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Original article

## Catalytic degradation of toluene on manganese oxide catalyst loaded on a natural zeolite support

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### ABSTRACT

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The aim of the present study was the investigation of catalytic oxidation of toluene over manganese oxide supported on a natural zeolite (clinoptilolite). The catalyst was synthesized by the impregnation method and calcining at 450°C, and then characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The effects of the toluene concentration, and space velocity were investigated at different reaction temperatures and the catalytic activity of the catalyst was compared with zeolite 13X. The results indicate that Mn/Clino catalyst, with 10wt% loading, shows proper catalytic activity for degradation of toluene. This study claims that Mn/Clino exhibited relatively a good catalytic activity in comparison with Mn/Z13X.

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## 1. Introduction

Volatile organic compounds (VOCs) are considered to be the most important group of air contaminants. The VOCs are vented from a variety of industrial and commercial processes, such as metal decorating, printing, dry cleaning, oil supplying, paint drying, manufacturing of organic compounds and polymers, metal degreasing, and food processing, etc. (Park and Ledford, 1998). Exposure to VOCs might cause symptoms, such as the sick building syndrome including headache, fatigue, mucous membrane irritation, respiratory tract irritation, dizziness and nausea and might cause toxic effects to central nervous system and internal organs (Auvinen and Wirtanen 2008; Mo et al., 2009).

Among the different removal technologies for VOCs, catalytic oxidation is probably the most effective and economically viable way for reducing the emissions of VOCs in a wide range of concentrations and gas flow rates (Barzegar Shangol et al., 2013; Ozcelik et al. 2009). This way can be classified into two main categories: supported noble metals which possess high activity but are expensive (Avgouropoulos et al., 2006; Maldonado-Hodar et al., 2004; Santos et al., 2010c; Tsou et al., 2005) and transition metal oxides (bulk or supported forms) which are cheaper but less active (Santos et al., 2010a; Santos et al., 2010b; Vu et al., 2008; Yang et al., 2007). Nevertheless, in some cases, these catalysts show performances as high as or higher than supported noble metal catalysts (Lahousse et al., 1998). Among the transition metals, manganese is an interesting metal to be applied in catalytic oxidation reactions because of its multiple oxidation states.

Among suggested substrate for catalysts, natural zeolites are renowned valuable inorganic materials (microporous crystalline hydrated aluminosilicates) with wide range of applications from molecular sieves adsorbents to ion-exchangers and catalysts. Generally, chemical formula of zeolites can be shown as:  $M_2/nOAl_2O_3 \cdot xSiO_2 \cdot yH_2O$ , where M is the mobile cation with valence of n, x is 2.0 or more, and y representing moles of water. Natural zeolitic minerals possess selective adsorption, cation-exchange, dehydration-rehydration, and catalysis properties, which contribute directly to their industrial applications. Clinoptilolite with the simplified ideal formula of  $(Na, K) 6Si_{30}Al_6O_{72} \cdot nH_2O$ , is the most abundant zeolitic mineral found as sedimentary rocks of volcanic origin having a tremendous commercial interest because of its purity, stability and accessibility. Zeolite structure has a negative charge responsible for adsorbing of cations in micro pores channels and cavities by means of ion exchange mechanism. Pb, Cd and Hg cations are typical toxic heavy metal that can be captured by zeolitic materials (Faghihian et al., 1999; Kazemian and Mallah, 2008; Mahabadi et al., 2007). Zeolites have been claimed as promising supports to stabilize transition metals, because of their availability, special porous structures, different composition and hydrophobicity degree, active sites acidic properties and location of exchanged cations (Corma and Navarro, 2002). The specific characteristics of zeolites make them a potential multifunctional materials for environmental remediation purpose that are suitable for adsorption of oxyanions (Menhaje-Bena et al., 2004) organic molecules such as BTEX (Seifi et al., 2011; Torabian et al., 2010) and MTBE (Ghadiri et al., 2010).

In this study, we used natural clinoptilolite as a support, because of its availability, special properties and low cost. Toluene, as a good represent of VOCs, has been chosen for the catalytic test on samples. Manganese oxide, as a catalyst, was chosen because of its high catalytic oxidation activity of VOCs. Therefore, the aim of the present work was to study the catalytic combustion of toluene vapour over natural clinoptilolite modified by manganese oxide.

## 2. Materials and methods

Clinoptilolite mineral was obtained from Semnan in Iran. The clinoptilolite was characterized by using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The chemical composition of clinoptilolite determined by X-ray fluorescence (XRF) measurements was as follows: SiO<sub>2</sub>, 60.7%; Al<sub>2</sub>O<sub>3</sub>, 9.95%; Fe<sub>2</sub>O<sub>3</sub>, 1.94%; TiO<sub>2</sub>, 0.223%; CaO, 3.23%; MgO, 0.94%; Na<sub>2</sub>O, 2.25%; K<sub>2</sub>O, 3.9%; P<sub>2</sub>O<sub>5</sub>, 0.045%; SO<sub>3</sub>, 2.924; Cl, 0.291%; Sr, 0.053%; Zr, 0.02%; Ba, 0.111%. Clinoptilolite samples with a size range of 0.5-1 mm were treated with 1M NH<sub>4</sub>Cl solution at 70°C on a magnetic mixer for 24h. Then, clinoptilolite samples were washed with warm distilled water several times. Samples were dried in an oven at 110°C for 16h.

Clinoptilolites were converted to H form by calcining in air at 450°C for 4h. In addition, an artificial zeolite, 13X, has been used for comparison purposes. H form 13X zeolite was prepared like clinoptilolite samples.

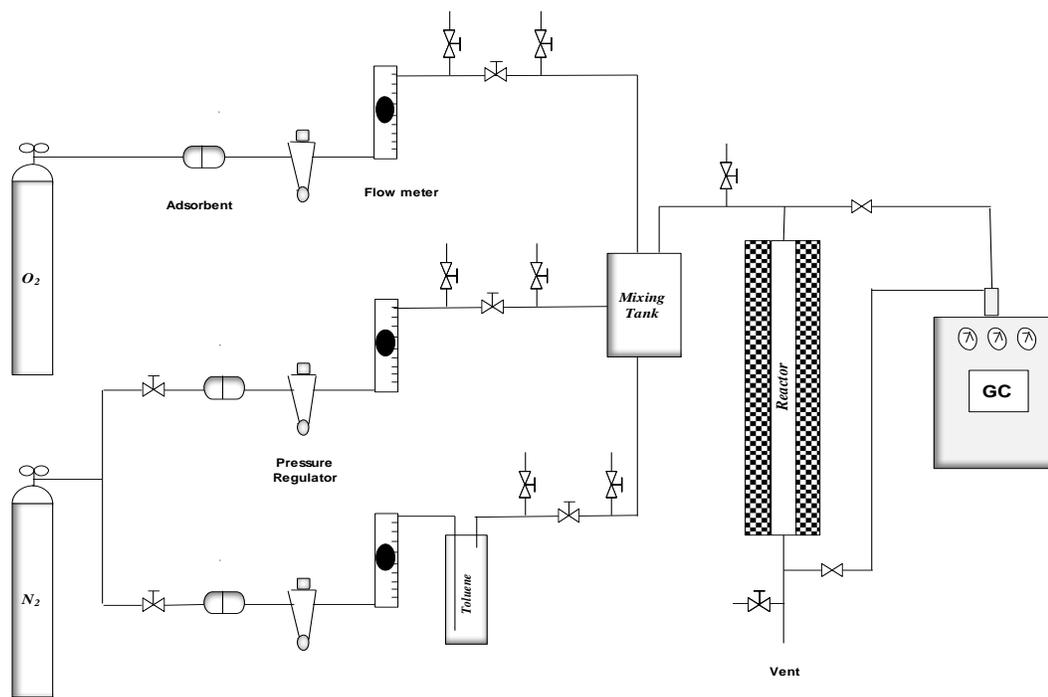
Transition metal solution was prepared by dissolving  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Merck) and in distilled water. Catalysts containing nitrates of Mn were prepared by incipient wetness impregnation of ion exchanged zeolites. The impregnated supports were dried at 105°C for 14h, and they were calcined in air at 450°C for 4h. Metal oxide loading of the catalysts were nominally 10wt%. In order to confirm the size of the modified zeolites, they were sieved at the definite size range after modification. In this stage, the samples were denoted as Mn/Clino and the artificial one as Mn/Z13X.

The modified clinoptilolite was characterized by using X-ray diffraction (XRD) and scanning electron microscopy (SEM) after treatment.

Catalytic activities were measured in a fixed-bed steel tubular reactor with 10 mm diameter and 10 cm length. The schematic of the experimental set-up is shown in Fig. 1. Prior to catalytic tests, catalyst precursors were heated in the flowing air at 400°C for 1h. The reaction mixture consisting of toluene (50, 100 and 1000 ppm),  $\text{O}_2$  (21% by volume) and  $\text{N}_2$  (79% by volume) was passed continuously through a 5 g catalyst sample layer with a total flow rate of 1 and 2 lit/min. Catalytic activity was measured over the range 150-450°C, and temperatures were measured by means of a K-type thermocouple placed just beneath the catalyst bed. Conversion data were calculated by the differentiating between inlet and outlet concentrations. Conversion measurements and product profiles were taken at steady state, typically after 30min on stream. The inlet and outlet toluene concentration were analysed after stepwise changes in the reaction temperatures by an on-line gas chromatograph (Bruker GC-450) equipped with a FID detector using a Cp-sil 5CB capillary column (30m × 0.25mm × 0.25µm). In all cases, data points presented here are averages of at least three measurements. Conversion of toluene was calculated based on inlet and outlet measured concentrations using the following expression:

$$\text{Toluene conversion} = (C_{\text{in}} - C_{\text{out}}) \times 100 / C_{\text{in}} \quad (1)$$

, where  $C_{\text{in}}$  and  $C_{\text{out}}$  are the inlet and outlet concentrations of toluene, respectively. It should be noted that the only reaction product detected under the present experimental conditions was  $\text{CO}_2$ .



**Fig. 1.** The schematic diagram of experimental set-up using for toluene elimination.

### 3. Results

XRD patterns of the synthesized Mn/clino catalyst and the parent natural zeolite are presented in Fig. 2. It was observed that manganese oxide was loaded on natural clinoptilolite samples. The main crystalline zeolitic phase of the produced catalyst was clinoptilolite, and the crystallinity of the zeolite substrate was 30.78% after treatment with manganese oxide.

SEM was used to study the morphological structures of natural and manganese oxide loaded clinoptilolite samples. The SEM micrographs are illustrated in Fig. 3. Fig. 3a indicates the presence of particles with some crystal faces with various particle sizes. It is clear that a uniform morphology of micron-sized granules can be observed on the sample with smaller crystals on the surface which could be ascribed to manganese oxide after thermal treatment at 450°C and loading with manganese oxide (Fig. 3b).

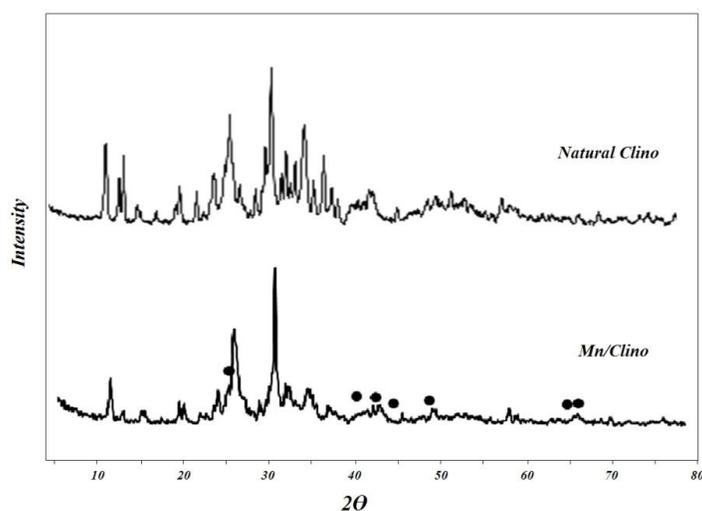


Fig. 2. XRD pattern of Mn/clino catalyst; (●) Manganese oxide.

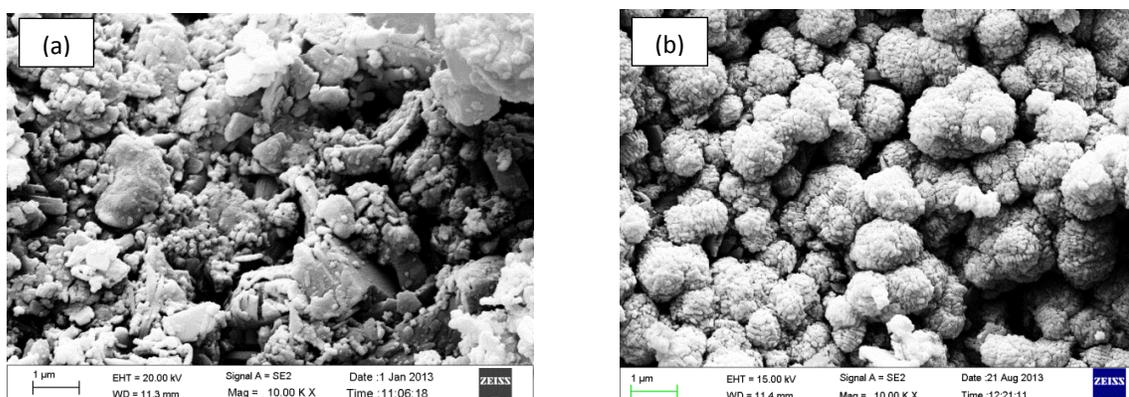
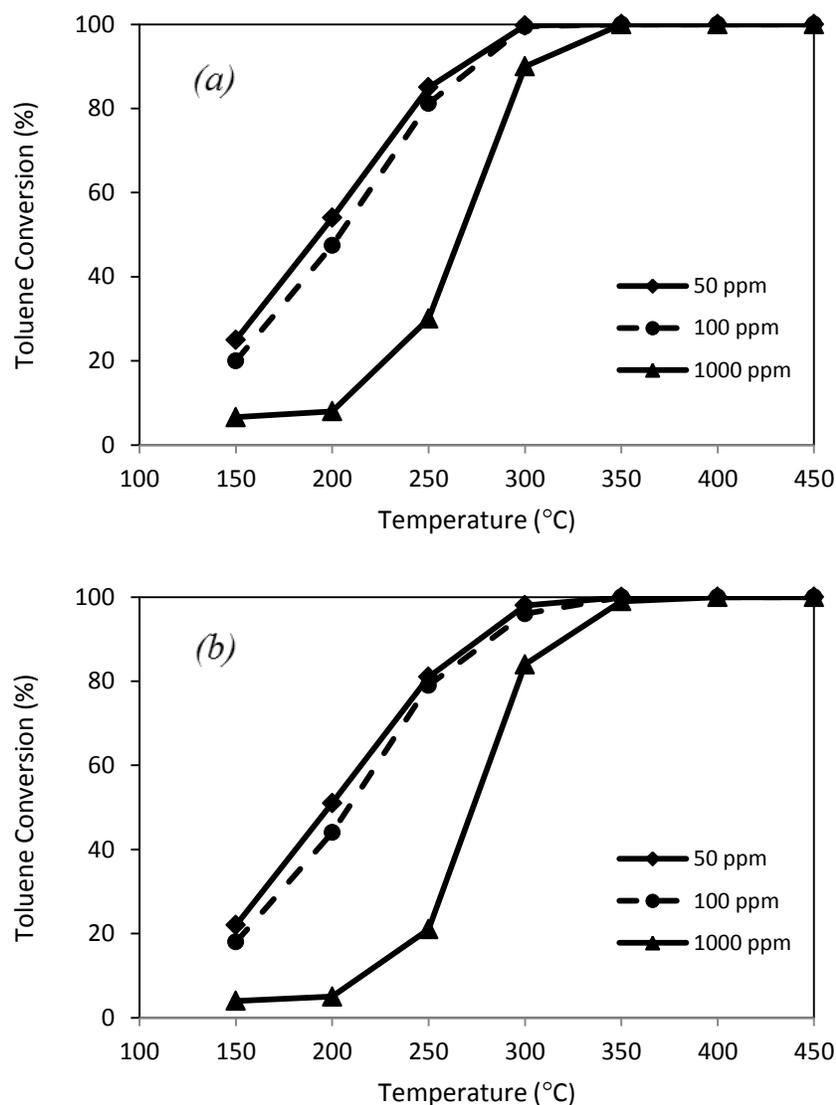


Fig. 3. SEM images of natural (a) and manganese oxide loaded (b) clinoptilolite.

Fig. 4 shows the conversion as a function of temperature over natural clinoptilolites modified by manganese oxide under different conditions. It could be observed that the highest activity is related to 50 ppm concentration of toluene. When the concentration was reached to 100 ppm, the toluene conversion at the same temperatures was decreased slightly, especially at low temperatures. For a toluene concentration of 1000 ppm, the conversion was the lowest but it seemed had an acceptable activity. So that the conversion percent was 90% at a reaction temperature of 300°C and the total conversion into

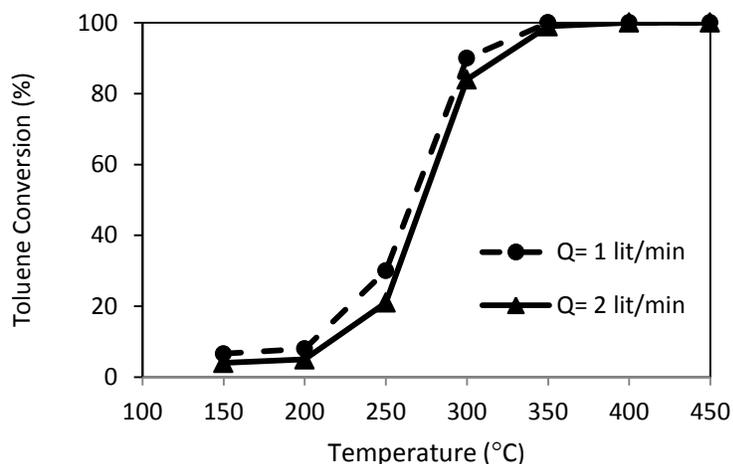
CO<sub>2</sub> was achieved at a reaction temperature of 350°C. This was at a situation that the total flow rate was 1 lit/min (Fig. 4a).

The activity of toluene conversion was decreased because of increasing the total flow rate from 1 lit/min to 2 lit/min (Fig. 4a and 4b). This point has been shown better in Fig. 5. The space velocity was 7643 and 15286 h<sup>-1</sup> (2.12 and 4.24 S<sup>-1</sup>) under total flow rate of 1 and 2 lit/min, respectively. The residence time of toluene in our reactor was 0.471 and 0.2355 S under total flow rate of 1 and 2 lit/min, respectively.

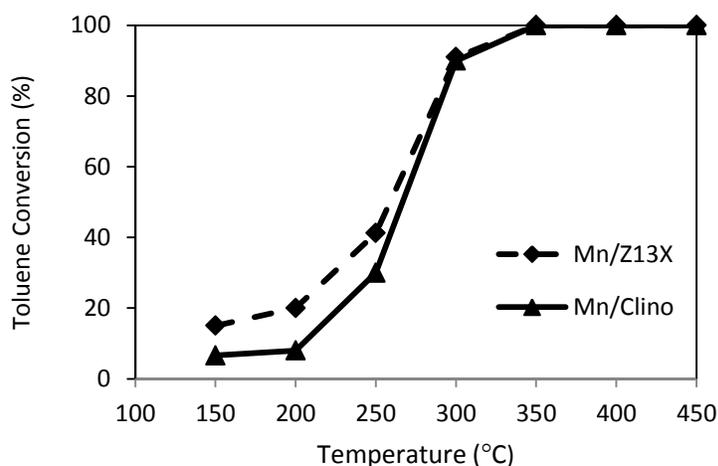


**Fig. 4.** Toluene conversion vs. reaction temperature over the Mn/clino samples under various toluene concentrations: Reaction condition: catalyst weight = 5 g; total flow rate = 1 lit/min (a), 2 lit/min (b).

Moreover the activity of Mn/clino was compared with Mn/Z13X. As shown in Fig. 6, the activity of Mn/Z13X is higher than Mn/clino especially at low temperatures up to 300°C. But at the temperatures higher than 300°C, the activities were equal.



**Fig. 5.** Toluene conversion vs. reaction temperature over the Mn-clino sample under various flow rates. Reaction condition: catalyst weight = 5 g; toluene concentration = 1000 ppm.



**Fig. 6.** Toluene conversion vs. reaction temperature over the Mn/Clino and Mn/Z13X samples. Reaction condition: catalyst weight = 5 g; total flow rate = 1 lit/min; toluene concentration = 1000 ppm.

#### 4. Discussion

The results indicated that increasing reactant concentration results in decreasing activity. Such a phenomenon is usual for catalytic oxidation of VOC, i.e. the lower the concentration, the lower the light-off temperature (Li, et al., 2008; Vesper, et al., 1999).

The activity of toluene conversion was decreased because of increasing the total flow rate. Decreasing activity is related to decreasing residence time of toluene in the reactor. These results are in agreement with literature (Li, et al., 2008).

The developed Mn/clino catalyst has shown efficient catalytic activity for toluene degradation which is comparable with other similar report (Kim, 2002). Nevertheless, slightly lower activity of Mn/clino catalyst compared to some reports (Soylu, et al., 2010) can be attributed to the difference in the reaction condition and particularly because of the fact that we used larger particle size and higher flow rate in this work. The larger particle size of the zeolitic support materials might result lower catalytic activity for VOC degradation because of decreasing available active sites and reactants intra and inter particle diffusion. On the other hand, using of larger particle size of zeolite as a support material for reducing the pressure drop is necessary because the smaller particle size will cause larger pressure drop.

## 5. Conclusion

In this study, the catalytic combustion of toluene over manganese oxide supported on a natural zeolite was investigated in different conditions. It has been found that manganese oxide exhibited relatively a good catalytic activity in comparison with Mn/Z13X, especially at higher temperatures. Two reaction parameters including the concentration of toluene and the flow rate (space velocity) were shown direct influence on the catalytic oxidation efficiency.

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