

Application of Different Catalysts for Oxidation of Toluene in Absence and Presence of Ozone

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In this study removal of vapourization organic compounds (VOC) from polluted air by using ozone and zeolite -NaX, -HX and -NaY, α - and γ -alumina and ZrO_2 with a self-oscillatory behaviour observed on zeolite -NaX. The self-oscillatory behaviour was examined by means of continuous flow reactions, temperature-programmed oxidation. The complete oxidation of toluene in the absence of ozone for different catalyst bases was between 400-650 °C that by means of different concentration of ozone as an oxidation factor, this range was decreased to 300-450 °C. It was observed that by increasing of ozone concentration, the perfect oxidation of toluene occurred in lower temperature. The products of toluene oxidation by using different catalysts are CO_2 , CO and HCOOH.

Key Words: Ozone, Toluene, Zeolite, Oxidation.

INTRODUCTION

Over the last 25 years, health complaints related to indoor climate have increased¹. Poor indoor air quality can be attributed to physical (humidity), chemical (organic and inorganic), physical-chemical (particulate matter) and biological (molds) agents. Buildings are being sealed more tightly to reduce thermal energy losses. Concentrations of indoor pollutants can build up because there is a low turnover rate of indoor air². It proved that the level of indoor pollutants is 2-10 times higher than outdoor. In general volatile organic compounds (VOCs) can be given off by office products, insulating materials, synthetic furniture, cleaning and maintenance products, pressed wood, *etc.* or may originate from tobacco smoke³. Much effort has been devoted to characterize the levels of indoor air pollutants. Concentrations are known to be random variables because of their dependence on several sources and the fluctuations of emission variables⁴. Associations to adverse health effects such as allergic reactions, headache, eye, nose and throat irritation, dry cough, dizziness and nausea, concentration problems, tiredness⁵ and even cancer⁶ have been made to a poor indoor air quality⁷. These symptoms affect human health severely and lead to economic losses⁸. It estimated that the 'sick building syndrome' results in a productivity decrease of average 6.5 % in offices. Mechanical or electronically filters can

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effectively trap particulate contaminants and remove them from the circulating air. Ionic air purifiers emit ions enhancing the agglomeration of smaller particles into larger ones, which then gravitationally settle. Ionization may also cause attraction between particles and grounded surfaces resulting in electrostatic precipitation⁹. It has been proven that accumulation of pollutants, may serve as nutrient source for moulds and bacteria. These organisms are able to produce VOCs such as aldehydes, ketones, alcohols, furans, esters and acids^{10,11}. Sorption media (*e.g.*, activated carbon) only transfer VOCs to another phase rather than eliminating them¹². The use of adsorbents implies the change, disposal or regeneration of the adsorbents¹³. The Self oscillatory behaviour in toluene oxidation on zeolite-NaX¹⁴ and metallic mixed oxides (Pt, Mn or Cr) as catalysts for the gas-phase toluene oxidation¹⁵ has been reported.

Einaga and Futamura¹⁶ have reported that benzene is oxidized on supported manganese oxide catalyst to form CO_x and various types of partially oxidized by products at room temperature (295 K) and that the build-up of these by products on the catalyst surface is the cause of catalyst deactivation. In other paper, they carried out benzene oxidation with ozone over ion-exchange zeolite catalysts, Mn-Y, Mn-B, Mn-MoR and Mn-ZSM-S to further investigate the effect of catalyst support on the reaction¹⁷. To select an optimal catalyst support for the catalytic oxidation of toluene, we studied. Zeolite -NaX, -HX and -NaY, α - and γ -alumina and ZrO₂. The candidacy of zeolite-NaX and -NaY was specifically affiliated with the large pore channel system¹⁸⁻²⁰ and high surface area²⁰.

In this work, zeolite-NaX, -HX and -NaY, α - and γ -alumina and ZrO₂ catalytic performances on the toluene oxidation in the absence and presence of ozone are investigated.

EXPERIMENTAL

The schematic flow chart of pilot employed for the omitting toluene, as shown in Fig. 1. Catalytic oxidation of toluene was carried out with a fixed-bed reactor. Reaction was carried out using mixture of toluene with air. The toluene concentration, catalyst weight and gas flow rate, were 500 ppm, 0.05 g and 1000 mL/min, respectively. Ozone was synthesized from O₂ by a silent discharge ozone generator (Ebara Jitsugyo Co., Ltd. O2SD-3000A). Ozone concentration in O₂ flow was controlled at 36 and 56 ppm by monitoring ozone concentration with an ozone generator. Reactor diameter was 7 mm. Before the catalytic reaction, the sample in a Pyrex glass reactor was heated in N₂ flow for 1 h.

Catalyst preparation: Zeolite -NaX and -NaY, α - and γ -alumina and ZrO₂ were obtained from Aldrich Chemical Company Inc. Zeolite-HX was prepared from zeolite-NaX by a conventional ion exchange technique, using 5 wt % NH₄Cl aqueous solution. The salt solution was taken in the aliquots of 15 mL/g of zeolite-NaX and a high degree of ion-exchange was achieved by five exchange treatments at 80 °C. The ion exchanged solid was filtered and washed thoroughly with distilled water to

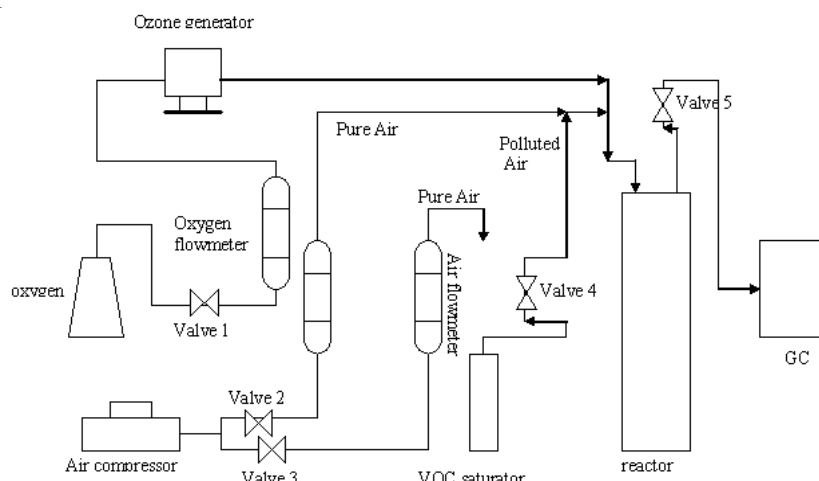


Fig. 1

remove chloride. The solid was then dried at 120 °C in an air oven for 12 h before being decomposed to zeolite-HX by calcination at 350 °C^{18,21,22}.

Experimental technique: In these tests, effects of reactor temperature, ozone concentration and different catalyst on the toluene omission percentage were inspected. At first contaminated air with toluene analyzed by GC machine. Then toluene oxidized with oxygen and ozone using different temperatures. The determination of toluene concentration, existing air sent to GC machine. The concentration of toluene was obtained by using the following equation:

$$C_{\text{toluene}} = 0.0066759 \times A$$

where C = toluene concentration in unit ppm, A = under surface of graph in GC machine that its unit is square meter.

This function obtained from linearity of data in calibration of machine with standard solutions. In each test, input and output of toluene measured by GC machine. The tests repeated approximately twice and toluene omission percentage was measured by using ozone at 100 to 700 °C.

The oxidation in natural air was measured at 100 to 700 °C. Every test began in high temperature and finished in lowest temperature. The main aim of this work was burnt the remaining probable fleas from the last test and prevent from toluene discharge. Also absorption occurs in the low temperatures. If the flow temperature can be used with toluene ascending disposal of high-temperature absorption level we are facing the disposal of toluene reduces test accuracy.

RESULTS AND DISCUSSION

As shown in Table-1, toluene is changed into CO₂, CO and HCOOH after oxidation. Through applying zeolite-NaY, toluene is transformed into CO, HCOOH after oxidation and in case of zeolite-NaX and-HX, the products derived from oxidation are CO

TABLE-1
PRODUCTS OF TOLUENE OXIDATION BY USING DIFFERENT CATALYST

Catalyst	Products	Catalyst	Products
NaY	HCOOH, CO ₂	γ -Al ₂ O ₃	CO, CO ₂ , HCOOH
NaX	CO, CO ₂	α -Al ₂ O ₃	CO, CO ₂ , HCOOH
HX	CO, CO ₂	ZrO ₂	CO, CO ₂

and CO₂. The γ -Al₂O₃ and α -Al₂O₃ oxidize toluene to form CO, CO₂ and HCOOH. Additionally, the products resulted from oxidation of toluene by means of catalyst ZrO₂ are CO and CO₂.

As can be seen in Figs. 1 and 2, among other catalysts applied, α -Al₂O₃ possesses the lowest transformation value of toluene. The complete oxidation of toluene by this catalyst occurs at 650 °C. Among the zeolites, the oxidation temperature of the -NaY for the complete transformation of the toluene is 600 °C. The lowest oxidation temperature of the catalysts applied belongs to HX-zeolite.

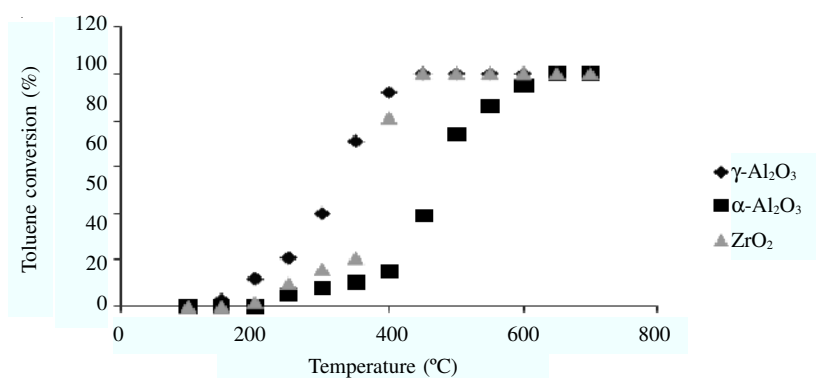


Fig. 2. Toluene removal at various temperatures in absence of ozone

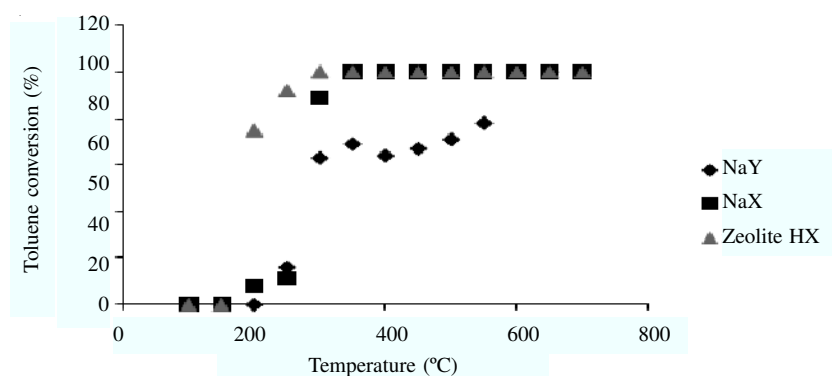


Fig. 3. Toluene removal at various temperatures in absence of ozone using zeolites

The results of toluene's oxidation in the presence of ozone have been shown in Figs. 4-7.

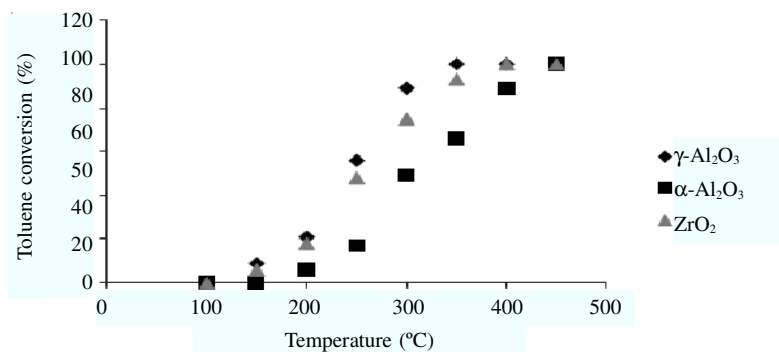


Fig. 4. Toluene conversion at various temperatures in presence of ozone (36 ppm)

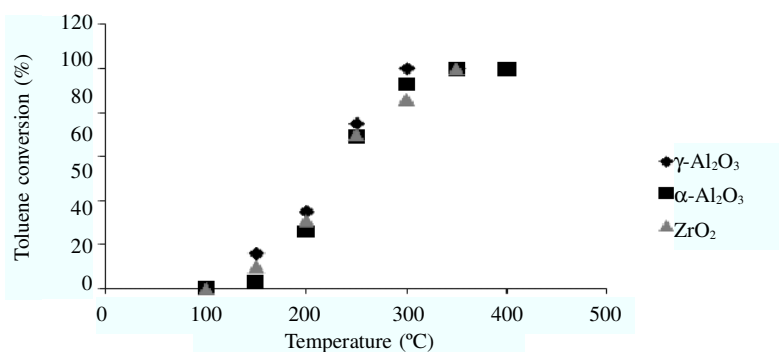


Fig. 5. Toluene conversion at various temperatures in presence of ozone (56 ppm)

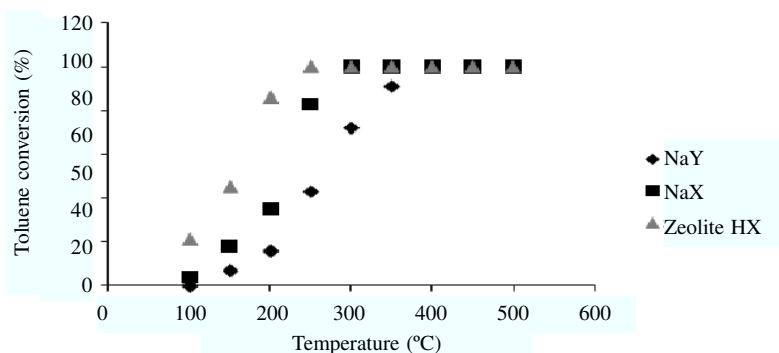


Fig. 6. Toluene conversion at various temperatures in presence of ozone (36 ppm) using zeolites

As the figures show, the oxidation temperature of toluene decreases by applying ozone and drop of the oxidation temperature raises more through an increase in concentration of ozone. The oxidation temperatures of toluene for the catalysts applied, in the presence of ozone, drop about 100 -150 °C as compared with that of oxidation in the absence of ozone. Through applying low concentration of ozone, the temperature drop becomes considerable therefore toluene's oxidation in the presence of ozone leads to more power saving.

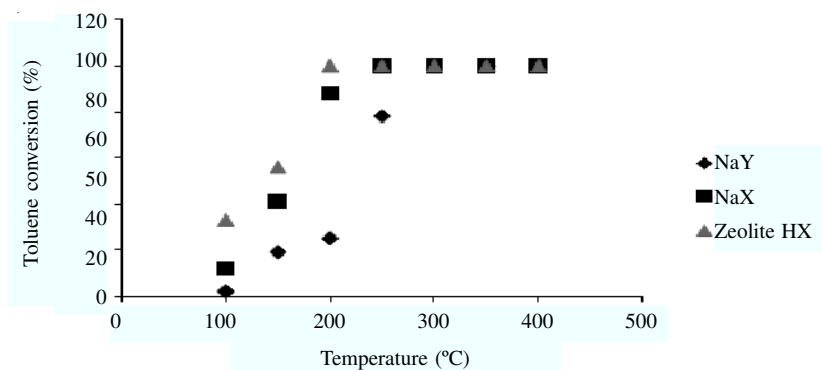


Fig. 7. Toluene conversion at various temperatures in presence of ozone (56 ppm) using zeolites

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REFERENCES

1. M.A. Isbell, R.J. Stolzberg and L.K. Duffy, *J. Sci. Environ.*, **345**, 31 (2005).
2. A.P. Jones, *Soc. Sci. Med.*, **47**, 755 (1998).
3. S. Aguado, A.C. Polo, M.P. Bernal, J. Coronas and J. Santamaria, *J. Membr. Sci.*, **240**, 159 (2004).
4. J.S. ParK and K. Ikeda, *Indoor Air.*, **14**, 413 (2004).
5. J. Mo, Y. Zhang and R. Yang, *Indoor Air.*, **15**, 291 (2005).
6. R.X. Luo, B. Wu, Y.N. Yi, Z.W. Huang, R.T. Lin, *Chin. Lung Cancer-J. IASLC.*, **14**, 113 (1996).
7. A.P. Jones, *Atmos. Environ.*, **33**, 4535 (1999).
8. P.O. Fanger, *Indoor Air.*, **10**, 68 (2000).
9. S.A. Grinshpun, G. Mainelis, M. Trunov, A. Adhikari, T. Reponen and K. Willeke, *Indoor Air.*, **15**, 235 (2005).
10. H.H. Jelen, C.K.J. Pirocha, E. Wasowicz and E. Kaininski, *Appl. Environ. Microb.*, **61**, 3815 (1995).
11. H. Schleichinger and H. Ruben, *Atmos. Environ.*, **33**, 4571 (1999).
12. J. Zhao and X. Yang, *Build. Environ.*, **38**, 645 (2003).
13. P. Pichat, J. Disdier, C. Hoang-Van, D. Mas and G. Goutailler, *Catal. Today*, **63**, 363 (2000).
14. J.D. Lee, N. Park, S.O. Ryu, K. Kim and T.J. Lee, *Appl. Catal.*, **275**, 79 (2004).
15. A.C.C. Rodrigues, *Catal. Com.*, **8**, 1227 (2007).
16. H. Einagan and S. Futamura, *J. Catal.*, **227**, 304 (2004).
17. H. Einagan and S. Futamura, *Catal. Commun.*, **8**, 557 (2007).
18. Y.C. Chang and A.N. Ko, *Appl. Catal. A*, **190**, 149 (2000).
19. M. Huang, A. Auroux and S. Kaliaguine, *Micropor. Mater.*, **5**, 17 (1995).
20. H.S. Fogler, *Elements of Chemical Reaction Engineering*, Prentice Hall PTR, Upper Saddle River, NJ (1989).
21. P.V. Zhdanov, *Surf. Sci. Rep.*, **45**, 231 (2002).
22. B.Y. Choi, W.C. Chang, K.S. Kim and T.J. Lee, *Hwahak Konghak*, **38**, 123 (2000).

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