Catalytic ozonation of nonyl phenol ethoxylates in water by octahedral molecular sieve OMS-2

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Abstract: In the present work the nonionic surfactant nonyl phenol ethoxylate (NPE) is used as the target polutant and its degradation in the ozonation process and cryptomelane-type manganese oxide of octahedral molecular sieve structure (OMS-2) catalytic ozonation was studied. OMS-2 material was synthesized by refluxing method. Characterisation of OMS-2 was made using XRD patterns and TGA profile. Nitrogen adsorption-desorption measurement gives BET specific surface of the catalyst is of 72 m^2/g. The influence of pH, initial NPE concentration, ozonation time and the amount of catalyst in ozonation process was also investigated. Results show that NPE removal by using OMS-2 is higher than that of using single ozonation. More than 95% NPE were removed within 10 min at pH of 11 at 30°C with an amount of OMS-2 catalyst of 0.1 g/L. Furthermore, in this condition 39% of total carbon of NPE was mineralized.

Keywords: Nonyl Phenol Ethoxylate, Catalyst, Ozonation, OMS-2, Mineralisation

Introduction:

Surfactants being the common contaminants of sewage are hardly removable by classical, both physicochemical and biological methods. Among them hard detergents are only weakly biodegradable and do not self decompose in storage reservoir of water**.** Nonylphenol ethoxylates (NPE) as hard surfactants are used anywhere there is a need for increased surface activity, and provide excellent all-purpose detergency and wetting, as well as solubilization and emulsification.They are useful components in industrial surfactants, detergents, phenolic resins, polymer additives, pesticides, chemicals, textiles**,** lubricants, pharmaceuticals…
Due to their persistence and inefficiency of third-stage treatment process, NPE are emitted to environment via wastewater and cause many harmful effect to many creatures and humans especially endocrine disruptive effects**.** It has been confirmed that generally non-ionic surfactants are more toxic than others[1]. Periods of long acclimation are required during the conventional treatment, and they typically result in a quite incomplete degradation. Finally, introduced into water ecosystem, some of the pollutants such as alkylphenyl polyethoxylate-type non-ionic surfactants, e.g. Triton X-100 (TX), are suspected to be the endocrine disrupters in aquatic organisms.

In order for the surfactants to be removed, the heterogeneous photocatalysis, as a one of the advanced oxidation processes (AOPs), can be applied successfully. The observed progress in the field of AOPs has made them as alternatives or as a complement to conventional wastewater treatment. Besides, nonylphenols (NPs) can be produced from the anaerobic or anoxic biotransformation of long chain NPE, by losing the whole ethoxylates group and NPs have a higher toxicity compared with their parent compound and this makes the presence of NPE become more and more dangerous.
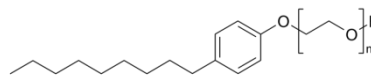
NPE structure

Although the use of NPE was banned in many countries, tonnes of them are still being manufactured everyday around the world [2]. Among the potential methods for treating NPE as well as other pollutants, ozonation and other advanced oxidation processes are paid more attention since they are "environmental friendly" which mean they can decompose the compounds into reaction products with less, or no, toxicological effect rather than simply separating them from the flow (such as adsorption or membrane processes). Ozonation is often applied in oxidation processes thanks to its advantages among other common oxidation agent. Additionally, some results have suggested that the surface reactive oxygen species might also play an important role in catalytic ozonation of ibuprofen, sodium dodecyl sulfonate...[3,4,5,6]. Many metallic oxides could afford this property. There have been several characterization and reactivity studies conducted on supported manganese oxides. Manganese oxides have been used for catalyzing several chemical reactions including the decomposition of nitrous oxide, isopropanol ; oxidation of methanol, ethanol, benzene, CO, ... Oxides of manganese are also being applied in air pollution control technology particularly the decomposition of ozone and volatile organic compounds (VOCs). Both molecular sieves and layered oxides materials have been paid attention for many years due to their well-known industrial applications, such as petroleum refining, gas cleansing, gas separation, etc. Manganese dioxides can exist in different crystal structures and

morphologies. Cryptomelane-type manganese oxide(OMS-2) is a form of manganese dioxide with a one-dimensional tunnel structure composed of 2×2 edge-shared MnO_6 octahedral chains, which are corner-connected to form 4.6×4.6 Å tunnels. Manganese is present in OMS-2 as Mn_{2+}, Mn_{3+}, and Mn_{4+} located in octahedral sides, and potassium ions reside in the tunnels along with a small amount of water to stabilize the tunnel structure. Cryptomelane-type manganese octahedral molecular sieves material (OMS-2) is being used as an excellent oxidation catalyst in many oxidation processes and can be applied in wastewater treatment process plants because of its advantages (significantly increase oxidation yield, catalyst recycling can be done easily without reducing catalytic activities, etc.). However, the combination of ozonation and OMS-2 catalyst are not investigated though they could potentially be efficient.[7-9]

In this work, batches of experiments were carried out to test the initial pH values, ozone dosages, initial NPE concentration in catalytic ozonation in the presence of OMS-2 as heterogeneous catalyst. For the removal of NPE9 contaminant from aqueous solution the mineralization in ozonation and catalytic stability (catalyst recycling) were also investigated.

Materials and methods:
All chemicals were analytical grade and used without further purification. Nonylphenol Ethoxylate (NPE9) was purchased from Merck. Ammonium thiocyanate, Potassium permanganate, Hydrochloric acid, Manganese (II) sulfate monohydrate, Sodium hydroxide, Sodium chloride, were products of Xilong Chemical Corp.

Preparation of catalyst: The OMS-2 material used as catalyst was prepared using refluxing method following our previous work [3]. In a typical experiment, 5.89 g $KMnO_4$ in 100 mL water was added to solution of 8.8 g $MnSO_4.H_2O$ in 30 mL water and 3 mL of concentrated HNO_3 (70%). The mixture is refluxed at 100^oC for 24 hours. The product is filtered, washed with a lot of water and then dried at 120^oC for 24h and heated at 450^oC for 5h. This solid product is ready for use as catalyst in ozonation. For catalyst recycling, OMS-2 catalyst should be carefully filtered, washed with water and organic solvent (ethanol and acetone) then dried at 100^oC for several hours before reuse.

X-ray diffraction (XRD) was used to determine the crystallinity of OMS-2. An ASC (0007 model) diffractometer using Cu Ka radiation source was used. The samples were scanned from $2\theta = 10\text{-}70^o$ at a rate of 0.03^o s^{-1} (1° min^{-1}). The x-ray power was operated with a current of 40 mA and a voltage of 45 kV. Nitrogen adsorption-desorption measurement was also made at 77K using BET method for specific surface area of the catalyst.

Ozonation of NPE9 with OMS-2
Ozone was produced from dry air by use of Vina Ozone Generator model VN3 using Cold Plasma Technology. Ozone flow was measured by a ball flow rate meter. The concentration of ozone in aqueous solution was determined by UV-Vis spectrometer model T70+ manufactured by PG instrument Ltd. at 258 nm (molar extinction coefficient of 2950 $cm^{-1}M^{-1}$.

The flask containing NPE9 placed on a magnetic stirrer at 80rpm was used as ozonation reactor. The superflous ozone was adsorbed by activated carbon in aqueous absorption flask. The pH of the solution was adjusted by HCl or NaOH. The Ozone flowrate was controlled by needle valves.

After ozonation, in order to avoid the influence of organic compounds in the mixture, residual ozone concentration was determined by indirect method in place of UV method : Ozone reacts with KI in solution to produce I_2 which rapidly forms complex with p-phenylenediamine for a UV-VIS absorption at $\lambda = 540$ nm and using Beer-Lambert equation $A = \varepsilon \cdot l \cdot C$ where A is the absorbance measured (unitless), ε is the molar absorption coefficient($\varepsilon = 3300$ $mol^{-1}cm^{-1}$), l is the cuvette length (cm), C is the concentration of ozone (mole/L) [9].

Determination of NPE9 concentration:
A solution of given NPE9 concentration diluted from 1000 mg/L NPE stock solution was used as wastewater sample. The concentrations of NPE9 were determinedby HPLC equipped with a UV detector (Waters UK). After degassing, acetonitrile and 0.2 acetic acid (v/v) buffered Milli-Q water were used as solvent with a gradient program (5–100% of organic solvent). The flowrate of the solvent was kept at 1 ml min^{-1} and a C18 column(4.6 · 15 mm, 5 lm) was used, supplied by Waters UK. A UV detector wavelength of 224 nm was employed, which was found to give the maximum response for NPE. The effects of initial NPE9, reaction time, O_3 flowrate, amount of catalyst, initial pH on ozonation were investigated through NPE9 conversion yield (H%) calculated on the basis of the following equation:

$$NPEconversion = \frac{C_o - C}{C_o} \times 100\%$$

Mineralization of ozonation was investigated by measuring the mass of the CO_2 gas in absorption of a 0.5M $Ba(OH)_2$ solution. The barium carbonate precipitate was dried at 110^oC for an hour until constant weight. All the experiments were performed under ambient conditions in an environmentally controlled laboratory where the room temperature was 30 ± 1 ^oC. Noncatalytic ozonation (without OMS-2) experiments were carried out in addition to catalytic ozonation (with OMS-2) experiments for comparison. It is noted that according to our preliminary studies, there were no adsorption of NPE on heterogeneous surface OMS-2.
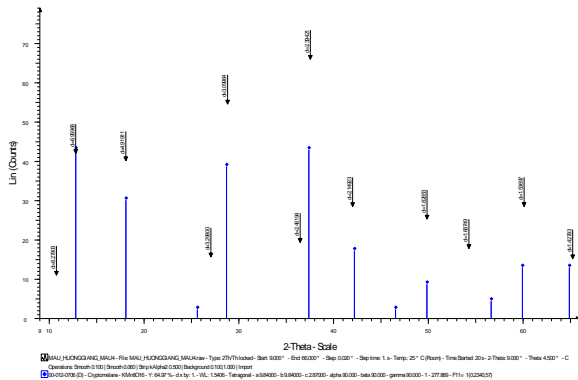
Results and Discussion:
Formation of OMS-2

Fig. 1. XRD pattern of cryptomelane OMS-2

The diffractogram of crystalline OMS-2 cryptomelane on Fig. 1 showed the largest characteristic intensites at 2θ = 12.8, 18.1, 29, 37.6, 50 and 60 degree (JCPDS No. 29–1020). Specific surface area of the catalyst measured by BET method is of 72 m^2/g. The size of OMS-2 crystal calculated from the line broadening of XRD peaks using Sherrer's formula (d= $0.9\lambda/\beta cos\theta$) is of 45 nm.

Fig,2 showed the typical fibrous morphology of OMS-2 as analysed by SEM image with the small particles with average diameter about 40-50nm, which is consistent with XRD result. In addition, in preparation of OMS-2, sulfate groups in the solution and the surface OH groups on the manganese oxide materials may have formed bonds, which could cause the isolation of manganese oxide particles from each other by the surrounding groups and prevent further aggregation.
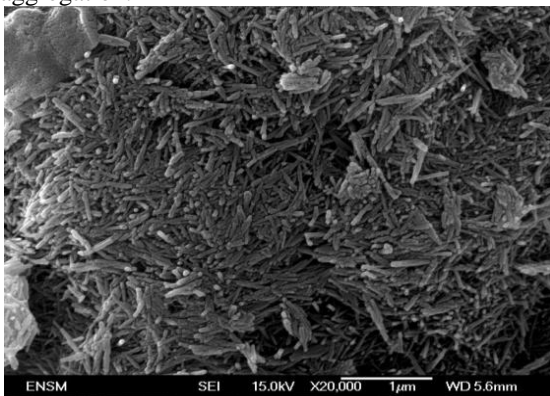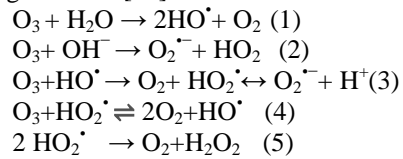

Fig.2   SEM image of OMS-2

Effect of initial pH on catalytic NPE ozonation

The condition of pH in the range of 4 -11 was chosen to investigate the NPE catalytic ozonation yield. In general, in aqueous solution, ozone reacts with organic compounds via two ways. Being an oxidant, the molecular ozone is a selective electrophile that reacts quickly with amines, phenols and double bonds in aliphatic compounds. Besides, the ozone decomposition may also generate secondary oxidants (mainly hydroxyl radicals) to oxidize molecules as following reactions[10]:

$$O_3 + H_2O \rightarrow 2HO^\bullet + O_2 \quad (1)$$
$$O_3 + OH^- \rightarrow O_2^{\bullet -} + HO_2 \quad (2)$$
$$O_3 + HO^\bullet \rightarrow O_2 + HO_2^\bullet \leftrightarrow O_2^{\bullet -} + H^+ (3)$$
$$O_3 + HO_2^\bullet \rightleftharpoons 2O_2 + HO^\bullet \quad (4)$$
$$2\ HO_2^\bullet \rightarrow O_2 + H_2O_2 \quad (5)$$

The rate of formation of hydroxyl radicals depends largely on the aqueous matrix. The •OH radicals are stronger oxidants with faster reaction rates but they react less selectively than molecular ozone [9]. Thus the pH value would control the ozone decomposition and the formation of hydroxyl radical. The fact that the quantity of hydroxyl radicals could be favored in alkaline pH can be seen from Fig. 3. After 10 minutes, with OMS-2 as catalyst, the NPE ozonation yield reached 98% at pH=11 in comparison to 60% at pH=8. Without catalyst the ozonation are less efficient. It is mentioned that the mixed valency of manganese atoms in OMS-2 catalyst was important for electron transport because the efficiencies of catalysts, especially for redox reactions are usually controlled by their ability to transform between various oxidation states of the cationic ions.[54].
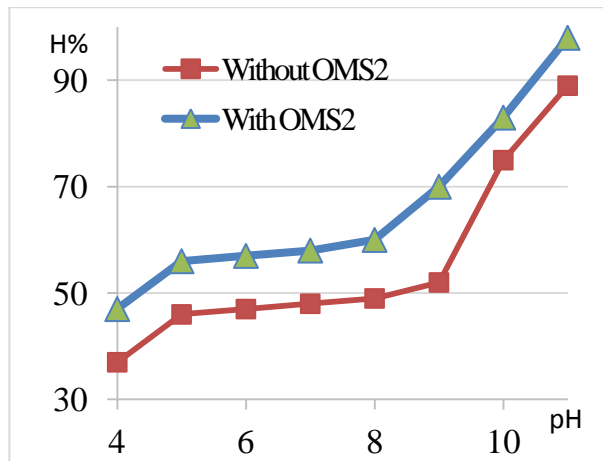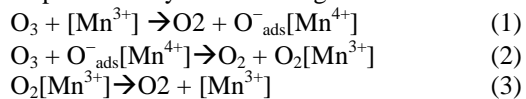

Fig.3 Effect of pH on NPE ozonation yield H%
(t = 10 min, V_{O3} = 3.5 L/min, [OMS-2] = 0.1 g/L, [NPE9]$_o$ = 10 mg/L)

Ozone decomposition on the surface of OMS-2 could be presented by the following reaction scheme:

$$O_3 + [Mn^{3+}] \rightarrow O2 + O^-_{ads}[Mn^{4+}] \qquad (1)$$
$$O_3 + O^-_{ads}[Mn^{4+}] \rightarrow O_2 + O_2[Mn^{3+}] \qquad (2)$$
$$O_2[Mn^{3+}] \rightarrow O2 + [Mn^{3+}] \qquad (3)$$

In their report, Liu et al. presented a linear correlation between ozone decomposition and Mn^{3+} content [8]. The more the quantity of Mn^{3+} on the surface of the catalyst, the more the ozone decomposition could be favored. It is known that the existence of various manganese cations from OMS-2 would be dependent on pH values, their participation into the above cycle between Mn^{3+} and Mn^{4+} may be beneficial for the ozone decomposition.
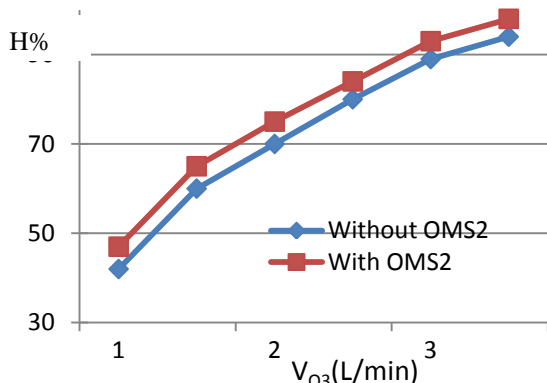
Effect of ozone flowrate:

Fig.4 Effect of ozone flow rate on NPE ozonation yield (t = 10 min, [NPE]o= 10 mg/L, [OMS-2] = 0.1 g/L, pH = 7)

The ozone flowrate controls ozone dosage for the NPE decomposition. The range of 1 – 3.5L/min is due to limit of the flowmeter in the set-up system. With an increase of O_3 flowrate, the ozone concentration could increase then the NPE ozonation yield would increase. Higher flowrate could be used for reducing reaction time. After 10 minutes, in the presence of OMS-2, the degradation yield of NPE was nearly 50% with ozone flowrate of 1L/min. At an flowrate of 3.5L/min, the yield reached 98%. The effect of ozone flowrate on NPE9 degradation without catalyst is similar as shown in Fig.4.

Effect of initial NPE concentration:

According to previous researches on pollutants in the Saigon River, the NPE content may be often in the range of 5-15 mg/L. The effect of initial NPE concentration is described in the figure 6. Overall, the ozonation yield decreased gradually with the increasing of initial NPE concentration. The decreasing yield's slope is larger with high NPE concentraton. Because ozone dosages are the same but the quantity of NPE is increased, the reaction yield is diminished. Higher NPE concentration solutions will make the foam layer become thicker and more stable which makes ozone stream flows more difficult through the solution.
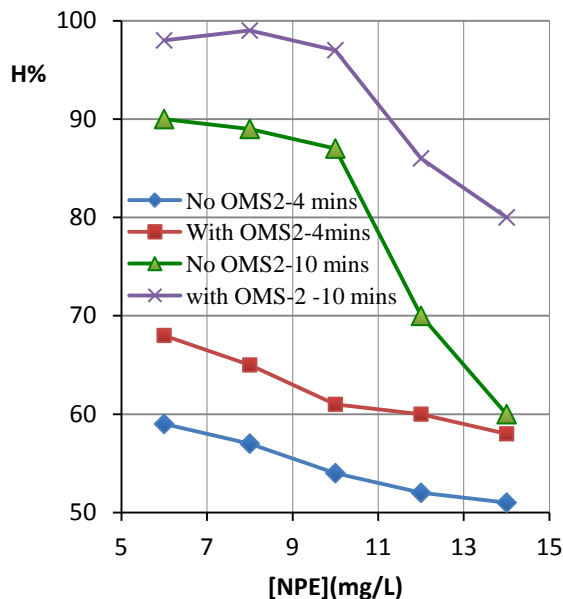

Fig.5 Effect of initial NPE concentration on ozonation yield (V_{O3} = 3.5 L/min, [OMS-2] = 0.1 g/L, pH = 7)

Effect of catalyst content

As presented above, the most possible mechanism of heterogeneous catalytic ozone decomposition can be based on active surface sites (denoted *):
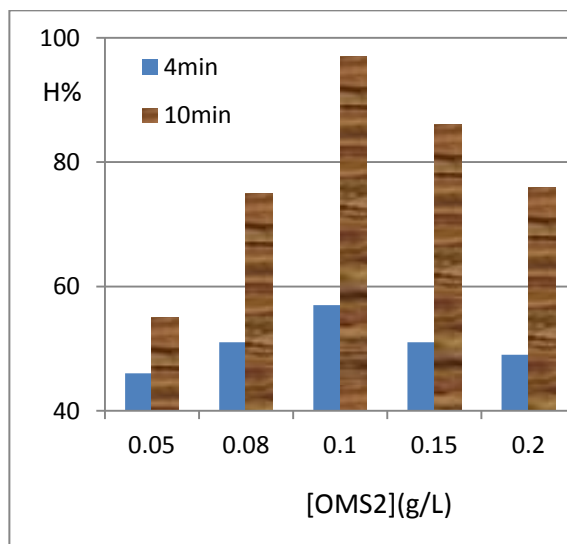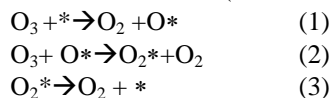
$$O_3 + * \rightarrow O_2 + O* \qquad (1)$$
$$O_3 + O* \rightarrow O_2* + O_2 \qquad (2)$$
$$O_2* \rightarrow O_2 + * \qquad (3)$$

Fig.6 Effect of catalyst content on NPE9 ozonation yield (V_{O3} = 3.5 L/min, pH = 7, [NPE9]o= 10 mg/L).

In step (1) ozone decays and the finding that the adsorbed ozone does not desorbs ascertains the irreversibility of steps (1) and (2). Further peroxide particles are formed in accordance with step (2) and then oxygen is desorbed from the catalytic surface – step (3). The finding that the peroxide species could not be formed from molecular oxygen at any conditions shows the irreversibility of step (3). The increase of OMS-2 content with small particles can introduce more defects and enhance the active surface sites, the NPE decomposition yield thus increase (Fig.6). If the NPE content exceeds a certain value the yield slightly decreases. This could derive from the mass trasnfer of ozone in a dense suspension.

Effect of ozonation time

The yield of NPE ozonation increased with the increase of reaction time until the maximum value . Many works proved that the ozonation follows the rule of first order reaction [6,7].

Table 1. Kinetic data of NPE ozonation

t (min)	0	2	4	6	8	10
C (mg/L)	10	7.2	3.97	2.12	0.74	0.28
k (min^{-1})		0.695	0.63	0.785	1.69	3.62

A pseudo-first order model is applied to determine reaction rate constant by the formula $\ln(C_o/C) = k.t$, where C_0 and C are the initial NPE concentration and NPE concentration at t, respectively (assume that ozone is in excess compared to NPE in this experiment). The average value of reaction rate constant k is of 0.703 min^{-1} (for the 3 first points). Ozonation is a rapid oxidation method, more than 95% NPE was converted just within 10 min (Fig.7). The kinetic data and effect of reaction time on NPE ozonation yield are described in Table 1 and Fig. 7.
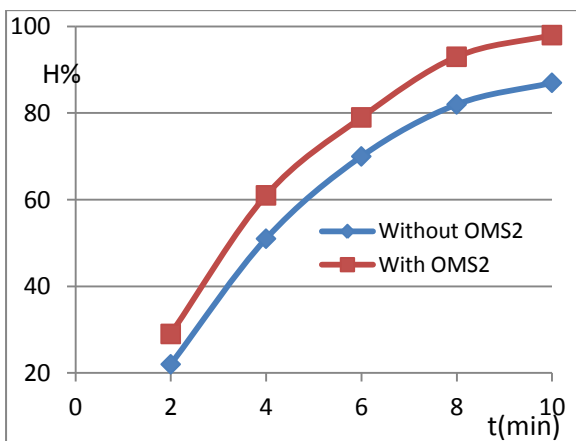

Fig.7 .Effect of reaction time on NPE9 ozonation yield

Mineralization investigation

In the treatment of pollutants, mineralization is always desired; however, in general AOPs are very difficult to transform all the pollutants including the intermediates to inorganic compounds. The mineralization was investigated by measuring the outlet CO_2 and compared to theoretical amount of carbon in NPE (Note that blank sample was ozone stream alone at the same condition). The effect of time on mineralization yield is presented on figure 8.
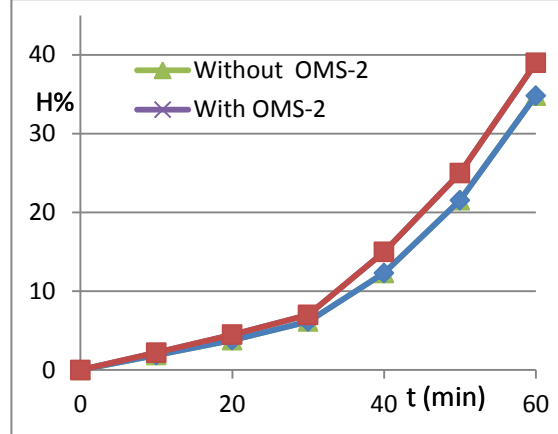

Fig.8 Effect of time on mineralization yield ((V_{O3} = 3.5 L/min, pH = 7, [OMS-2] = 0.1 g/L,[NPE]o = 10 mg/L)

A duration of 60 min is spent in this work for investigation of mineralization in ozonation process. The change of mineralization can be described by two stages: At the early stage of process (t < 30 min) the mineralization efficiency is not significant. NPE structure has a long chain of ethoxylates and a nonyl chain connected with an aromatic ring. In this stage, it is thought that NPE was decomposed into shorter chain of NPE and NPs were gradually formed. After that, hydroxyl radicals created by ozone continuously reacted with NPs and other decomposed product to create other products. A small amount of these species (approximate 7% at 30 min) is mineralized into CO_2. At the later stage of ozonation process (t > 30 mins), the mineralization yield increased with a higher rate. In this stage, most remained compounds are minor compounds and hydroxyl radicals can easily oxidize them into CO_2 (approximate 39% of total carbon in NPE is mineralized after 60 mins).

During ozonation treatment, the control of physical properties of the aqueous solution was fulfilled. The conductivity was increased from 1.5 to 19.8 µS/cm in 12 min while pH was slightly decreased from 7.02 down to 6.75 (Fig.9). It could be thought that the intermediate products of NPE9 ozonation process may rather contribute into increase of H$^+$ concentration as well as of the conductivity of the solution. The catalytic ozonation using metallic oxides can increase the yield of ozonation just by creating more hydroxyl radicals on the surface of catalyst, that means the mechanisms of ozonation are

nearly the same between catalytic ozonation and basic ozonation. Therefore the products of catalytic ozonation and ozonation would be the same, with a different yield. In fact, preliminary results from HPLC analysis of a reaction mixture after ozonation showed the existence of products with content in microgram/L. They are NPE4, NPE5,NP9,.... It is interesting that there are no NP in the products. The study on the distribution of products in degradation ozonation has been continued.
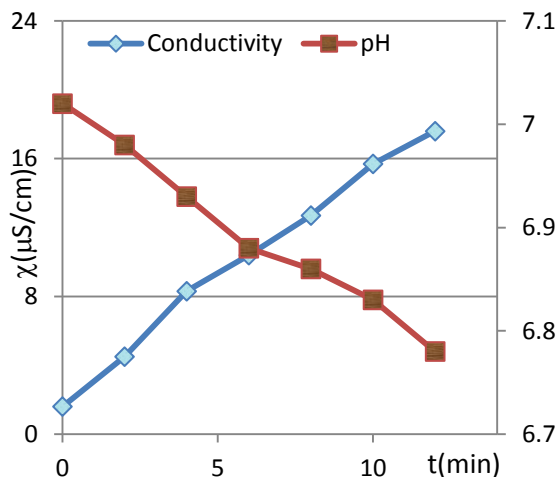

Fig.9 .Conductivity and pH change in the NPE9 ozonation degradation (V_{O3} = 3.5 L/min, pH = 7, [OMS-2] = 0.1 g/L,[NPE]o = 10 mg/L)
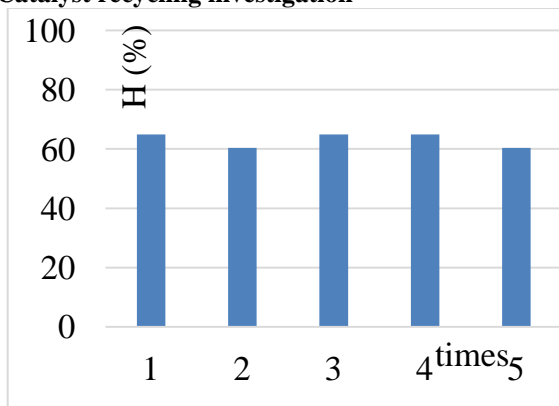
Catalyst recycling investigation

Fig.10. Investigation of catalyst recycling (((V_{O3} = 3.5 L/min, pH = 7, [OMS-2] = 0.1 g/L,[NPE]o = 10 mg/L)

After recycling, OMS-2 catalyst still have the same catalytic activities as depicted in Fig. 10. Since OMS-2 catalyst can be easily recycled with unchanged catalytic activity, this catalyst is reliable and can be applied in large scale model.

Conclusion:
The degradation ozonation of NPE in the presence of OMS-2 as heterogeneous catalyst was investigated. The best ozonation yield over 95% was achieved at temperature of 30°C, during the reaction time of 10 mins, with an amount of catalyst about 0.1

g/L, at pH of the solution of 11, using inlet ozone flow rate of 3.5 L/min, along with the initial NPE concentration of 10 mg/L. The mineralization yield was nearly 40% after 60 min of treatment. OMS-2 catalyst was easily recycled with negligible reduction of catalytic activities. In conclusion, OMS-2 catalytic ozonation is a reliable method that can be used as an addition stage in wastewater treatment processes to remove NPE from wastewater.

References:
[1] Liwarska-Bizukojc, E.; Miksch, K.; Malachowska-Jutsz, A. & Kalka, J. 2005. Acute toxicity and genotoxicity of five selected anionic and nonionic surfactants. Chemosphere, 58: 1249–1253.
[2] Saiena J., Ojaghlooa, Z. A.R. Soleymania, M.H. Rasoulifardb, Homogeneous and heterogeneous AOPs for rapid degradation of Triton X-100 in aqueous media via UV light, nano titania hydrogen peroxide and potassium persulfate; Chem. Eng. J. 167 (2011) 172–182
[3] Nguyen, G.H; Nguyen-Ngoc, H,Oxidation of CO over M-OMS-2, J.Sci,Devel.; 2008, 11, 13-16.
[4] Sun, H, Chen,S.; Wang, P; Quan, X . Catalytic oxidation toluen over Manganese Oxide Octahedral Molecular Sieves; Chem.Eng.J. 2011, 178, 191.
[5] Bower, K.C., Garner, K.H., Miller, C.H. and Kong, L.J.(2001) In situ colloidal MnO2 deposition and ozonation of 2,4-Dinitrotoluene. Environ Engin. Sci. 18, 259-265.
[6] Ikehata, K. and El-Din M.G. (2004) Degradation of recalcitrant surfactantss in wastewater by ozonation and advances oxidation processes: A review. Ozone Sci. Engin. 26, 327-343.
[7] Kasprzyk-Hordern, B., Ziolek,M and Nawrocki, J.(2003) Catalytic ozonation and methods of enhancing molecular ozone reactions inwater treatment: A review, Appl.Catal B: Environ 46, 639-669.
[8] Liu,Y., Li, X.,Zhu, A. M. Ozone Catalytic Oxidation of Benzene over Ag/HZsm-5 Catalyst at Room Temperature: Effects of Mn Loading and Water Content. Chin.J.Cata.2014, 35, 1465-1474.
[9] Li, J.H.; Wang,R.H; hao, J.M.Role of lattice Oxygen and Lewis Acid on Ethanol Oxidation over OMS-2 Catalyst. J.Phy. Chem.C2010,114, 10544-10650.
[10] B Kasprzyk-Hordern, M Ziółek, J Nawrocki. Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment ; Applied Catalysis B: Environmental 46 (4), 639-669.