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

Amir Ikhlaq^{a, b}, Barbara Kasprzyk-Hordern^{c,1}

^aUniversity of Huddersfield, Department of Chemical and Biological Sciences, School of Applied Sciences, Queensgate, Huddersfield HD1 3DH, UK

^bUniversity of Engineering and Technology, Institute of Environmental Engineering and Research, Lahore, Pakistan

^cUniversity of Bath, Department of Chemistry, Faculty of Science, Bath BA2 7AY, UK

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.

Keywords: catalytic ozonation, VOCs, zeolites, alumina, chlorides

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 findings 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].

¹Corresponding author: E-mail: b.kasprzyk-hordern@bath.ac.uk; Fax: +44(0) 1225 386231; Tel: +44 (0) 1225 385013

1 However, others have hypothesised that both zeolites and alumina catalyse the decomposition of ozone
2 leading to the production of hydroxyl radicals [15, 17, 22-25]. It is important to mention here that a lack
3 of ozone decomposition does not indicate a lack of catalytic activity [16]. Some reports have suggested
4 that Lewis and Bronsted acid sites of zeolites play a vital role in ozone decomposition leading to the
5 production of hydroxyl radicals [15, 25]. However, according to some recent findings, ZSM-5 zeolites
6 do catalyse the degradation of pollutants by molecular ozone reactions with pollutants [4, 6].
7 Furthermore, it has been suggested that adsorption of pollutants plays an important role in the catalytic
8 ozonation process [9, 13]. Studies of the catalytic activity of alumina indicate that alumina does show
9 catalytic activity for the degradation of certain pollutants [13, 17, 26], while it does not catalyse the
10 removal of other pollutants such as hydrocarbons [17, 19, 27]. Recently, Nawrocki et al [11] suggested
11 that alkaline impurities present in alumina oxides may be responsible for ozone decomposition and
12 hydroxyl radicals generation [10]. Therefore, it is important to monitor pH during the catalytic ozonation
13 process.

14 This paper aims to provide further understanding of the mechanisms of ozonation of volatile organic
15 chemicals (VOCs) such as cumene, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene on zeolites and
16 alumina. For this purpose a comparative study has been conducted to verify the removal of cumene and
17 chlorobenzenes from water.. Chlorinated aromatic compounds are highly toxic, widely used and are
18 known to be highly resistant to ozonation as compared to non-chlorinated compounds (benzene) [29].
19 This may be due to the steric effects of attached chlorinated groups. This paper is a continuation of our
20 previous studies which concerned the removal of VOCs in the presence of zeolites [6] and alumina [17].
21 It has been hypothesised that zeolites catalysed the removal of VOCs by direct ozone attack on the
22 surface of zeolites [6]. Alumina was found to be ineffective in the degradation of VOCs [17]. The present
23 study focusses on new important aspects of catalytic ozonation, which are key to fully understanding the
24 catalytic process. These include mechanistic studies of VOCs decomposition and chloride ions (Cl⁻)
25 formation during the catalytic ozonation process in the presence of zeolites and alumina. The monitoring
26 of the generation of chloride ions in ozonation and catalytic ozonation processes may further help to
27 study the actual degradation of chlorinated organic compounds during the catalytic process [30].
28 Additionally, VOCs decomposition rates and chlorides generation have been studied in the presence of
29 TBA, a hydroxyl radical scavenger to further understand the catalytic process. Furthermore, the rate
30 equations have been calculated to investigate the order of reactions. In order to verify the catalytic
31 processes occurring on alumina and zeolites, the effect of initial pH and the effect of hydroxyl radical
32 scavengers on the removal of VOCs and generation of chloride ions have also been investigated.

33 2. Experimental

34 2.1 Materials and reagents

35 The ZSM-5 zeolites were supplied by Zeochem Switzerland and γ -alumina was supplied by Alcoa Inc,
36 USA. VOCs were obtained from Sigma-Aldrich. All chemicals were of analytical grade and were used
37 without further purification.

38 2.2 Ozonation experiments

39 Ozonation experiments were performed in a semi-continuous mode at room temperature (20°C) (column
40 length, 70 cm; width, 51 mm; catalyst bed height, 5 cm) [6]. Possible loss of VOCs due to volatilization
41 was also determined. A saturated solution (490 mL) of VOCs was used in the ozonation experiments
42 and was prepared by directly spiking of VOCs to a flask containing 1 L of ultrapure water [6]. VOCs
43 solution (cumene, 19.1 ± 0.5 mg/L; 1,2-dichlorobenzene, 3.5 ± 0.3 mg/L; 1,2,4-trichlorobenzene, $0.5 \pm$
44 0.1 mg/L) was transferred to the column containing 5.0 g of catalyst, and was recirculated at a flow rate
45 of 15 mL/min over the period of 30 minutes. Ozone was produced by a corona discharge method from
46 pure oxygen by AZCO HTU-5000GE-120 ozone generator. By the aid of a ceramic sparger, ozone was
47 continuously bubbled through the column at a flow rate of 0.1 mL/min. Samples were collected at 5

1 minutes intervals and quenched with 0.025M Na₂SO₃ in order to remove residual ozone. All the samples
2 were filtered (PTFE 0.45 µm syringe filter) prior to the analysis.

3 **2.3. Analytical procedures**

4 **2.3.1. Ozone dose**

5 Gas phase ozone concentrations were determined by the iodometric method [31]. For this purpose the
6 gaseous ozone was bubbled through a ceramic sparger into two sets of glass bottles, each filled with 200
7 mL of 2% KI [31]. Solutions were acidified with 10 mL of 1N HCl and the liberated iodine was titrated
8 with standard 0.005N Na₂S₂O₃ using a starch indicator.

9 **2.3.2. Analysis of VOCs**

10 VOCs were quantified by gas chromatography coupled with mass spectrophotometry (GC/MS, Agilent)
11 as described previously [6]. The method was validated. The RSD was found to be less than 5 %.

12 **2.3.3. Analysis of chloride ions**

13 Chlorides concentrations were determined by ion chromatography using a DIONEX DX-120 system
14 with Ion Pac As14 analytical column (4 × 250 mm) and Ion Pac AG14 guard column (4 × 250 mm)
15 coupled to an ED-50A electrochemical detector (Dionex, USA). The limits of detection and
16 quantification for phosphates were 0.05 ppm and 0.2 ppm respectively. The RSD was less than 5 %.

17 **3. Results and discussion**

18 **3.1. Physicochemical properties of zeolites and alumina**

19 Data regarding physical properties of zeolites were obtained from Zeochem Switzerland (Table 1). The
20 point of zero charge (pH_{PZC}) of zeolites and alumina were determined using potentiometric mass titration
21 method [32]. The point of zero charge of alumina was found to be 8.9 while the point of zero charge of
22 zeolites ranged from 5 to 9.5 (Fig 1). The average pore size was found to be 47.8 Å and the surface area
23 of alumina used was 190 m²/g.

24 **3.2. Catalytic ozonation of VOCs**

25 **3.2.1. Kinetic study**

26 Catalytic ozonation of VOCs on alumina and ZSM-5 zeolites with different silica to alumina ratios were
27 studied at selected pH values: 3.0, 6.2 and 13.0. The results presented in Figure 2 show that alumina
28 does not have catalytic activity for VOCs, while ZSM-5 zeolites show significant catalytic activity
29 especially at pH 3 (Figure 2).

30 Kinetic studies of catalytic ozonation for the removal of cumene, 1,2- dichlorobenzene and 1,2,4-
31 trichlorobenzene were undertaken (Table 2). The catalytic process was found to follow the first order
32 kinetics as indicated by the linear regression values in Figure 4. Therefore, first order rate constants for
33 the removal of VOCs have been determined (Table 2). The results clearly indicate that VOCs
34 decomposition rates are higher in the case of catalytic ozonation in the presence of zeolites (Table 2)
35 when compared with single ozonation and ozonation in the presence of alumina (at pH 3 and 6.2). For
36 example, first order decomposition rate constant for dichlorobenzene was calculated to be 15 times
37 higher in the case of ozonation on zeolites when compared with ozonation alone (Table 2). The results
38 further show that the rate constant values for ozonation in the presence of zeolites were found to be the
39 highest at pH 3 when compared with pH 6.2 and 13 (Table 2). This may be due to the stability of
40 molecular ozone at low pH which results in its higher adsorption on the zeolites surface, and which
41 subsequently leads to faster decomposition of adsorbed pollutants [6]. It is worth noting that zeolites
42 having higher silica to alumina ratios (Z1000H, Z900Na) are found to be more affective when compared
43 with those with lower silica to alumina ratio (Z25H, Z25Na). This phenomenon can be explained by
44 higher hydrophobicity of high silica zeolites leading to higher sorption of VOCs on their surfaces [12].

1 The results further show that higher decomposition rates on zeolites at pH 3.0 were observed for cumene
2 when compared with chlorobenzenes. For example, the rate constant for VOCs degradation on
3 Z1000H/O₃ at pH 3.0 was $9.55 \times 10^{-2} \text{ min}^{-1}$, $8.17 \times 10^{-2} \text{ min}^{-1}$, $8.21 \times 10^{-2} \text{ min}^{-1}$ for cumene,
4 dichlorobenzene and trichlorobenzene respectively (Table 2). This may be due to higher adsorption of
5 cumene on studied zeolite when compared with chlorobenzenes [6]. Other explanation could be that
6 chlorinated VOCs may be more resistant to ozone attack due to steric effects.

7 Previous kinetic studies [17] on heterogeneous process in the presence of alumina indicated that surface
8 reactions are important in the catalytic process. Therefore, it is hypothesised that adsorption on the
9 surface of the catalyst is vital in the catalytic ozonation process [17]. Furthermore, we postulate that
10 molecular ozone reactions are fundamental to achieving effective VOCs oxidation with ozone while
11 using zeolites as catalysts. It is important to mention here that ozone decay rates in the absence of
12 pollutants were investigated by our group in previous studies [4]. The results indicated that alumina
13 possesses high aqueous ozone decomposition rates when compared with zeolites. However,
14 interestingly, in this work alumina did not show any significant catalytic activity for VOCs removal.
15 This may be due to the lack of adsorption of VOCs on alumina. In our previous work, we reported that
16 adsorption of studied VOCs on alumina [17], as opposed to ZSM-5 zeolites [6], is limited. Furthermore,
17 as already mentioned, zeolites with high silica to alumina ratios have higher adsorption capacity towards
18 VOCs. This is in correlation with our results which indicates that high silica zeolites (Z1000H, Z900Na)
19 show higher catalytic activity as compared with low silica zeolites (Z25H, Z25Na). Qi et al [11] has
20 recently studied the catalytic ozonation of phenacetin on manganese ferrite and nickel ferrite. It was
21 observed that adsorption of a pollutant and its intermediates play an important role in catalytic ozonation
22 process. It was suggested that possible desorption of the pollutant and its intermediates from the surface
23 of manganese ferrite may be one of the reasons for its lower catalytic activity as compared with nickel
24 ferrite. This further supports our hypothesis that adsorption plays a key role in the catalytic ozonation
25 process. The other explanation could be that molecular ozone reactions are favoured in the case of
26 studied VOCs which agrees with our hypothesis that VOCs ozonation on zeolites occurs via molecular
27 ozone reactions.

28 3.2.2. pH changes during the ozonation and catalytic ozonation process

29 The presence of contaminants on the catalysts may change the initial pH of water and hence can affect
30 the experimental results. It has been recently reported that alkaline contaminants present on the surface
31 of alumina lead to higher ozone decomposition in the presence of alumina when compared with
32 ozonation alone [11]. Therefore, it is important to monitor pH during the ozonation and catalytic
33 ozonation process. In this study pH changes were studied in the presence of pollutants. The results
34 presented in Figure 3 indicate that despite small variations from initial pH no significant change in pH
35 ($\text{pH}_0 \pm 0.3$) was observed during ozonation alone and catalytic ozonation on ZSM-5 zeolites and
36 alumina. It can be therefore concluded that observed negligible variations of pH during catalytic
37 ozonation do not affect the overall process.

38 3.2.3 Formation of chloride ions

39 The formation of chlorides was studied during catalytic ozonation of VOCs (cumene, 1,2-
40 dichlorobenzene and 1,2,4-trichlorobenzene) on alumina and ZSM-5 zeolites at selected pH values. The
41 formation of chlorides during ozonation and catalytic ozonation processes may help to verify
42 degradation of VOCs, which may further lead to better understanding of mechanisms governing both
43 catalytic systems [30]. The results presented in Figure 5 show that the formation of chlorides in the case
44 of ozonation in the presence of alumina was very low when compared with zeolites. This may be due to
45 the low adsorption of chlorinated VOCs on alumina [17]. As previous findings indicate [17], surface
46 reactions are considered to be important in the effective degradation of pollutants on alumina. Low
47 formation of chlorides during ozonation on alumina might be also linked with the fact that alumina

1 facilitates ozone decomposition but molecular ozone reactions are favoured in the case of VOCs
2 degradation. Among the zeolites, high silica zeolites (Z1000H, Z900Na) showed significantly higher
3 chlorides formation (Figure 5). This clearly suggests that high silica zeolites lead to higher degradation
4 of chlorinated VOCs when compared with their low silica equivalents (Z25H, Z25Na). From these
5 results it can be hypothesized that adsorption of pollutants on the surface of the catalyst is a critical stage
6 of the catalytic process [5]. The results further indicated that at pH 13.0 the chlorides formation was
7 similar to single ozonation (Fig 5). This may be due to the lack of catalytic activity at this pH [14]. It is
8 also important to mention that no significant change in the pH of solution was observed in all
9 experiments throughout 30 minutes reaction time.

10 **3.4. Mechanisms of catalytic ozonation**

11 **3.4.1 Effect of tert-butyl alcohol on the VOCs removal rates**

12 A comparative study of VOCs ozonation has been conducted on a selected zeolite (Z1000H), alumina
13 and using ozonation alone in the presence and absence of tert-butyl alcohol (TBA). Pseudo first order
14 VOC decomposition rate constants are presented in Tables 2 and 3. The results clearly indicate that
15 VOCs removal on Z1000H/O₃ remained unaffected in the presence of TBA (Table 2, 3). However, in
16 the case of alumina conclusive results have not been obtained, as there was no significant removal of
17 VOCs in the case of alumina as compared to ozonation alone (Table 2, 3). This may be due to the lack
18 of adsorption of VOCs on alumina's surface [17].

19 It is important to highlight here that the lack of catalytic activity at pH 13 for both zeolites and alumina
20 is to be expected as at a higher pH, due to the presence of hydroxide ions, free hydroxyl radicals are
21 more readily formed. Such observations indicating the inhibition of catalytic activity of zeolites and
22 alumina have been reported in previous studies [6, 14, 17].

23 **3.4.2 Effect of tert-butyl alcohol on the formation of chloride ions**

24 In order to investigate the mechanism of catalytic ozonation in the presence of zeolites and alumina, the
25 formation of chlorides as a result of degradation of the chlorinated compounds was investigated in the
26 presence and absence of TBA. The results presented in Figure 6 show that formation of chlorides as a
27 result of ozonation of chlorinated VOCs on Z1000H was not affected to a high extent in the presence of
28 TBA at pH 3 and 6.2. For example, the concentration of chlorides was 1.6 mg/L after 30 minutes when
29 solution was ozonated on Z1000H at pH 6.2 and it was 1.5 mg/L in the presence of TBA under similar
30 conditions. In contrast to experiments undertaken at pH 3 and 6.2, formation of chlorides was reduced
31 in Z1000H/O₃ at pH 13 (Figure 6). For example, the concentration of chlorides was about 1.1 mg/L and
32 it was reduced to 0.44 mg/L in the presence of TBA after 30 minutes. Interestingly, similar decrease in
33 the chlorides formation was observed in the presence of TBA in both catalytic and single ozonation
34 experiments (Figure 6). This suggests that the decrease of chlorides formation in the case of Z1000H/O₃
35 at pH 13.0 takes place, similarly to ozonation alone, due to the influence of scavenging effect of TBA
36 on radicals produced in bulk solution. It is also important to emphasise that a significant reduction in
37 chlorides formation was also observed at pH 6.2 in the case of Al₂O₃/O₃ (for example the concentration
38 of chlorides was 0.66 mg/L after 30 minutes without TBA and it was 0.34 mg/L in the presence of TBA
39 at pH 6.2, Figure 6). These results further support our hypothesis that ozonation in the presence of
40 alumina operates through the radical mechanism while ZSM-5 zeolites facilitate degradation of VOCs
41 through molecular ozone reactions on their surface. It is important to mention here that the above
42 hypothesis is in agreement with recent findings [6, 17].

43 **3.4.3 Proposed mechanism**

44 Previous studies on VOCs ozonation indicate that zeolites catalyse the removal of VOCs when compared
45 with ozonation alone. In contrast, alumina does not remove VOCs [6, 17]. However, it is important to
46 mention, that some reports imply that alumina does catalyse the removal of VOCs in water [18, 20]. It

1 was reported that adsorption of pollutants on the alumina surface was found to be an important step in
2 the catalytic process [20]. In current study the lack of catalytic activity of alumina towards VOCs
3 (cumene, dichlorobenzene and trichlorobenzene) may be due to the lack of adsorption of studied VOCs
4 on alumina's surface [17]. The results presented in this work provide further evidence. The significantly
5 higher concentrations of chlorides formed in the presence of ZSM-5 zeolites when compared with
6 ozonation alone and ozonation on alumina clearly suggest that zeolites catalyse the degradation of
7 VOCs. Furthermore, the concentration of chlorides during VOCs ozonation on zeolites in the presence
8 of hydroxyl radical scavengers (TBA) was found not to remain constant when compared with ozonation
9 on zeolites without TBA. This clearly suggested that zeolites do not promote ozone decomposition
10 leading to the formation of hydroxyl radicals. Furthermore, it was found that catalytic activity of zeolites
11 was the highest in the case of zeolites with high silica content. This may be due to high adsorption of
12 VOCs on the surface of zeolites followed by their reactions with molecular ozone [5, 6]. The mechanism
13 of catalytic ozonation in the presence of zeolites has been proposed (based on this and previous findings)
14 as indicated in Figure 7. It clearly indicates that adsorption of VOCs plays a vital role in the catalytic
15 ozonation process.

16 In contrast to zeolites, ozonation on alumina does not lead to increased generation of chlorides when
17 compared with ozonation alone at studied pH values. This may be due to the lack of adsorption of VOCs
18 on the alumina surface. Surface reactions are considered to be important in the catalytic ozonation
19 process. This suggests that alumina may not be an effective catalyst for the removal of studied VOCs.
20 This is in agreement with some of the previous findings [17]. Previous reports have also indicated that
21 alumina may decompose aqueous ozone leading to the production of active oxygen species [14, 22, 24].
22 It is further reported that surface hydroxyl groups may be the active sites [14, 22, 24]. However, some
23 reports have contradicted this and suggested that aqueous ozone is not decomposed by alumina [21]. Qi
24 et al [23] confirmed that alumina promotes the generation of hydroxyl radicals but the group claimed
25 that surface hydroxyl groups of alumina do not interact with ozone. Other reports further suggested that
26 molecular ozone reactions may be involved [9, 16]. The results presented in this work clearly indicate
27 that alumina is not an effective catalyst for studied VOCs and this may be due to the lack of adsorption
28 of VOCs on alumina's surface. The lack of generation of chlorides on alumina in comparison with
29 zeolites further supports this hypothesis.

30 **4. Conclusions**

31 The following are the main conclusions.

- 32 1. ZSM-5 zeolites, as opposed to alumina, are the effective catalysts of VOCs degradation during
33 ozonation. The surface reactions were found to be important in the catalytic ozonation process
- 34 2. The ZSM-5 zeolites with high silica to alumina ratios were found to be more effective in the
35 decomposition of VOCs when compared to low silica zeolites.
- 36 3. Catalytic ozonation on ZSM-5 zeolites proceeds via direct attack of molecular ozone on the
37 adsorbed chlorinated pollutants leading to the generation of chlorides.
- 38 4. TBA, a hydroxyl radical scavenger, does not influence catalytic activity of zeolites.
- 39 5. The decomposition of pollutants occurs via pseudo first order kinetics.

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42 University of Huddersfield (United Kingdom) is gratefully acknowledged.

43 **References**

- 44 [1] A.A. Goncalves, Brazilian Archives Of Biology and Technology 52 (2009) 1527-1539.[2] P.C.C. Faria, J.J.M.
45 Órfão, M.F.R. Pereira, Applied Catalysis B: Environmental 79 (2008) 237-243.
- 46 [3] T. Merle, J.S. Pic, M.H. Manero, S. Mathé, H. Debellefontaine, Catalysis Today 151 (2010) 166-172.

- 1 [4] A. Ikhlaq, D.R. Brown, B. Kasprzyk-Hordern, *Applied Catalysis B: Environmental* 123–124 (2012) 94-106.
2 [5] H. Fujita, J. Izumi, M. Sagehashi, T. Fujii, A. Sakoda, *Water Research* 38 (2004) 166-172.
3 [6] A. Ikhlaq, D.R. Brown, B. Kasprzyk-Hordern, *Applied Catalysis B: Environmental* 154–155 (2014) 110-122.
4 [7] D.H. Quiñones, A. Rey, P.M. Álvarez, F.J. Beltrán, P.K. Plucinski, *Applied Catalysis B: Environmental* 144 (2014)
5 96-106.
6 [8] F.J. Beltrán, F.J. Rivas, R. Montero-de-Espinosa, *Applied Catalysis B: Environmental* 39 (2002) 221-231.
7 [9] J. Nawrocki, *Applied Catalysis B: Environmental* 142–143 (2013) 465-471.
8 [10] J. Nawrocki, L. Fijołek, *Applied Catalysis B: Environmental* 142–143 (2013) 533-537.
9 [11] F. Qi, B. Xu, W. Chu, *Journal of Molecular Catalysis A: Chemical* 396 (2015) 164-173.
10 [12] J. Reungoat, J.S. Pic, M.H. Manéro, H. Debellefontaine, *Separation Science and Technology* 42 (2007) 1447-1463.
11 [13] M. Ernst, F. Lurot, J.-C. Schrotter, *Applied Catalysis B: Environmental* 47 (2004) 15-25.
12 [14] A. Ikhlaq, D.R. Brown, B. Kasprzyk-Hordern, *Applied Catalysis B: Environmental* 129 (2013) 437-449.
13 [15] H. Valdés, R.F. Tardón, C.A. Zaror, *Chemical Engineering Journal* 211–212 (2012) 388-395.
14 [16] B. Kasprzyk-Hordern, U. Raczek-Stanisławiak, J. Świetlik, J. Nawrocki, *Applied Catalysis B: Environmental* 62
15 (2006) 345-358.
16 [17] A. Ikhlaq, D.R. Brown, B. Kasprzyk-Hordern, *Applied Catalysis B: Environmental* 165 (2015) 408-418.
17 [18] J. Vittenet, W. Aboussaoud, J. Mendret, J.-S. Pic, H. Debellefontaine, N. Lesage, K. Faucher, M.-H. Manero, F.
18 Thibault-Starzyk, H. Leclerc, A. Galarneau, S. Brosillon, *Applied Catalysis A: General* 504 (2015) 519-532.
19 [19] B. Kasprzyk, J. Nawrocki, *Ozone: Science & Engineering* 24 (2002) 63-68.
20 [20] W. Aboussaoud, M.-H. Manero, J.-S. Pic, H. Debellefontaine, *Ozone: Science & Engineering* 36 (2014) 221-228.
21 [21] J. Lin, A. Kawai, T. Nakajima, *Applied Catalysis B: Environmental* 39 (2002) 157-165.
22 [22] F. Qi, Z. Chen, B. Xu, J. Shen, J. Ma, C. Joll, A. Heitz, *Applied Catalysis B: Environmental* 84 (2008) 684-690.
23 [23] F. Qi, B. Xu, Z. Chen, L. Feng, L. Zhang, D. Sun, *Chemical Engineering Journal* 219 (2013) 527-536.
24 [24] F. Qi, B. Xu, Z. Chen, J. Ma, D. Sun, L. Zhang, *Separation and Purification Technology* 66 (2009) 405-410.
25 [25] N. Brodu, M.-H. Manero, C. Andriantsiferana, J.-S. Pic, H. Valdés, *Chemical Engineering Journal* 231 (2013) 281-
26 286.
27 [26] C.A. Guzman-Perez, J. Soltan, J. Robertson, *Journal of Environmental Science and Health, Part B* 47 (2012) 544-552.
28 [27] B. Kasprzyk-Hordern, P. Andrzejewski, A. Dbrowska, K. Czaczyk, J. Nawrocki, *Applied Catalysis B: Environmental*
29 51 (2004) 51-66.
30 [28] H.S. Brown, D.R. Bishop, C.A. Rowan, *American Journal of Public Health* 74 (1984) 479-484.
31 [29] Y. Pi, L. Zhang, J. Wang, *Journal of Hazardous Materials* 141 (2007) 707-712.
32 [30] M. Lim, Y. Son, J. Khim, *Ultrasonics Sonochemistry* 18 (2011) 460-465.
33 [31] A.D. Eaton, L.S. Clesceri, E.W. Rice, A.E. Greenberg, *Standard methods for the examination of water & waste water*,
34 21 ed., (2005).
35 [32] K. Bourikas, J. Vakros, C. Kordulis, A. Lycourghiotis, *The Journal of Physical Chemistry B* 107 (2003) 9441-9451.

1 **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

Tables 2 First order decomposition rates of cumene, dichlorobenzene and trichlorobenzene in O₃, zeolites and Al₂O₃/O₃ processes.

Process	K _{overall} × (10 ⁻² min ⁻¹)								
	pH = 3.0			pH = 6.2			pH = 13.0		
	Cumene	Dichlorobenzene	Trichlorobenzene	Cumene	Dichlorobenzene	Trichlorobenzene	Cumene	Dichlorobenzene	Trichlorobenzene
O ₃	2.65±0.2 (R ² = 0.912)	1.95±0.3 (R ² = 0.953)	3.06±0.3 (R ² = 0.805)	3.03±0.2 (R ² = 0.933)	3.06±0.2 (R ² = 0.802)	3.28±0.2 (R ² = 0.897)	3.92±0.3 (R ² = 0.910)	5.86±0.3 (R ² = 0.909)	4.87±0.3 (R ² = 0.812)
Al ₂ O ₃ /O ₃	2.75±0.2 (R ² = 0.901)	1.60±0.2 (R ² = 0.939)	2.68±0.2 (R ² = 0.950)	3.00±0.3 (R ² = 0.916)	1.95±0.3 (R ² = 0.906)	2.89±0.3 (R ² = 0.820)	4.12±0.3 (R ² = 0.862)	5.27±0.2 (R ² = 0.901)	5.18±0.3 (R ² = 0.848)
Z25H/ O ₃	7.35±0.3 (R ² = 0.911)	6.33±0.3 (R ² = 0.743)	4.05±0.2 (R ² = 0.875)	3.46±0.2 (R ² = 0.867)	3.89±0.2 (R ² = 0.917)	4.05±0.2 (R ² = 0.904)	3.71±0.2 (R ² = 0.876)	3.73±0.3 (R ² = 0.832)	3.56±0.3 (R ² = 0.847)
Z1000H/ O ₃	9.55±0.3 (R ² = 0.930)	8.17±0.4 (R ² = 0.915)	8.21±0.3 (R ² = 0.884)	6.85±0.3 (R ² = 0.8904)	5.92±0.3 (R ² = 0.840)	6.35±0.2 (R ² = 0.879)	4.66±0.3 (R ² = 0.873)	6.14±0.3 (R ² = 0.903)	4.03±0.2 (R ² = 0.885)
Z25Na/ O ₃	5.62±0.3 (R ² = 0.980)	6.87±0.4 (R ² = 0.932)	3.09±0.3 (R ² = 0.883)	3.75±0.2 (R ² = 0.901)	3.76±0.4 (R ² = 0.806)	3.09±0.2 (R ² = 0.948)	4.34±0.4 (R ² = 0.887)	4.37±0.4 (R ² = 0.868)	2.6±0.3 (R ² = 0.757)
Z900Na/ O ₃	9.72±0.4 (R ² = 0.928)	8.35±0.4 (R ² = 0.949)	7.92±0.3 (R ² = 0.875)	5.97±0.3 (R ² = 0.883)	6.41±0.3 (R ² = 0.905)	6.81±0.3 (R ² = 0.908)	4.40±0.3 (R ² = 0.870)	5.69±0.5 (R ² = 0.776)	4.66±0.2 (R ² = 0.912)

Tables 3 Effect of TBA on the first order decomposition rates of cumene, dichlorobenzene and trichlorobenzene in O₃, zeolites and Al₂O₃/O₃ processes

Process	K _{overall} × (10 ⁻² min ⁻¹)								
	pH = 3.0			pH = 6.2			pH = 13.0		
	Cumene	Dichlorobenzene	Trichlorobenzene	Cumene	Dichlorobenzene	Trichlorobenzene	Cumene	Dichlorobenzene	Trichlorobenzene
O ₃ (TBA)	3.24±0.3	1.75±0.3	2.95±0.2	2.02±0.1	2.45±0.2	2.95±0.2	2.95±0.2	4.91±0.2	4.01±0.3
Al ₂ O ₃ /O ₃ (TBA)	3.01±0.3	1.68±0.2	2.54±0.2	2.03±0.2	1.81±0.3	2.61±0.2	3.12±0.2	4.65±0.2	3.85±0.2
Z1000H/O ₃ (TBA)	9.31±0.4	7.13±0.4	8.35±0.3	6.65±0.2	5.56±0.3	6.01±0.3	3.92±0.4	5.65±0.3	3.65±0.3

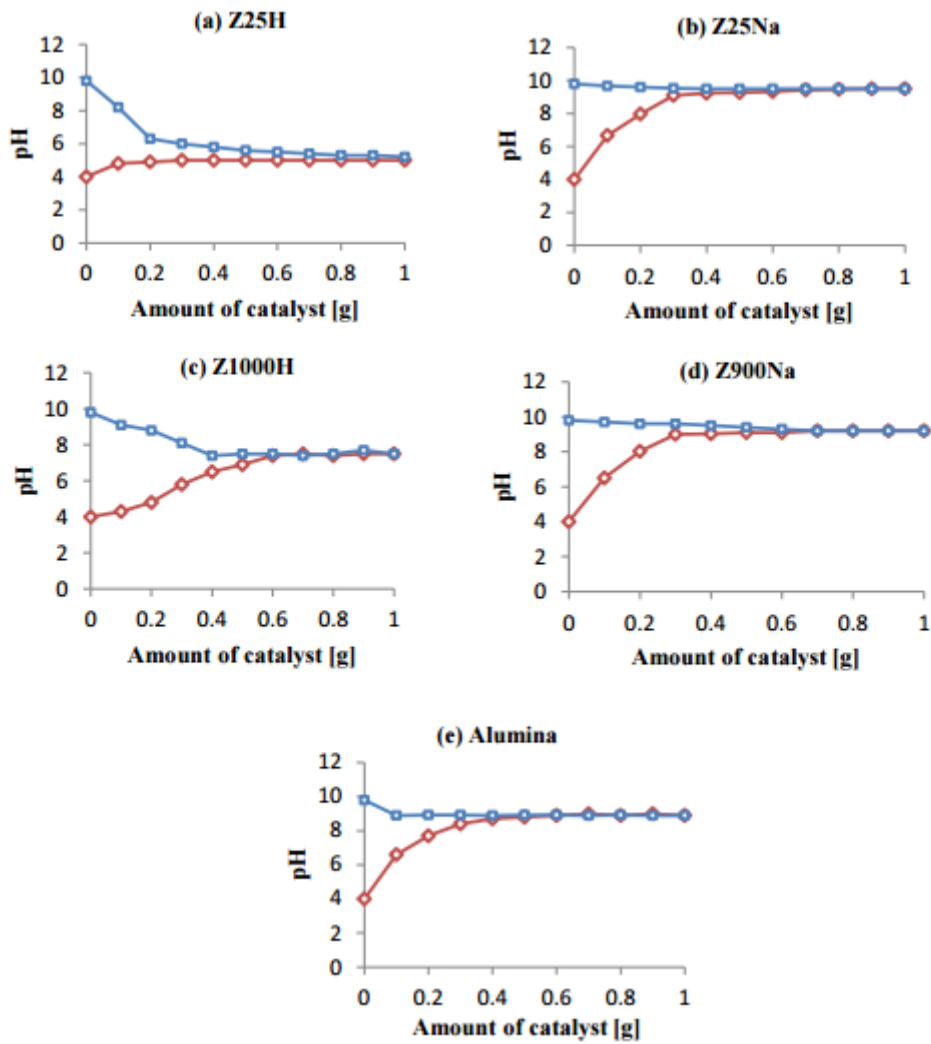


Figure 1 Point of zero charge (pH_{pzc}) of ZSM-5 zeolites and alumina (Catalyst = 0.1-1.0g; $T = 25^\circ\text{C}$; electrolyte $\text{NaCl} = 10^{-3} \text{ mol/dm}^3$; $V = 190 \text{ mL}$)

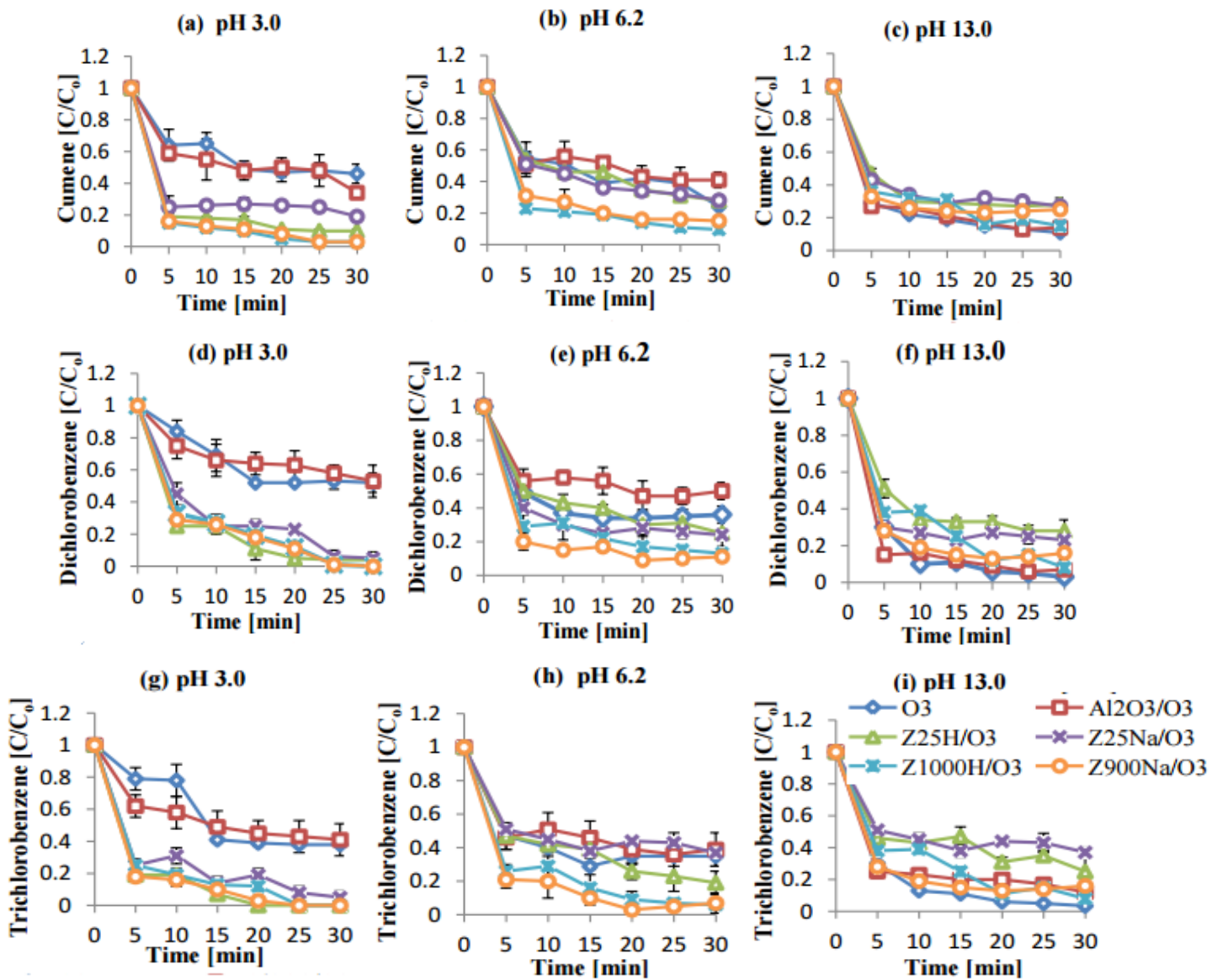


Figure 2 Effect of pH on VOCs removal by ozonation alone and ozonation in the presence of ZSM-5 zeolites and alumina (C_0 (cum) = 19.2 ± 0.5 mg/L, C_0 (DCB) = 3.5 ± 0.2 mg/L, and C_0 (TCB) = 0.5 ± 0.1 mg/L; $T = 20^\circ\text{C}$; pH = 3.0, 6.2 and 13.0; $\text{pH}_{30\text{min}} = \text{pH}_0 \pm 0.3$; catalyst amount = 5 g; $V = 490$ mL; $\text{O}_3 = 0.1$ mg/min) [5, 11].

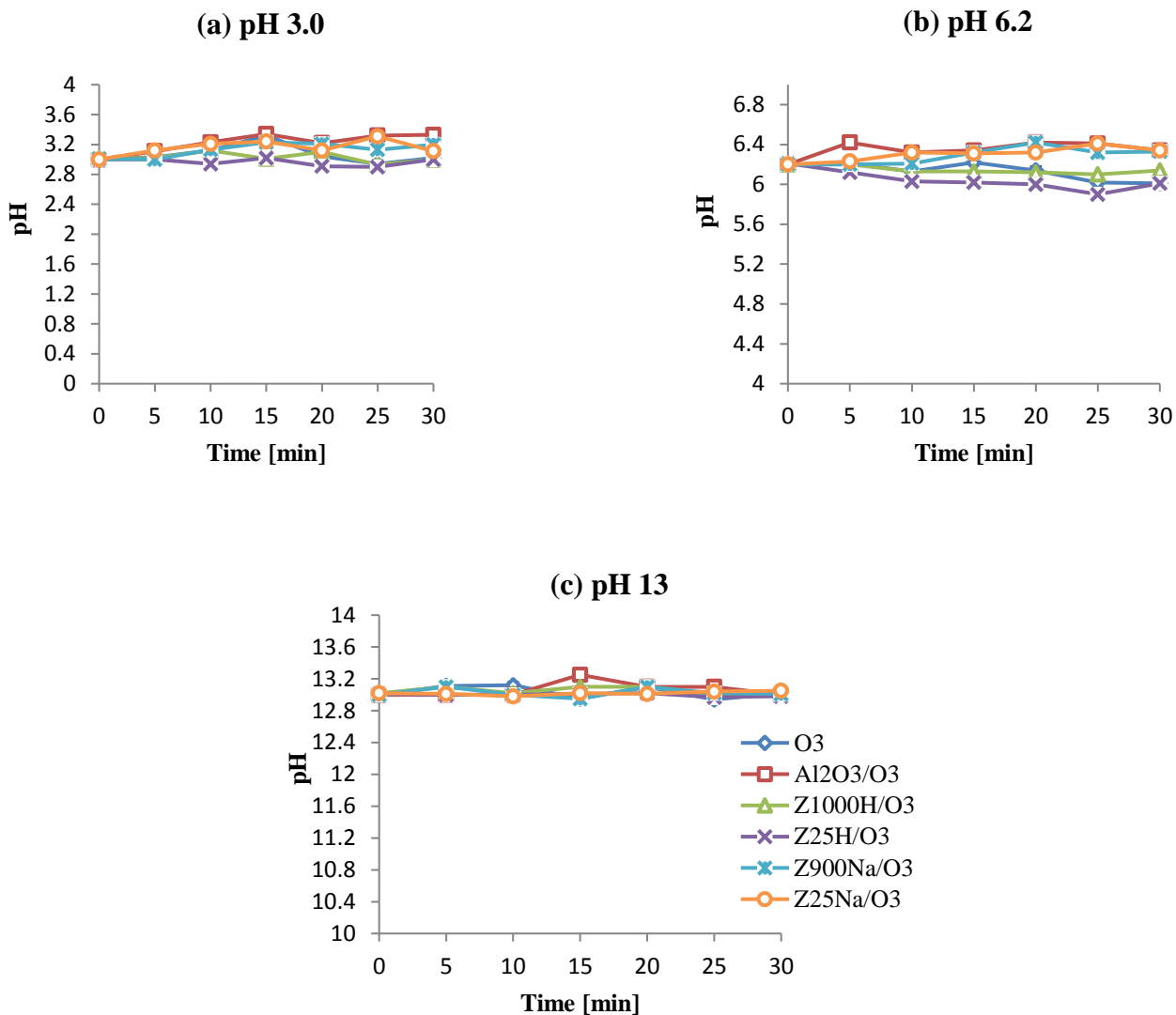


Figure 3 pH changes during the removal of VOCs by ozonation alone and ozonation in the presence of ZSM-5 zeolites and alumina (C_o (cum) = 19.2 ± 0.5 mg/L, C_o (DCB) = 3.5 ± 0.2 mg/L, and C_o (TCB) = 0.5 ± 0.1 mg/L; $T = 20^\circ\text{C}$; pH = 3.0, 6.2 and 13.0; $\text{pH}_{30\text{min}} = \text{pH}_o \pm 0.3$; catalyst amount = 5 g; $V = 490$ mL; $\text{O}_3 = 0.1$ mg/min).

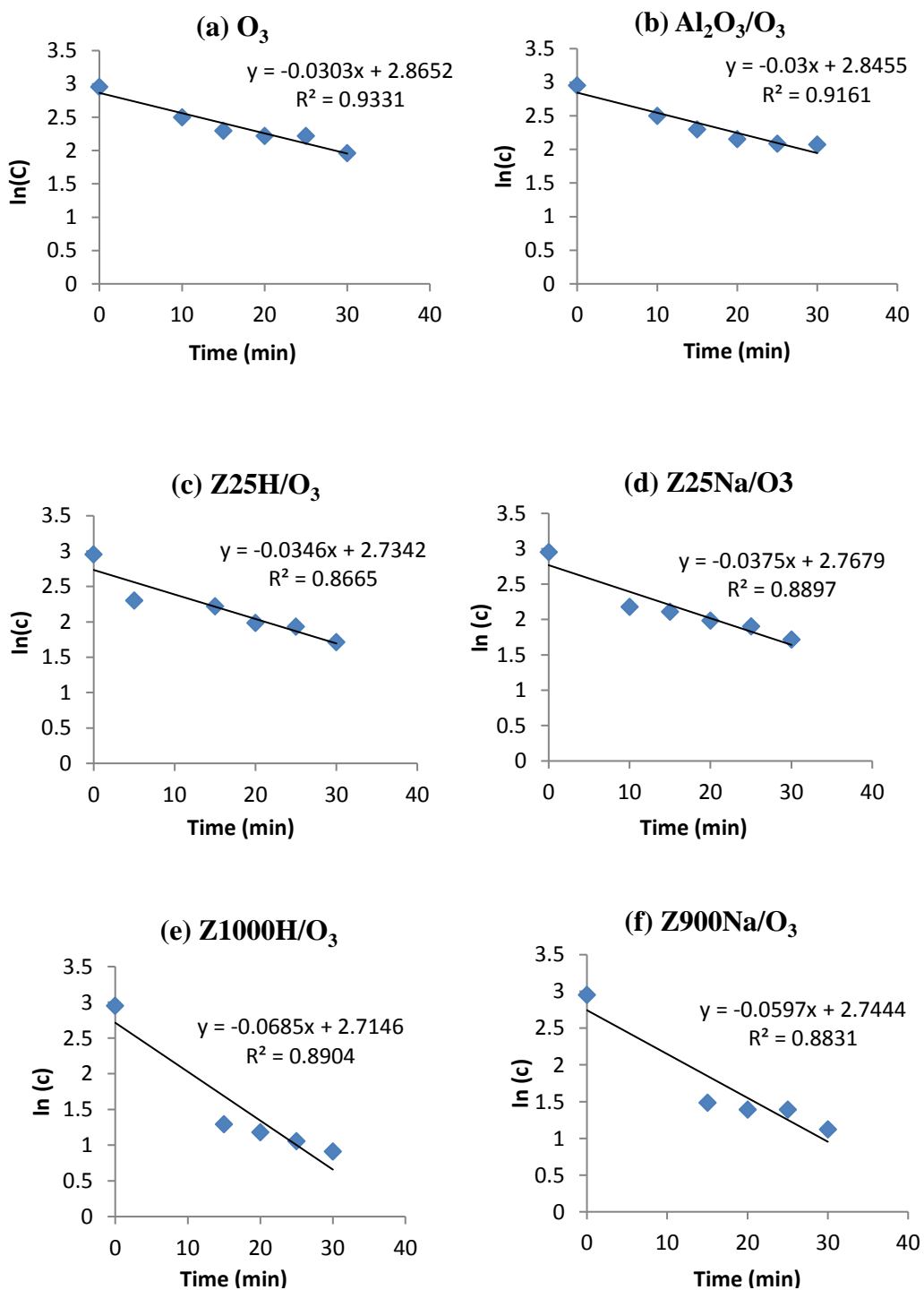


Figure 4 First order plots for the removal of cumene in ozonation alone and ozonation in the presence of ZSM-5 zeolites and alumina (C_0 (cum) = 19.2 ± 0.5 mg/L; $T = 20^\circ\text{C}$; $\text{pH} = 6.2$; catalyst amount = 5 g; $V = 490$ mL; $O_3 = 0.1$ mg/min).

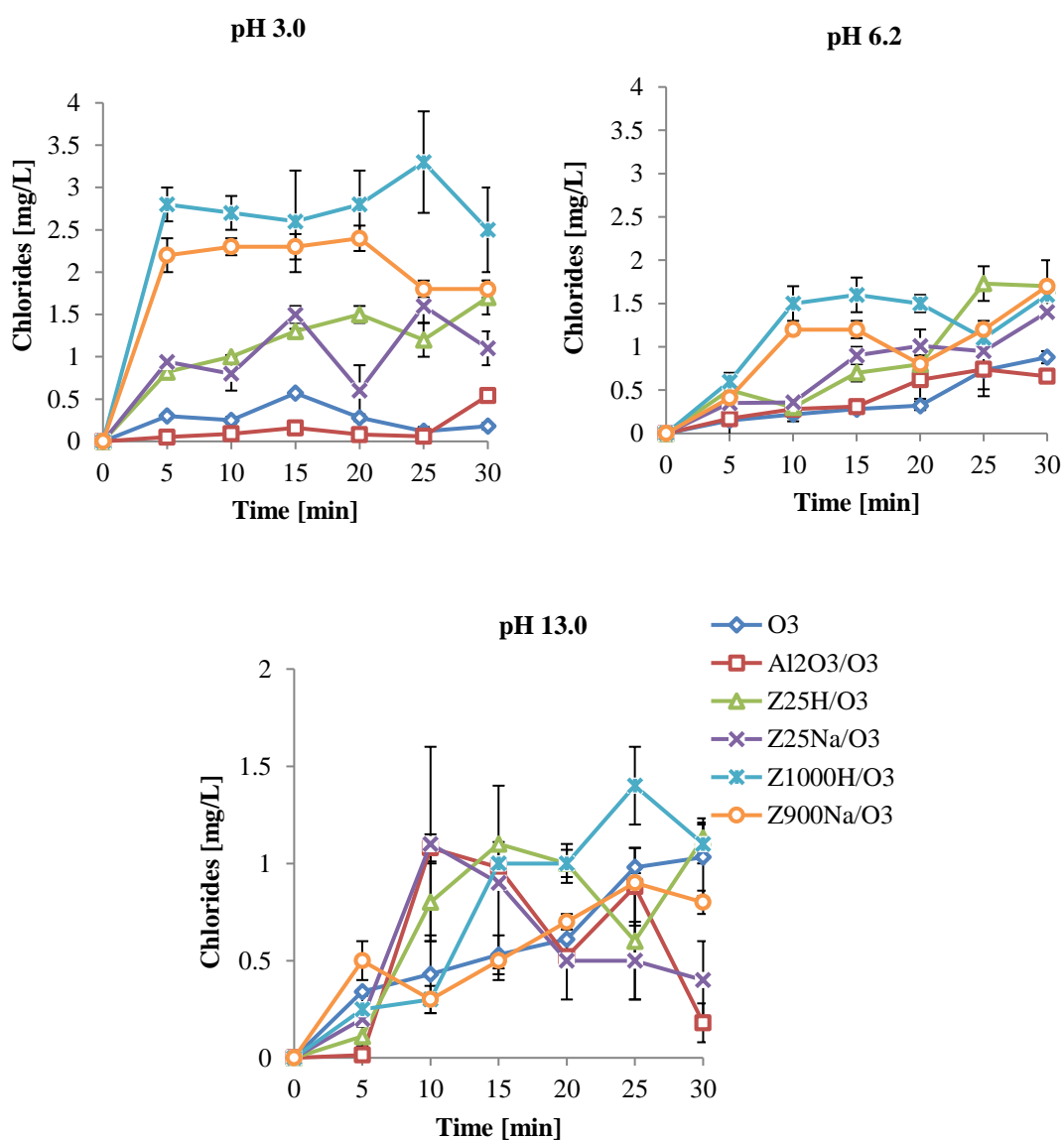


Figure 5 Effect of pH on chlorides formation during VOCs ozonation alone and ozonation in the presence of ZSM-5 zeolites and alumina (C_o (cum) = 19.2 ± 0.5 mg/L, C_o (DCB) = 3.5 ± 0.2 mg/L, and C_o (TCB) = 0.5 ± 0.1 mg/L; $T = 20^\circ\text{C}$; $\text{pH} = 3.0, 6.2$ and 13.0 ; $\text{pH}_{30\text{min}} = \text{pH}_0 \pm 0.3$; catalyst amount = 5 g; $V = 490$ mL; $\text{O}_3 = 0.1$ mg/min).

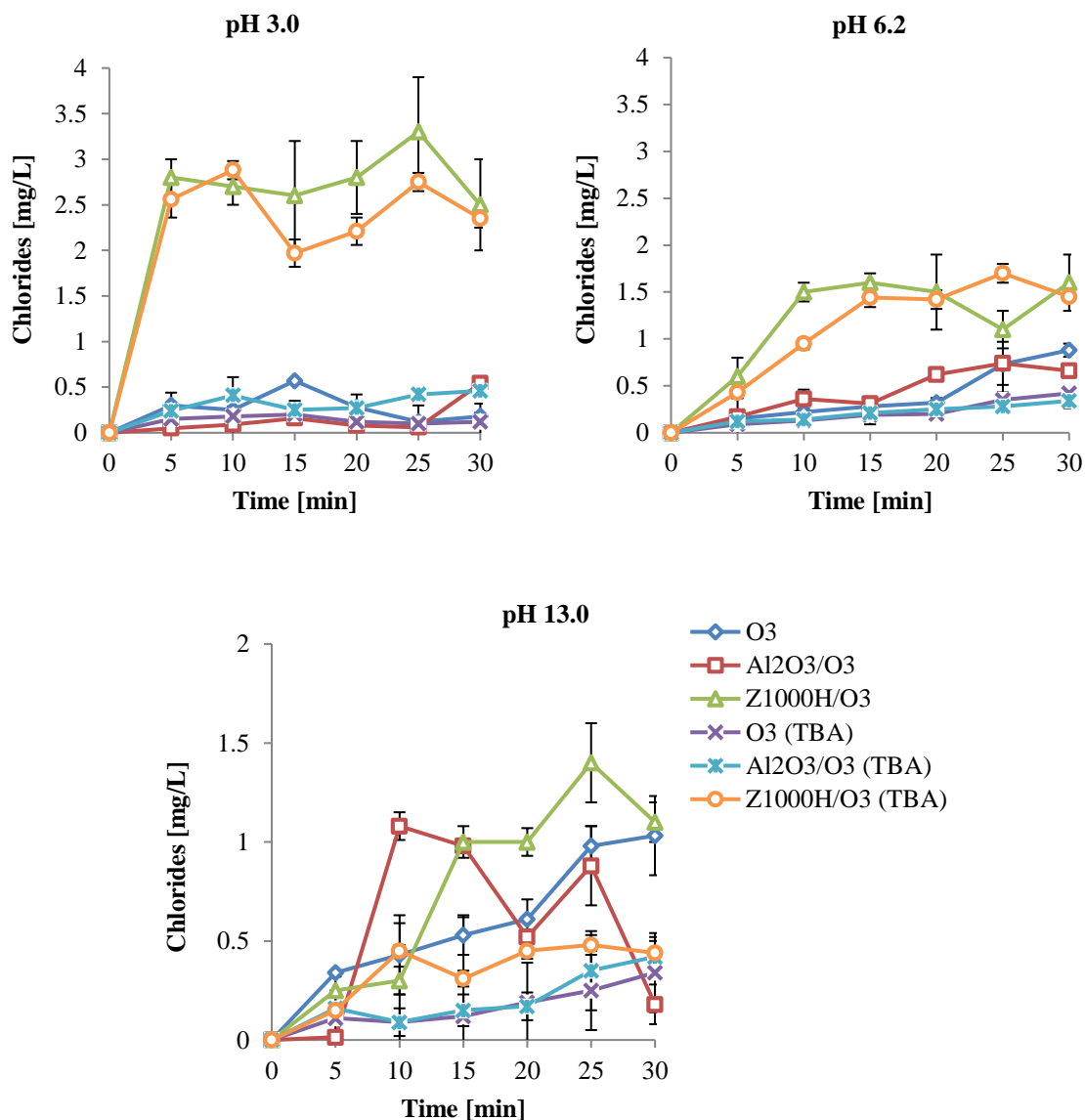


Figure 6 Effect of TBA on chlorides formation during VOCs ozonation alone and ozonation in the presence of ZSM-5 zeolites and alumina (C_o (cum) = 19.2 ± 0.5 mg/L, C_o (DCB) = 3.5 ± 0.2 mg/L, and C_o (TCB) = 0.5 ± 0.1 mg/L; $T = 20^\circ\text{C}$; $\text{pH} = 3.0, 6.2$ and 13.0 ; $\text{pH}_{30\text{min}} = \text{pH}_o \pm 0.3$; catalyst amount = 5 g; $V = 490$ mL; $\text{O}_3 = 0.1$ mg/min; TBA = 50 mg/L).

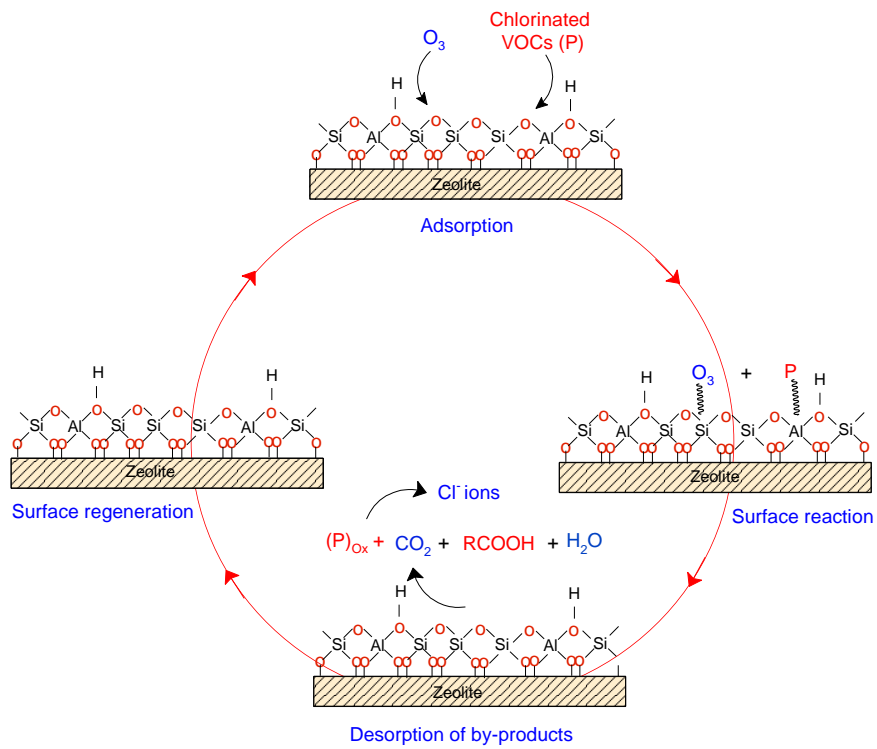


Figure 7 Proposed mechanism of VOCs ozonation on zeolites