Jurnal Teknologi, 44(C) Jun 2006: 13–22

CATALYTIC OZONATION OF 2-HYDROXY-1,2,3-PROPANETRICARBOXYLIC ACID

NORZITA NGADI[1]*, NOR AISHAH SAIDINA AMIN[2], KHEW SHIH TAK[3],
LAI SIOK LIAN[4] & LAU KOK KEONG[5]

Abstract. Catalytic ozonation is an Advanced Oxidation Processes (AOP) where the ozone is applied together with catalyst in homogeneous or heterogeneous form. The heterogeneous catalytic ozonation of 2-hydroxy-1,2,3-propanetricarboxylic acid using powdered HZSM-5, Cu-ZSM-5, Mn-ZSM-5 and V-ZSM-5 with different mole ratio of SiO_2/Al_2O_3 as catalyst were studied. The effectiveness of catalytic ozonation compared with non-catalytic ozonation, the effect of loaded metal onto ZSM-5 and the performance of each catalyst are tested in this work. The effect of ozone gas bubble size is also investigated. The experiment had been carried out in an agitated semibatch reactor under some fixed experimental parameters. Acid-base titration was used to analyze the collected product. The results show that the presence of catalyst has improved the ozonation rate of 2-hydroxy-1,2,3-propanetricarboxylic acid by 25% as compared to the results of non-catalytic ozonation. Different catalysts with different mole ratio of SiO_2/Al_2O_3 have different performance in this catalytic ozonation. However, most of the catalysts show the highest conversion rate at SiO_2/Al_2O_3 mole ratio of 80. In overall, V-ZSM-5 catalyst could promote the ozonation process better than Cu-ZSM-5 and Mn-ZSM-5. The results also show that ozone gas with smaller bubble size gave better performance.

Keywords: Catalytic ozonation, advanced oxidation processes, ZSM-5, wastewater treatment, 2-hydroxy-1,2,3-propanetricarboxylic acid

Abstrak. Pengozonan bermangkin adalah proses di mana ozon digunakan bersama-sama dengan kehadiran mangkin yang berada dalam bentuk homogen atau pun heterogen. Pengozonan heterogen bermangkin asid 2-hidroksi-1,2,3-propanetrikarbosilik menggunakan HZSM-5, Cu-ZSM-5, Mn-ZSM-5 dan V-ZSM-5 dengan nisbah SiO_2/Al_2O_3 yang berbeza sebagai mangkin telah dikaji. Perbandingan kecekapan antara pengozonan bermangkin dan pengozonan tanpa mangkin, kesan penambahan logam kepada ZSM-5 dan prestasi setiap mangkin akan dikaji dalam kajian ini. Kesan saiz ozon turut juga dikaji. Uji kaji dijalankan di dalam reaktor separa kelompok. Penitratan asid-bes digunakan untuk menganalisa produk yang terhasil. Keputusan yang diperolehi menunjukkan bahawa kehadiran mangkin dapat meningkatkan lagi kadar pengozonan asid 2-hidroksi-1,2,3-propanetrikarbosilik sehingga 25% berbanding dengan pengozonan tanpa mangkin. Mangkin yang berbeza nisbah SiO_2/Al_2O_3 turut memberikan prestasi yang berbeza dalam pengozonan bermangkin ini. Walau bagaimanapun, kebanyakan mangkin memberikan kadar penukaran tetinggi pada nisbah SiO_2/Al_2O_3, 80. Secara keseluruhannya, mangkin V-ZSM-5 lebih mampu merangsang proses pengozonan berbanding Cu-ZSM-5 dan Mn-ZSM-5. Keputusan uji kaji juga menunjukkan bahawa saiz gelembung ozon lebih kecil memberikan hasil yang lebih baik berbanding dengan gelembung ozon yang bersaiz besar.

[1,2,3,4&5] Chemical Reaction Engineering Group (CREG), Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM, Skudai, Malaysia
*Corresponding author: Tel: 07-5535480, Fax: 07-5581463, Email: norzita@fkkksa.utm.my

Kata kunci: Pengozonan bermangkin, proses pengoksidaan termaju, ZSM-5, perawatan air sisa, asid 2-hidroksi-1,2,3-propanetrikarbosilik

1.0 INTRODUCTION

Ozonation technology has been used for several years ago mainly for drinking water treatment in European countries. Nowadays, ozonation is an attractive and increasing important technology in wastewater treatment for the removal of organic pollutants and as a disinfectant. The application of ozone for purification of industrial wastewaters from various manufacturers is based on its high oxidation-reduction potential, which determines its destructive action on a wide range of organic and inorganic compounds. The properties of ozone have been widely studied in literatures [1,2]. In aqueous solution, the unstable property of ozone enables it to undergo spontaneous decomposition that is also known as auto-decomposition. Auto-decomposition of ozone is a complex chain reaction process that involves few free radical species. Hydroxyl radical, $OH^{\bullet}$, one of the intermediate products from the auto-decomposition of ozone is the strongest chemical oxidants and able to react fast with organic and inorganic components.

In aqueous solution, ozone reacts with organic compounds in two ways; direct reaction of ozone molecule and radical type reaction that involves hydroxyl radical, $OH^{\bullet}$ from the decomposition of ozone in solution (Equations 1-5).

$$O_3 + \text{Organic compound} \rightarrow \text{Product} \tag{1}$$

$$OH^- + O_3 \rightarrow O_2^- + HO_2^{\bullet} \tag{2}$$

$$HO_2^{\bullet} \longleftrightarrow H^+ + O_2^- \tag{3}$$

$$O_3 + O_2^- \rightarrow O_3^- + O_2 \tag{4}$$

$$O_3^- + H^+ \rightarrow OH^{\bullet} + O_2 \tag{5}$$

Direct reaction involving ozone molecule is very selective. Ozone reacts instantly with certain species such as alkenes but very slowly with other species such as benzene. On the other hand, hydroxyl radical is non-selective and reacts very fast with most of the species [3,4].

However, some refractory pollutants such as phenol are very difficult to degrade using ozone alone. Thus, more attention is being focused on the Advanced Oxidation Processes (AOP) involving catalysts systems such as O_3/H_2O_2, UV/O_3, UV/H_2O_2, Fenton's reagent and photocatalytic oxidation with TiO_2 [5-9]. Since these AOPs may require more complex equipment and higher operating costs and may be difficult to use in practice, alternative lower costing of AOP with a relatively simpler operation need to be developed for the degradation of refractory organic pollutants in wastewater.

Catalytic ozonation is one such example of the AOPs that can fulfill the listed criteria because it is easy to operate and the apparatus needed is simple. The use of heterogeneous catalyst, which could improve the ozone capability for the degradation of refractory organic pollutants, is continuously attracting the attention of an increasing number of researchers. Literature review showed that the application of ozone in the presence of catalyst in the form of metal oxide such as TiO_2 and MnO_2 [10-12] or salt such as Mn^{2+}, Mn^{4+} and Fe^{2+} [12-15] has increased the ozonation rate of organic compounds as compared to ozonation alone.

Studies on the heterogeneous catalytic decomposition of ozone in water show the high capacity of ozone to decompose on the surface of catalyst [11]. Thus this work presented the study of the heterogeneous catalytic ozonation removal of 2-hydroxy-1,2,3-propanetricarboxylic acid from water using ZSM-5 based catalyst. It involves ozone in gas phase, 2-hydroxy-1,2,3-propanetricarboxylic acid in liquid phase and catalyst in solid phase. 2-hydroxy-1,2,3-propanetricarboxylic acid is chosen because it represents one of the typical end products formed from beet sugar molasses.

In this study, four different types of catalysts were synthesized namely, HZSM-5, Cu-ZSM-5, Mn-ZSM-5 and V-ZSM-5. For each sample, the mole ratio of SiO_2/Al_2O_3 were varied between 30, 80 and 280. All the catalysts were then tested in the catalytic ozonation removal of 2-hydroxy-1,2,3-propanetricarboxylic acid and their performance was compared with ozonation alone. The effect of the size of the ozone gas bubble on the reaction performance was also investigated.

2.0 METHODOLOGY

2.1 Catalyst Preparation

HZSM-5 is prepared by calcinations process of ZSM-5 at 550°C for 5 hours. ZSM-5 catalyst is obtained commercially from Sigma. The metal-ZSM-5 is prepared by wet-impregnation method. Metal ions that are impregnated in the ZSM-5 support are copper, vanadium and manganese with 1% (w/w) each. The method of wet-impregnation is as follows: distilled water (X mL) is mixed with y gram of metal salt for 1 hour to produce metal salts precursor solution. HZSM-5 (Z gram) is added into the precursor solution and stirred for 5 minutes. The mixture is then dried in the oven at 110°C for 12 hours. Finally, the dried product is calcined in the furnace at 550°C for 5 hours and cooled to produce metal-ZSM-5 with 1% (w/w) metal. The exact amount of x, y and z used to produce 1% (w/w) of metal in the ZSM-5 support are: Cu-ZSM-5(38.5 ml, 0.385 g, 10 g), V-ZSM-5(23.2 ml, 0.2319 g, 10g) and Mn-ZSM-5(46.2 ml, 0.46134 g, 10 g).

2.2 Experimental Procedure for Catalytic Testing

Simulated wastewater containing standard 2-hydroxy-1,2,3-propanetricarboxylic acid solution (0.008 M) was prepared. The pH of the solution was measured. The standard solution was then titrated using 0.02 M NaOH solution and the titration volume was recorded. 250 ml of standard solution was transferred into the ozonation reactor. Then, 1 gram of catalyst was added into the reactor and the temperature of the mixture was held around 30°C. The mixture was stirred at 300 rpm. Ozone stream at 1.5 g/hour was fed into the mixture using a gas diffuser. Samples of 2-hydroxy-1,2,3-propanetricarboxylic acid solution were collected at the reaction time intervals of 10 to 50 minutes. Finally, the collected sample was filtered and analyzed. The schematic diagram of the ozonation reactor is shown in Figure 1.

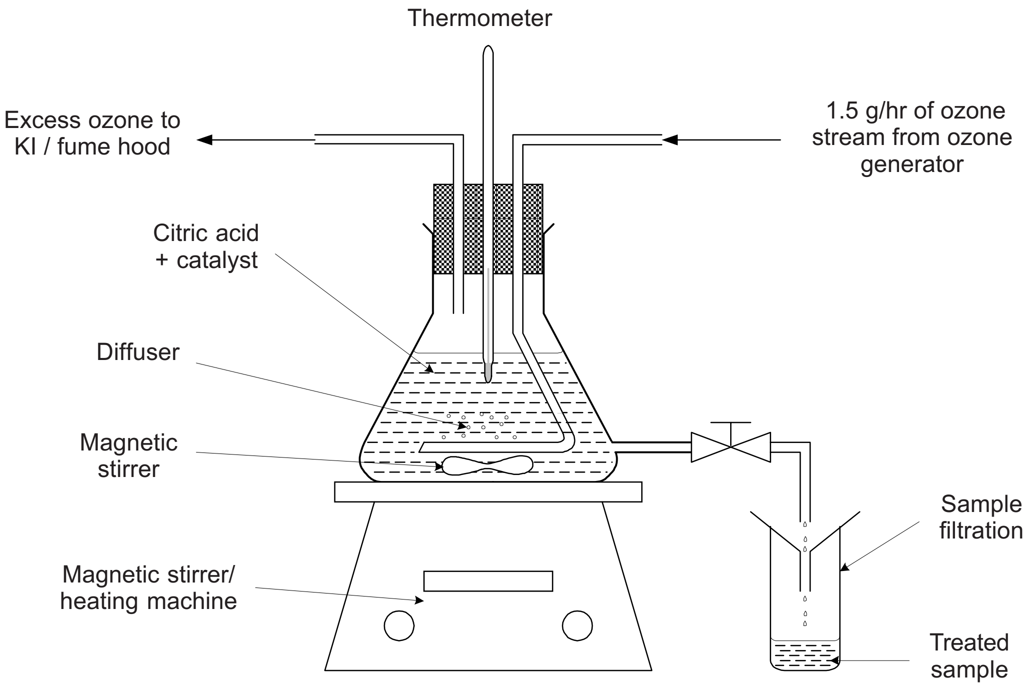


Figure 1 Schematic diagram for the ozonation reactor

2.3 Sample Analysis

The collected sample was titrated with NaOH solution using phenolphthalein as the indicator. The volume of NaOH used in the titration is proportional to the residual 2-hydroxy-1,2,3-propanetricarboxylic acid in the reaction sample. The conversion of the reaction was calculated as follows:

$$\text{Conversion, } X = (\text{Initial } V_{NaOH} - \text{Final } V_{NaOH}) / \text{Initial } V_{NaOH}$$

where;

Initial V_{NaOH} = volume of NaOH required to neutralize 2-hydroxy-1,2,3-propanetricarboxylic acid at t = 0
Final V_{NaOH} = volume of NaOH required to neutralize the collected sample

3.0 RESULTS AND DISCUSSIONS

3.1 Effect of Catalyst on 2-hydroxy-1,2,3-propanetricarboxylic acid Conversion

Figure 2 shows that the ozonation of 2-hydroxy-1,2,3-propanetricarboxylic acid in the presence of catalyst HZSM-5 led to a significant increase of reaction conversion compared to the ozonation alone, up to 25% discrepancy. Ozone reacts with organic compounds in aqueous directly through molecular or selective reactions with specific functional groups (double bonds, nucleophilic positions) and through free radicals (hydroxyl radicals) generated from ozone decomposition [3,4]. Since 2-hydroxy-1,2,3-propanetricarboxylic acid is a double bond in structure (see Figure 3), both direct and indirect reaction took place in this ozonation process. Under acidic

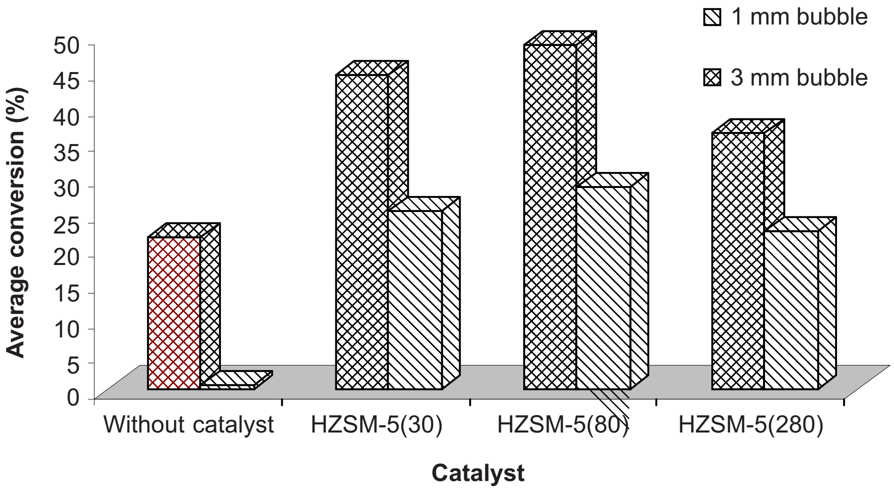
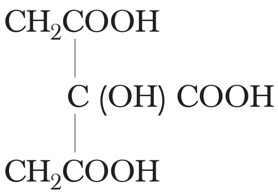


Figure 2 Average conversion of the 2-hydroxy-1,2,3-propanetricarboxylic acid during its catalytic ozonation with different SiO_2/Al_2O_3 mole ratio in catalyst HZSM-5 comparing to ozonation alone



$$\begin{array}{l} CH_2COOH \\ \quad| \\ \quad C\ (OH)\ COOH \\ \quad| \\ CH_2COOH \end{array}$$

Figure 3 2-hydroxy-1,2,3-propanetricarboxylic acid structure conditions, however, the generation of hydroxyl radicals from non-catalytic ozone decomposition is limited [12]. Then, it seemed that the poor conversion of 2-hydroxy-1,2,3-propanetricarboxylic acid in the non-catalytic ozonation process was due to the dominating of direct ozone reaction over free radical reaction. Furthermore, when the catalyst was present, ozone could also be adsorbed on a catalyst surface to yield another oxidation agent such as superoxide ion, O_2^- and ozonide ion, O_3^- making the catalytic-ozonation more superior than ozonation alone [16].

Besides that, SiO_2/Al_2O_3 ratio also affected 2-hydroxy-1,2,3-propanetricarboxylic acid conversion. The use of catalyst HZSM-5 with SiO_2/ Al_2O_3 mole ratio of 80 and 30 in the reaction gives a higher conversion compared to HZSM-5 mole ratio of 280. Even though HZSM-5 (30) catalyst has more acidic sites [17], catalytic ozonation with catalyst HZSM-5 (80) achieved the highest average conversion, which is about 49%. HZSM-5 (280) catalyst has very few acidic sites for reaction to take place as compared to HZSM-5 (30) and HZSM-5 (80). Therefore, catalytic ozonation with catalyst HZSM-5 (280) gave the lowest average conversion, which is only 36%.

The bubble size of ozone seemed to play a big role in catalytic ozonation. The increase in bubble size led to a decrease in oxidation rate. For ozonation alone, the activity is almost zero with 3 mm bubble. It is well accepted that the mass transfer rate of ozone is always inversely proportional to the gas bubble size [2]. It can be proved by following equations (6-7):

$$N_A = ka\ (C'_L - C_L)\ V \tag{6}$$

$$a = 6/d_B\ (h/1-h) \tag{7}$$

where;

N_A = mass transfer rate
k = mass transfer coefficient
a = specific conversion area
C = substrate concentration
V = liquid volume
d_B = bubble gas diameter
h = gas retention

Figure 4 shows the catalytic ozonation with the presence of Cu-ZSM-5. Like ZSM-5, the increase of ozone gas bubble size led to a significant decrease of reaction conversion. However, the amount of metal impregnated to zeolite seemed not to give any significant effect on the degradation of 2-hydroxy-1,2,3-propanetricarboxylic acid as shown by Cu-ZSM-5 (30), Cu-ZSM-5 (80) and Cu-ZSM-5 (280), gave similar conversion in 2-hydroxy-1,2,3-propanetricarboxylic acid conversion that is 51%, 50% and 48% respectively. Even though Cu-ZSM-5 (30) catalyst has more active acidic sites compared to the other two catalysts [18], its performance did not improve much.

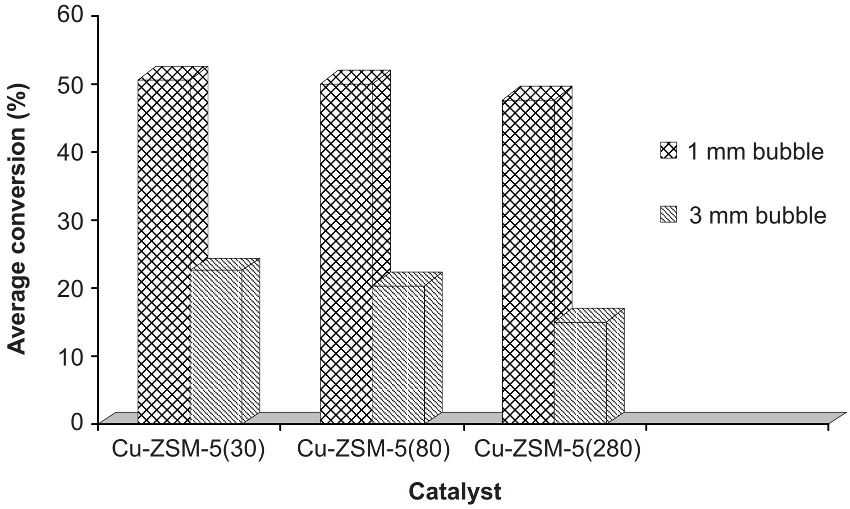


Figure 4 Average conversion of the 2-hydroxy-1,2,3-propanetricarboxylic acid during its catalytic ozonation with different SiO_2/Al_2O_3 mole ratio in catalyst Cu-ZSM-5

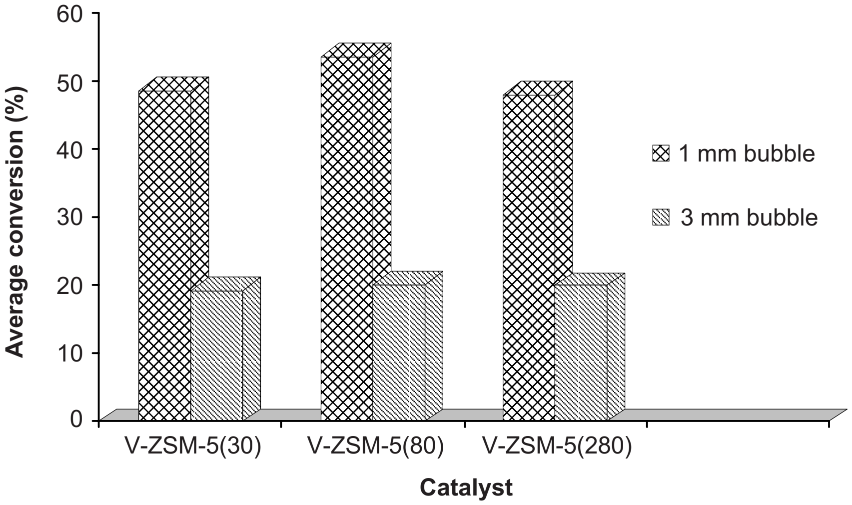


Figure 5 Average conversion of the 2-hydroxy-1,2,3-propanetricarboxylic acid during its catalytic ozonation with different SiO_2/Al_2O_3 mole ratio in catalyst V-ZSM-5

Catalytic ozonation with V-ZSM-5 (80) catalyst gave the highest acid conversion, 55% compared to V-ZSM-5 (30) and V-ZSM-5 (280), 50% and 49% respectively as can be seen in Figure 5. The result obtained is quite similar with Cu-ZSM-5 except on SiO_2/Al_2O_3 mole ratio of 80 where V-ZSM-5 (80) gives 55% conversion whilst Cu-ZSM-5 (80), only 50% conversion.

It is interesting to note that with SiO_2/Al_2O_3 mole ratio of 280, catalyst Mn-ZSM-5 gives the highest average conversion in catalytic ozonation, which is 45%

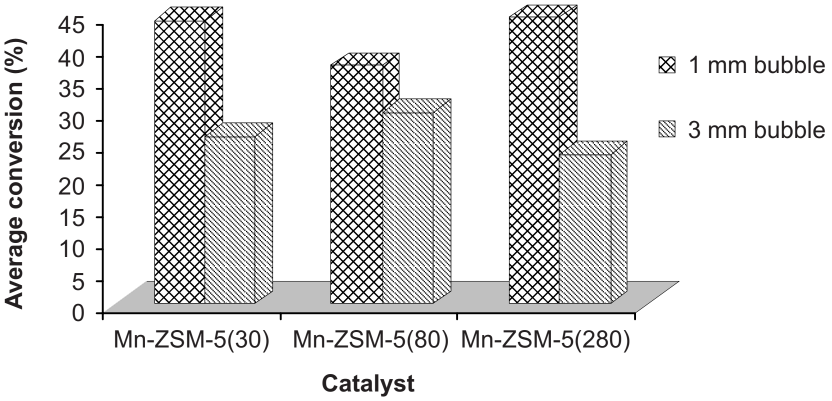


Figure 6 Average conversion of the 2-hydroxy-1,2,3-propanetricarboxylic acid during its catalytic ozonation with different SiO_2/Al_2O_3 mole ratio in catalyst Mn-ZSM-5

as shown in Figure 6. It can be seen that the result obtained is totally different from the case using catalyst HZSM-5, Cu-ZSM-5 and V-ZSM-5. It is believed that different metal being impregnated to ZSM-5 has different effects on the acid conversion during its catalytic ozonation.

Overall, it can be concluded that V-ZSM-5 could promote the ozonation process better than Cu-ZSM-5 and Mn-ZSM-5. This may be due to the electron configuration structure of V-ZSM-5, which enables it to release its electron valence easily to produce radical $OH^\bullet$. It is believed that metal oxides does not involve directly in degradation process. Besides that, the degradation of 2-hydroxy-1,2,3-propanetricarboxylic acid is not affected much by the acidity of the catalyst as shown by HZSM-5 and metal-ZSM-5. They give almost similar conversion rate even though metal-ZSM-5 is less acidic compared to HZSM-5. It is believed that the balance of hydropobicity-hydrophilicity of the HZSM-5 is the most important in order to attract 2-hydroxy-1,2,3-propanetricarboxylic acid (polar molecule) towards the surface of the catalyst before reaction take place rather than the presence of the metal oxides or the mole ratio of SiO_2/Al_2O_3.

4.0 CONCLUSIONS

Catalytic ozonation leads to a higher average conversion rate than ozonation alone, which is about 25% discrepancy. The decrease of bubble size yields a better conversion for all the catalysts. Metal-ZSM-5 can achieve better performance than HZSM-5 using certain type of metal only. Different metal-ZSM-5 catalysts with different SiO_2 $/Al_2O_3$ mol ratio appeared to have different effects on the acid conversion during catalytic ozonation. Overall, V-ZSM-5 with SiO_2/Al_2O_3 could promote the ozonation process better than Cu-ZSM-5 and Mn-ZSM-5. The balance of hydropobicity-hydrophilicity of the HZSM-5 seemed to be the most important in order to attract 2-hydroxy-1,2,3- propanetricarboxylic acid (polar molecule) towards the surface of the catalyst before reaction take place rather than the presence of the metal oxides or the mole ratio of SiO_2/Al_2O_3.

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