



Catalytic ozonation of chlorinated VOCs on ZSM-5 zeolites and alumina: Formation of chlorides



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ABSTRACT

This study aims to understand the mechanisms and kinetics of chlorinated volatile organic chemicals (VOCs) removal during the catalytic ozonation process on γ -alumina and ZSM-5 zeolites. Both the H-ZSM-5 and Na-ZSM-5 types with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and counter ions (Z1000H: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1000$, Z900Na: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 900$, Z25H: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$ and Z25Na: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$) were studied. In order to fully understand the mechanisms behind the catalytic processes, degradation of VOCs and chlorides formation were investigated during both ozonation alone and catalytic ozonation on alumina and zeolites. The effects of pH and hydroxyl radical scavengers on the efficiency of catalytic ozonation on alumina and zeolites were also studied. The results revealed that, as opposed to alumina, zeolites promoted decomposition of VOCs. Furthermore, the decomposition of chlorinated VOCs resulted in the generation of chlorides at significantly higher levels when compared with ozonation alone. The presence of hydroxyl radical scavengers had no significant effect on the removal rates of VOCs and the generation of chlorides in the presence of zeolites. It is therefore suggested that catalytic ozonation of organic VOCs on zeolites proceeds via a non-radical mechanism that involves reactions of molecular ozone with pollutants adsorbed on the surface of zeolites.

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1. Introduction

Ozonation is of considerable importance in water treatment due to its disinfection ability and the high oxidation potential of ozone. However, from an economic point of view, and due to higher removal efficiencies, heterogeneous catalytic ozonation is preferred over single ozonation [1]. Therefore, heterogeneous catalytic ozonation systems have been studied in recent years to improve the efficiency of ozonation. Degradation of many organic compounds has been studied by employing various heterogeneous catalytic systems such as ozonation in the presence of activated carbons [2,3], $\text{Al}_2\text{O}_3/\text{O}_3$ [4], zeolites/ O_3 [5,6] and TiO_2/O_3 [7,8]. However, there are many controversies regarding the understanding of the mechanisms of these processes [9,10]. For example, some reports suggested that adsorption plays an important role in catalytic ozonation process [6,11,12] while others suggested that the adsorption may have negative effect on catalytic ozonation process [13]. The role of the catalyst is also unclear. According to some find-

ings catalysts decompose aqueous ozone leading to the production of hydroxyl radicals [11,14,15]. While other reports suggested that catalysts act as adsorbents for both ozone and pollutants to facilitate surface reactions [6,12,16]. In addition to above, it is important to mention here that the same catalyst has been reported to be effective for some pollutants [17,18] and in some other reports it was found to be ineffective for other types of pollutants [17,19,20]. Therefore, it is indeed important to better understand the process of catalytic ozonation in order to scale-up this technology from lab to an industrial scale.

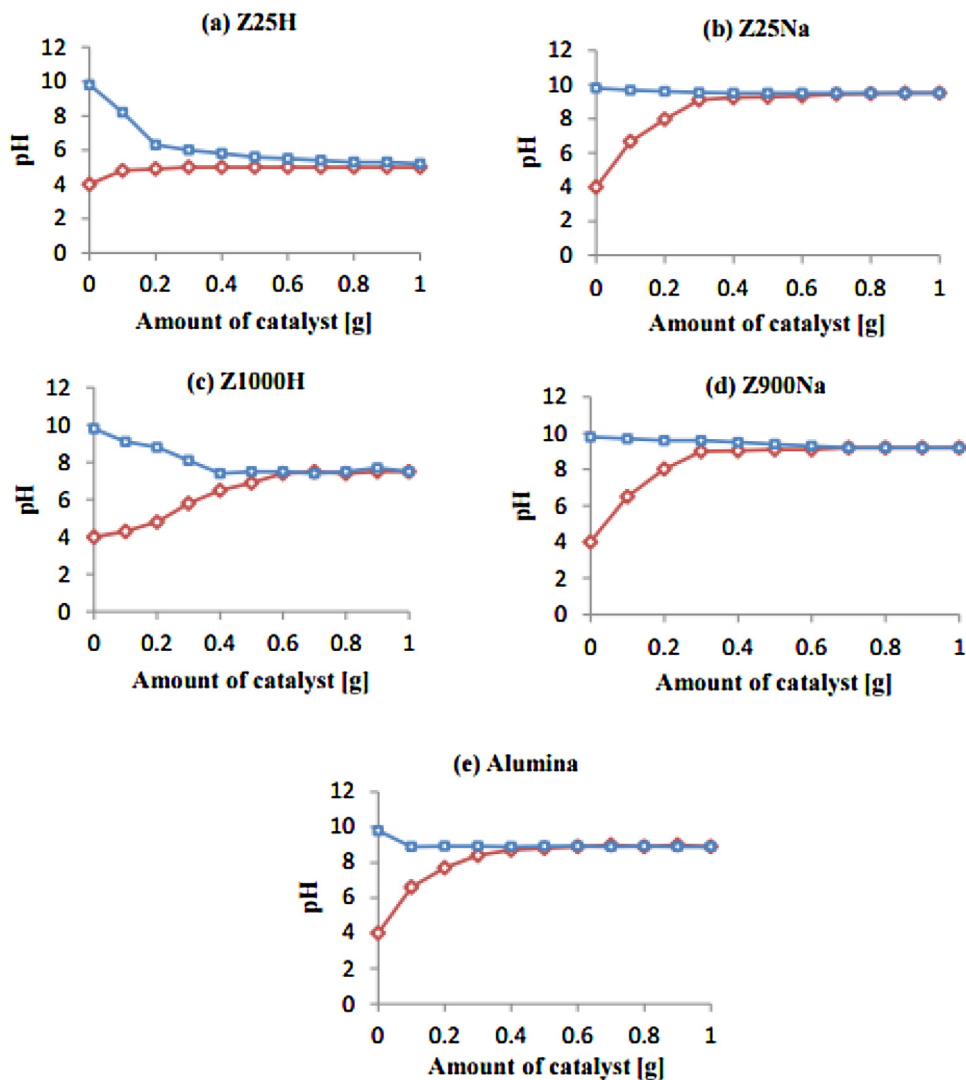
Different types of pollutants have been used to study the catalytic ozonation process in the presence of zeolites and alumina. There are however several, often contradictory, views on the catalytic activity of both catalysts. Some reports suggested that these catalysts do not decompose aqueous ozone [5,6,21]. However, others have hypothesised that both zeolites and alumina catalyse the decomposition of ozone leading to the production of hydroxyl radicals [15,17,22–25]. It is important to mention here that a lack of ozone decomposition does not indicate a lack of catalytic activity [16]. Some reports have suggested that Lewis and Bronsted acid sites of zeolites play a vital role in ozone decomposition leading to the production of hydroxyl radicals [15,25]. However, according to

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Table 1
Physical properties of alumina and zeolites [3].

Material	SiO ₂ (wt%)	Al ₂ O ₃ (wt%)	SiO ₂ /Al ₂ O ₃ mol ratio	Surface area (m ² /g)	Average pore size (Å)	Point of zero charge
γ-alumina	0	100	–	190	47.8	8.9 ± 0.1
Z25H	90	5.4	30 ± 5	300	5.3	5.0 ± 0.2
Z1000H	99	0.1	1000 ± 5	300	5.3	7.5 ± 0.2
Z900Na	98	5.4	900 ± 5	300	5.3	9.2 ± 0.1
Z25Na	90	0.2	30 ± 5	300	5.3	9.5 ± 0.1

**Fig. 1.** Point of zero charge (pH_{pzc}) of ZSM-5 zeolites and alumina (Catalyst = 0.1–1.0 g; $T = 25^\circ\text{C}$; electrolyte $\text{NaCl} = 10^{-3} \text{ mol/dm}^3$; $V = 190 \text{ mL}$).

some recent findings, ZSM-5 zeolites do catalyse the degradation of pollutants by molecular ozone reactions with pollutants [4,6]. Furthermore, it has been suggested that adsorption of pollutants plays an important role in the catalytic ozonation process [9,13]. Studies of the catalytic activity of alumina indicate that alumina does show catalytic activity for the degradation of certain pollutants [13,17,26], while it does not catalyse the removal of other pollutants such as hydrocarbons [17,19,27]. Recently, Nawrocki et al. [11] suggested that alkaline impurities present in alumina oxides may be responsible for ozone decomposition and hydroxyl radicals generation [10]. Therefore, it is important to monitor pH during the catalytic ozonation process.

This paper aims to provide further understanding of the mechanisms of ozonation of volatile organic chemicals (VOCs) such as cumene, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene on zeo-

lites and alumina. For this purpose a comparative study has been conducted to verify the removal of cumene and chlorobenzenes from water. Chlorinated aromatic compounds are highly toxic, widely used and are known to be highly resistant to ozonation as compared to non-chlorinated compounds (benzene) [29]. This may be due to the steric effects of attached chlorinated groups. This paper is a continuation of our previous studies which concerned the removal of VOCs in the presence of zeolites [6] and alumina [17]. It has been hypothesised that zeolites catalysed the removal of VOCs by direct ozone attack on the surface of zeolites [6]. Alumina was found to be ineffective in the degradation of VOCs [17]. The present study focusses on new important aspects of catalytic ozonation, which are key to fully understanding the catalytic process. These include mechanistic studies of VOCs decomposition and chloride ions (Cl^-) formation during the catalytic ozonation process in the

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