reveals that increasing the pollutant concentration causes the nanocatalyst activity or elimination of toluene to considerably decrease. This could be due to reduced toluene–oxygen interactions as a result of higher toluene accumulation on the nanocatalyst sites. The surface properties of

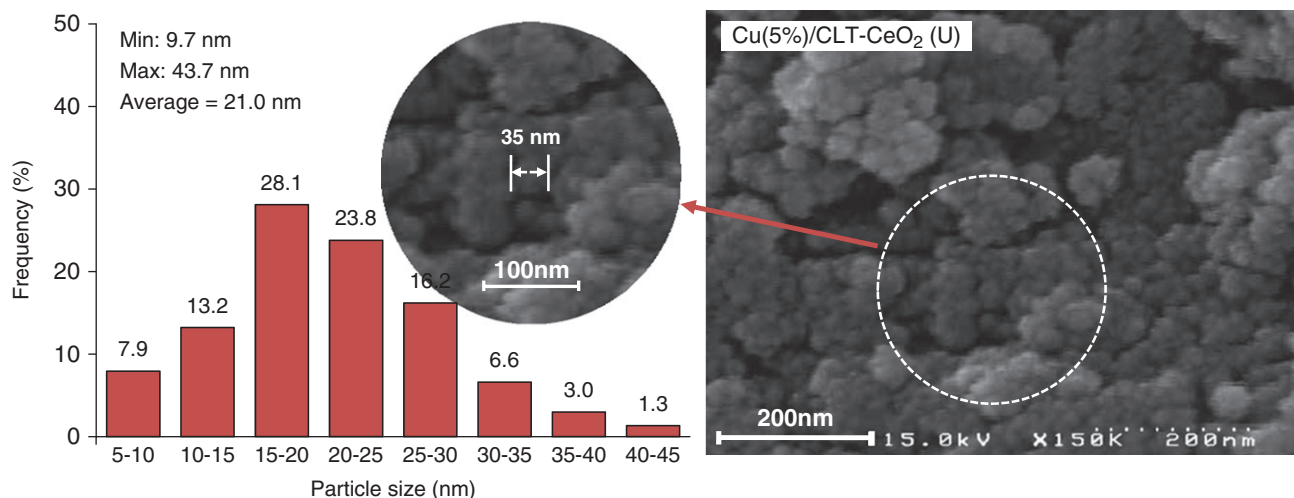


Figure 6. Size distribution histogram of Cu(5%)/Clinoptilolite–CeO₂ (U) nanocatalyst.

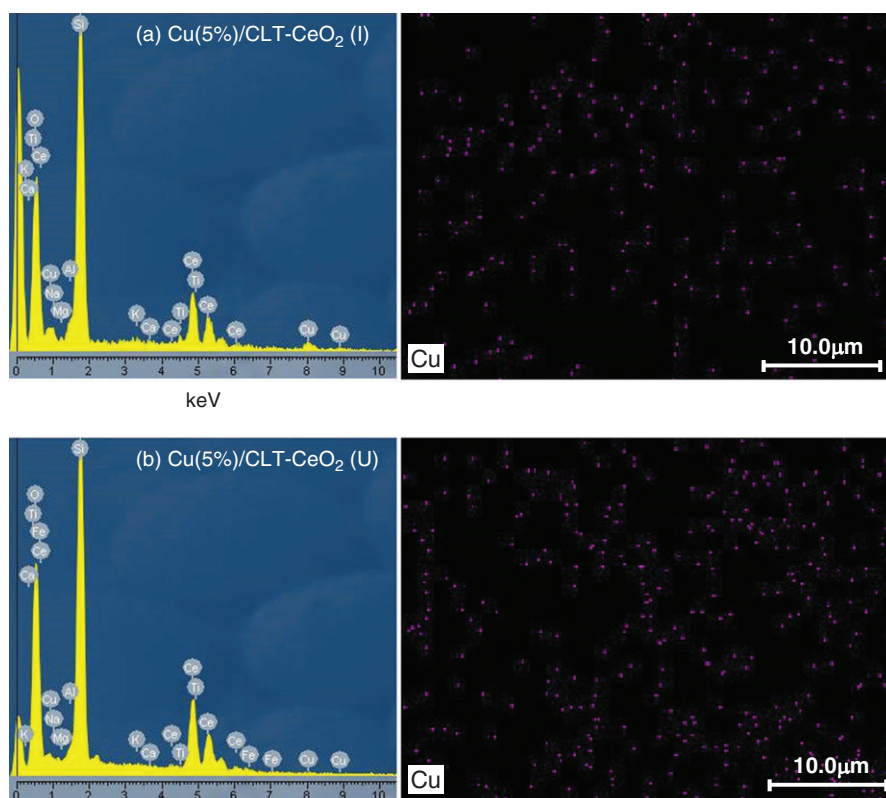


Figure 7. EDX Dot-Mapping analysis of Cu/Clinoptilolite–CeO₂ nanocatalyst with 5 wt% of Cu: (a) impregnation (b) ultrasound.

clinoptilolite play a vital role in VOC adsorption efficiency³⁵ and CeO₂ provides the required oxygen for oxidation by the reduction of Ce⁴⁺ to Ce³⁺.^{34,51,52} As can be noticed from trends of the curves in Fig. 11, by increasing the concentration in the temperature range of 150–350 °C, there is a decrease in the catalyst activity, although the nanocatalyst retains the ability to remove toluene even from highly polluted gas streams. As the figure shows, at high temperatures a conversion level of almost 96% is achieved for all concentrations of toluene tested. It seems that at high temperatures thermal decomposition of toluene occurs or there is more probability of reactant collisions due to the higher energy which helps in removal of the pollutant.

Based on the above explanations and in comparison with other researchers,^{35,50} using Cu(15%)/CLT–CeO₂ nanocatalyst for removing different loadings of toluene demonstrates the beneficial use of this research that leads to high activity of a low-cost nanocatalyst at low temperatures.

Time on stream performance

The stability of sonicated Cu(15%)/Clinoptilolite–CeO₂ nanocatalyst was investigated and results are presented in Fig. 12. The catalyst was tested at 350 °C and GHSV = 6000 h^{–1}. According to the figure, constant nanocatalyst activity and elimination approaching 98% was obtained over 1440 min. This indicates that

Table 1. BET surface area of the support and Cu/Clinoptilolite–CeO₂ nanocatalyst with various Cu-loadings

Support/Nanocatalyst	Nomenclature	Synthesis method	CeO ₂ loading (%)	Cu loading (%)	SBET (m ² g ⁻¹)
Clinoptilolite	CLT (NT)	Non-treated	-	-	13.1
Clinoptilolite	CLT	HCl-treated	-	-	23.7
Clinoptilolite–CeO ₂	CLT–CeO ₂	Precipitation	30	-	71.7
Cu/Clinoptilolite–CeO ₂	Cu(5%)/CLT–CeO ₂ (U)	Ultrasound	30	5	76.1
Cu/Clinoptilolite–CeO ₂	Cu(5%)/CLT–CeO ₂ (I)	Impregnation	30	5	54.2
Cu/Clinoptilolite–CeO ₂	Cu(10%)/CLT–CeO ₂ (U)	Ultrasound	30	10	80.1
Cu/Clinoptilolite–CeO ₂	Cu(15%)/CLT–CeO ₂ (U)	Ultrasound	30	15	85.1

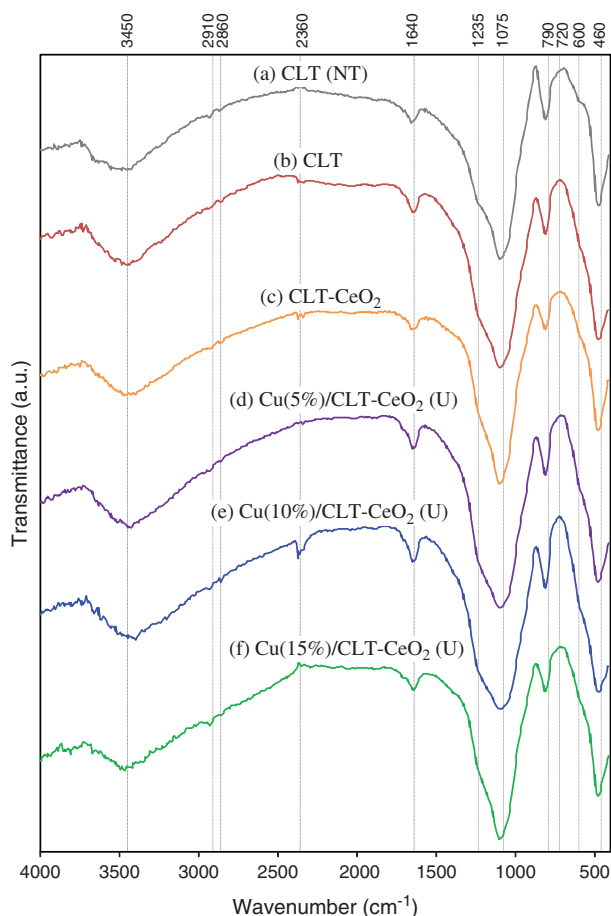


Figure 8. FTIR spectra of support: (a) non-treated clinoptilolite, (b) HCl-treated clinoptilolite, (c) CeO₂-doped clinoptilolite; and ultrasound assisted synthesized Cu/Clinoptilolite–CeO₂ nanocatalyst with various Cu loadings: (d) 5 wt%, (e) 10 wt% and (f) 15 wt%.

the well-defined morphology of the catalyst induces less deactivation of the nanocatalyst, probably due to less formation of carbon on the nanocatalyst during the toluene oxidation between active phase and carrier.³ The high stability of the nanocatalyst provides a suitable situation for toluene abatement with long operating time at an industrial scale.

CONCLUSIONS

Morphological analysis indicated the existence of nanoparticles and showed uniform morphology of the nanocatalyst structures

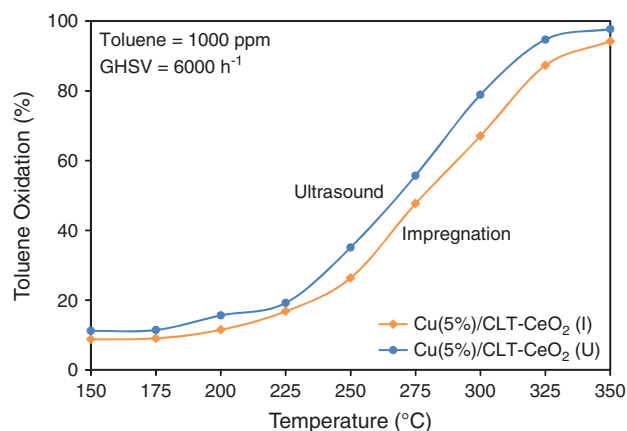


Figure 9. Effect of ultrasound irradiation on catalytic performance of Cu/Clinoptilolite–CeO₂ nanocatalyst in total oxidation of toluene at different temperatures.

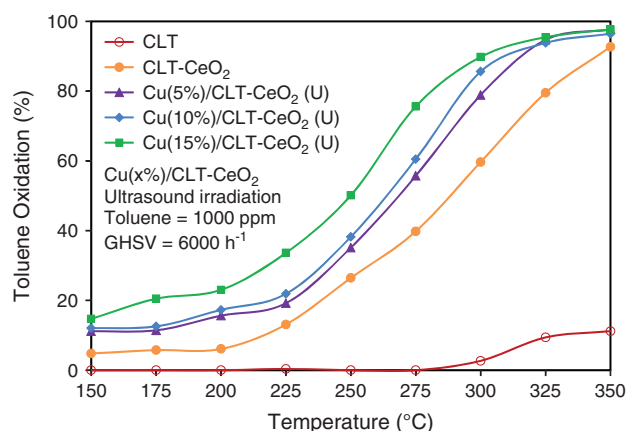


Figure 10. Effect of Cu-loading on catalytic performance of Cu/Clinoptilolite–CeO₂ nanocatalyst in total oxidation of toluene at different temperatures.

due to fine dispersion of active phase over the support by means of ultrasound. The BET results showed positive effects of acid treatment, loading of CeO₂, and ultrasound preparation method in providing considerable surface area for toluene oxidation. The results of catalytic tests demonstrated that a lower temperature catalytic activity and better catalytic performance was achieved with the highest loading (15%) of Cu over the clinoptilolite treated with the ultrasound method in comparison with conventional catalyst. Although increasing toluene concentration diminished

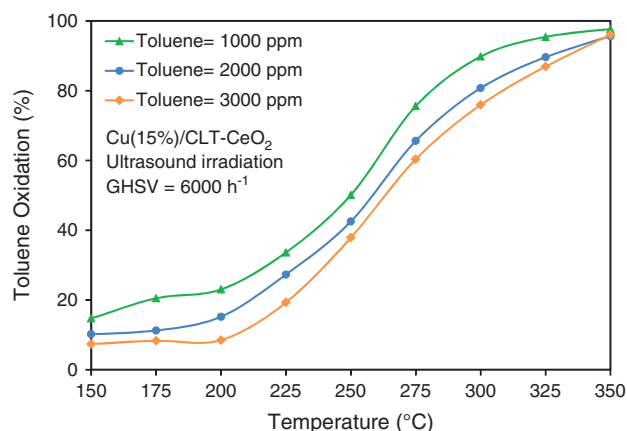


Figure 11. Effect of toluene concentration on catalytic performance of Cu/Clinoptilolite-CeO₂ nanocatalyst in total oxidation of toluene at different temperatures.

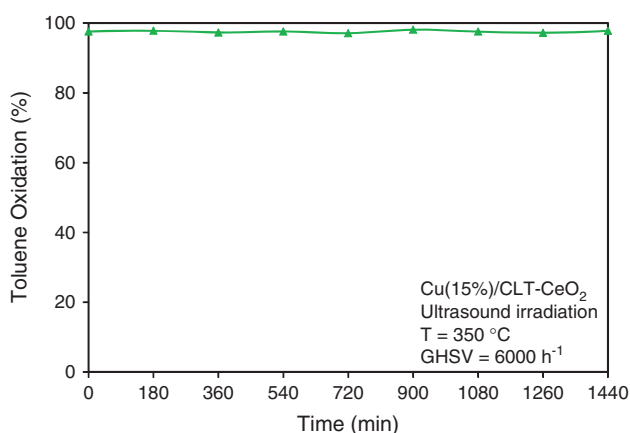


Figure 12. Time on stream performance of Cu/Clinoptilolite-CeO₂ nanocatalyst in total oxidation of toluene.

the elimination percentage, the nanocatalyst even at high concentrations of toluene has high removal ability. In addition, the time on stream test indicated a constant elimination percentage of 98% for about one day. Therefore, it is concluded that nanocatalyst (Cu(15%)/Clinoptilolite-CeO₂), because of its its high removal ability, greater stability, and inexpensive reaction conditions, is the most appropriate catalyst.

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