Catalytic Oxidation of Methyl tert-butyl Ether with Hydrogen Peroxide from Aqueous Solutions

CORINA BRADU1*, ION UDREA1, MARIAN NEATA1, NICOLETA MIHALACHE1, SORIN MARIUS AVRAMESCU1,
GABRIEL RACOVITEANU2, ELENA VULPASU2

1 University of Bucharest, Faculty of Chemistry, Organic Chemistry Department, 4-12 Regina Elisabeta Blvd., 030018, Bucharest, Romania
2 Technical University of Construction, Technical University of Civil Engineering of Bucharest, 124 Bd. Lacul Tei, 020396, Bucharest, Romania

The evaluation of catalytic activity of some homogeneous (FeSO₄, FeCl₃, CuO₂, MnSO₄) and heterogeneous (α-Fe₂O₃, CuO or MnO₂ supported on alumina) systems in the oxidation of methyl tert-butyl ether (MTBE) with hydrogen peroxide from aqueous solutions was the main purpose of this work. The experiments were carried out in a thermostated batch reactor equipped with a magnetic stirrer. The experimental temperatures were 10, 15 and 20°C, and the pH was varied from 2.0 to 9.0. In acid medium (pH around 3), FeSO₄ and FeCl₃ possess the highest activity. Among the heterogeneous systems, CuO based catalysts are the most efficient in the MTBE degradation. Irrespective to the nature of the catalyst, the identified byproducts were the tert-butyl alcohol (TBA) and acetone. The TBA does not act as an inhibitor for the catalytic oxidation process. Furthermore, the data of the oxidation of MTBA in the presence of ferrous sulfate or ferric chloride confirm a total removal of byproducts after 6-8 h (depending on the temperature and the H₂O₂ dose).

Keywords: water treatment, catalytic oxidation, MTBE removal

Methyl tert-butyl ether (MTBE) has been widely used as gasoline additive since the late 70s, in order to enhance octane index and consequently to decrease the emission of carbon monoxide and aromatic compounds resulted from an inefficient combustion. However, MTBE seems to have significant adverse impacts on watercourse and groundwater. The contamination is particularly relevant for groundwater because of accidental gasoline release from underground storage tanks and pipelines in petrochemical industrial sites [1,2]. In fact, there are many cases of surface water and groundwater contaminated with MTBE [3].

Due to its high solubility in water and poor biodegradability, MTBE persists for a long time in the water supply being difficult to be removed.

Chemical remediation methods, compared to the biological ones, are much faster in removing organic pollutants. Among them, advanced oxidation processes (AOPs) are known to be effective in removing a number of persistent organic pollutants, which are refractory to conventional oxidation with H₂O₂ or O₃. These techniques include: ozonation at elevated pH values (>8.5); oxidation using the couple H₂O₂/O₃; photochemical processes (such as: H₂O₂/UV; O₃/UV; O₂/H₂O₂/UV); catalytical (homogeneous and heterogeneous systems) and photocatalytical processes (such as: Photo-Fenton; UV/TiO₂).

Adequate uses of AOPs ensure a reduction of pollutant concentration from hundreds of ppm to less than 5 ppb. For this reason, some authors call them “the 21st century water treatment processes” [4].

The Fenton and Fenton-like processes are included in this category. A Fenton-like system involves the presence of a couple: transitional metal – hydrogen peroxide or other peroxides or hypo-halogenated acids supposed to generate oxidant high reactive species, which have been (and still are) the subject of many discussions.

In the classical Fenton system, two alternatives for the generated oxidant species are proposed: free hydroxyl radicals and Fe(IV) complexes, such as ferryl ion, FeO₄²⁻ [5].

Other metals as: Cu(II), Co(IV), Cr(IV) and Mn(IV) can form such intermediates [6,7].

Homogeneous catalytic systems based on iron or copper salts are the most studied for this type of process, but the role played by other metals cannot be neglected. On the other hand, the potential toxicity of the metal must be taken into consideration. Therefore, it has been found that cobalt and chromium, which may present a good activity in the oxidation processes with hydrogen peroxide, by Co(I) – Co(II) and Cr(II) – Cr(III) species, have a toxic and carcinogenic character [8-12]. For this reason, in the present study, we have not tested cobalt and chromium compounds.

The main purpose of this work was to evaluate the catalytic activity of some homogeneous and heterogeneous systems in the oxidation of MTBE from aqueous solutions with hydrogen peroxide. We have investigated also, the influence of: oxidizing agent dose, catalyst concentration, temperature and pH on the MTBE oxidation process.

Experimental part

Catalysts

The catalysts tested in this work are presented in table 1.

For heterogeneous catalysts, iron, manganese, and copper oxides were supported on alumina in order to ensure a good dispersion and consequently to enhance the contact surface with reactants.

The supported catalysts were obtained by: (i) solid-solid reaction (dry mixing) of active compounds for FeO₂-Al₂O₃ catalyst; (ii) precipitation-deposition for CuO-Al₂O₃; (iii) incipient wetness impregnation for

* email: corina.brada@g.unibuc.ro; Tel.: 4021.4105440

REV. CHIM. (București) ♦ 60 ♦ Nr.3 ♦ 2009
CuO/Al₂O₃ and Mn₃O₄/Al₂O₃ catalyst, followed by drying and final activation at 550°C [13, 14].

The experimental procedure and equipment

The MTBE oxidation with hydrogen peroxide was performed in a thermostated batch reactor with a capacity of 1L, equipped with a magnetic stirrer. The experimental setup is illustrated in figure 1.

All chemicals were of analytical purity grade. The 10 mg·L⁻¹ solutions of methyl tert-butyl ether (MTBE) and tert-butyl alcohol (TBA), one of the main by-products, were prepared using deionized water (0.1 μS).

The catalyst concentration was of 1.5 g·L⁻¹ for heterogeneous systems and of 0.25-1.0 mM for homogeneous systems.

For the experiments carried out in homogeneous systems, we prepared stock catalysts solution (MnSO₄; CuSO₄; FeSO₄; FeCl₃) of 5 g·L⁻¹ acidified with H₂SO₄ (0.1 M) until pH = 3 was reached, the desired catalyst concentration in the reaction medium being achieved by adding a corresponding volume of stock solution. All solutions were stored at 4°C in the dark.

A volume of 1L MTBE or TBA solution (initial concentration of 10 mg·L⁻¹) was used for each experimental run and the initial concentrations of hydrogen peroxide were between 3.5 mM and 140 mM. The experiments for the degradation of MTBE and TBA were carried out in a pH range of 2.0 – 9.0 (pH correction with H₂SO₄ or NaOH).

Taking into account the main purpose, MTBE removal from natural water (surface and ground water), the experimental temperatures were 10, 15 and 20°C (controlled within ±0.2°C of the set value).

Before each experimental run, to remove the air from reactor, the reactor was purged for 20 min under flowing N₂. Samples were taken from the aqueous solution and from the gas phase.

Analytical methods

The MTBE and TBA from the aqueous solution and from the gas phase were analyzed by GC using a Varian CP3800 chromatograph with FID detector, and a CP-WAX57CB (25mx0.25mm) column, with a N₂ flow rate of 1.5 mL·min⁻¹. The liquid samples were analyzed using headspace technique. To prevent further reaction at the end, an amount of 0.5 mL concentrated KNO₂ solution was added to each 5 mL of liquid sample.

The by products were also analyzed by GC-FID and identified by GC/MS. For GC/MS analysis a Varian 2100 T apparatus, equipped with split injector and a CP-SIL 8 CB capillary column has used in EI mode.

The evolution of the hydrogen peroxide concentration was monitored by permanganate titrimetric method.

All experiments were accomplished in three replicates, the presented results being an average of these results.

We mention that, in our experimental conditions, the most of MTBE and their byproducts are found in the aqueous solution. In consequence, the stripping of MTBE, TBA, and the other identified by products was assumed to be insignificant.

Results and discussion

The results obtained for the oxidative degradation process of MTBE are presented in figure 2. The investigation of homogeneous catalytic systems (MnSO₄, CuSO₄, FeSO₄, and FeCl₃) was carried out at pH = 3.0 in order to avoid the precipitation of metal ions as hydroxides and of heterogeneous systems (Mn₃O₄/Al₂O₃, CuO/Al₂O₃, CuO-Al₂O₃, and Fe₃O₄-Al₂O₃) at natural pH (6.5 - 7.0). These experimental runs were performed at 10°C. A blank experiment (MTBE solution without H₂O₂ and catalyst maintained at the same temperature) is also represented in the figure 2.
It was found that for the systems FeSO₄ – H₂O₂ and FeCl₃ – H₂O₂ a high reaction rate was attained, the total removal of MTBE taking place after 5-6 h.

Among the heterogeneous systems, catalysts based on CuO possess the highest activity, in given experimental conditions, insure for a 6 h reaction time a MTBE conversion of about 20%.

As presented in figure 2, MTBE is not stripped from the aqueous solution. Also it can be observed that the organic pollutant oxidation does not take place in the absence of the catalyst, suggesting that MTBE removal is produced only by catalytic way.

**Influence of the operating conditions**

**pH Effect**

The pH of reaction media may have a strong effect on the oxidation process efficiency [15].

The pH influence can act on:
- catalyst, by modification of solubility in the reaction media;
- H₂O₂ decomposition, by rising or diminishing the rate of hydroxyl radical generation;

It is well known that the hydroxyl radicals generation is favoured in alkaline media. The formed radicals are able to further initiate hydrogen peroxide decomposition, through radical chain mechanism:

\[
\text{HO}^+ + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^+ \\
\text{HO}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2^- + \text{HO}^+ 
\]

In addition, two HO₂⁻ radicals can combine to generate an ozone molecule:

\[
2\text{HO}_2^- \rightarrow \text{H}_2\text{O} + \text{O}_3 
\]

The last reaction is sustained by the presence of ozone trace, observed in many cases in the hydrogen peroxide decomposition [16].

The effect of pH on the oxidation of MTBE was studied for both homogenous and heterogeneous catalytic systems, for a reaction time varying from 0.5 to 3.0 h, at pH values ranging from 2.0 to 9.0.

In the case of heterogeneous catalyst no significant evolution of MTBE conversion with the pH was observed. On contrary, for the soluble catalysts (homogeneous system), the facts are completely different. They present maximum activity in a 3.0 – 4.0 pH range.

For the system FeSO₄ – H₂O₂, the optimal pH value is 3 (fig. 3). In a strong acid media (pH = 2.0) the reaction is stalled, probably due to the poor HO₂⁻ generation in this conditions. Also, at pH greater than 4, the reaction rate severely decreases, due to the ferrous ions precipitation.

![Fig. 2. Comparison of catalytic activity of different homogeneous and heterogeneous systems on MTBE oxidation (C₀ MTBE = 10 mg.L⁻¹ (0.11 mM), C₀ H₂O₂ = 70 mM; catalysts concentration: homogenous – 0.5 mM, heterogeneous – 1.5 g.L⁻¹; temperature = 10°C)](image)

![Fig. 3. pH effect on MTBE oxidation catalyzed by FeSO₄ (C₀ MTBE = 10 mg.L⁻¹ (0.11 mM), C₀ H₂O₂ = 70 mM; catalyst concentration = 0.5 mM, temperature = 10°C)](image)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H₂O₂ concentration, nM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (min)</td>
</tr>
<tr>
<td>CuO-Al₂O₃</td>
<td>1.65</td>
</tr>
<tr>
<td>CuO/Al₂O₃</td>
<td>2.80</td>
</tr>
<tr>
<td>Mn₃O₇/Al₂O₃</td>
<td>0.30</td>
</tr>
</tbody>
</table>

![Table 2: H₂O₂ CONCENTRATION AFTER HETEROGENEOUS CATALYTIC OXIDATION OF MTBE (H₂O₂ INITIAL CONCENTRATION = 14 mM)](image)
Effect of oxidizing agent and catalyst dose

In order to optimize the process, it is important to establish hydrogen peroxide dose and catalyst dose. Varying the H$_2$O$_2$ (33%) dose from 0.15 to 6.0 mL per liter MTBE solution, we have obtained concentrations of the oxidizing agent from 3.5 to 140 mM.

For small H$_2$O$_2$ concentration, 3.5 – 14 mM, in the heterogeneous catalytic process, the degradation of MTBE after 3 h reaction time is insignificant. It is interesting to mention that, in this condition, even CuO based catalysts, which generally have a high activity, doesn’t lead to MTBE degradation. Nevertheless, the rapid decrease of H$_2$O$_2$ concentration during the process catalyzed by CuO/Al$_2$O$_3$, CuO-Al$_2$O$_3$ and Mn$_2$O$_3$/Al$_2$O$_3$ suggest a high activity of these catalysts in the hydrogen peroxide decomposition (table 2). This supposition is sustained by the previous chemiluminescence measurement, which have emphasized a pro-oxidative character (by means of hydroxyl radical generation) for CuO based catalysts [17].

Under these circumstances, we assume a significant higher rate of hydrogen peroxide decomposition compared to the reaction rate of hydroxyl radicals with the organic pollutant, which leads to an inefficient H$_2$O$_2$ consumption. An effective heterogeneous catalytic degradation of MTBE can be achieved only at higher doses of hydrogen peroxide.

The influence of the oxidizing agent dose in the homogeneous catalytic process was studied for ferrous sulfate catalyst. The results presented in figure 4, show an increasing removal of MTBE with the H$_2$O$_2$ dose. This rise is important for hydrogen peroxide concentration up to 14 mM, becoming moderate subsequently.

Variations in catalyst concentration, in the range of 0.25 – 0.5 mM, induce a strong influence on MTBE homogeneous oxidation process (fig. 5).

Temperature

In order to work in conditions similar to those encountered in natural water, the oxidation test was carried out at reaction temperature of 10, 15 and 20°C.

The results for MTBE oxidation catalyzed by FeSO$_4$ and FeCl$_3$, at 14 and 70 mM H$_2$O$_2$ concentration are reported in figure 6. While for lower hydrogen peroxide concentration (14 mM), a rise of reaction temperature favoured the process catalyzed by FeSO$_4$, at higher H$_2$O$_2$ concentration (70 mM) both processes are considerably accelerated.
Byproducts

In order to assess the oxidation degree achieved, potential toxic character and biodegradability of the treated water, the identification of the byproducts resulted from the oxidation of organic pollutant from water is essential.

Irrespective of the nature of the catalyst, the identified byproducts were the tert-butyl alcohol (TBA) and acetone (fig.7). It should be mentioned that all chromatograms presented some unidentified peaks.

One of the byproducts, TBA, is presumed to manifest an inhibition effect on free radical reactions [18]. Due to this fact its evolution in the MTBE catalytic oxidation process was studied.

The results of the tests of the TBA (10 mg.L⁻¹) oxidation in the presence of FeSO₄ and FeCl₃, for a reaction time up to 3 h, are illustrated in figure 8. The
diminishing of the TBA concentration with the reaction time reveals the degradation of this compound by catalytic way, suggesting that no reaction inhibition occurs. Besides, the data of the oxidation of MTBA in the presence of ferrous sulfate or ferric chloride confirm a total removal of byproducts after 6-8 h (depending on the temperature and the H$_2$O$_2$ dose) (fig. 9).

Conclusions

As a result of the activity tests for homogeneous and heterogeneous catalytic systems in the oxidation of MTBE with hydrogen peroxide and of the evaluation of the operating condition influence on the process some conclusions can be draw. Catalytic oxidation with hydrogen peroxide can be considered an effective method for the MTBE removal from water.

Among the homogeneous catalysts, FeSO$_4$ and FeCl$_3$ possess the highest activity. The maximum of activity is achieved for a pH around 3.

CuO based catalysts, among the heterogeneous systems, are the most efficient in the MTBE degradation. Even though they present a lower conversion of MTBE in comparison with ferrous or ferric homogeneous catalysis, the CuO/Al$_2$O$_3$ catalysts possess the advantages of a greater operational pH range (3 – 9) and a more easy separation from the reaction media.

In the homogeneous catalysis, a rise of the reaction temperature from 10 to 20°C favors especially the process catalyzed by ferrous sulfate.

Irrespective of the nature of catalyst, the identified byproducts formed in the oxidation of MTBE were the tert-butyl alcohol (TBA) and acetone.

In the presence of ferrous sulfate or ferric chloride a total removal of degradation byproducts occurs, depending on the operating parameters, after 6-8 h.

Acknowledgments: Financial support from the Romanian Ministry of Education, Research and Youth under grant No. 622/2005 is gratefully acknowledged.

References
2. SIEDLECKA, E., WIECKOWSKA, A., STEPNOWSKI P., J. Haz. Mater. 147, 2007, p 497
13. UDREA, I., BRADU, C., Ozone Sci. & Eng., 25, nr. 4, 2003, p 335
15. SIMINICEANU, I., BOBU, M.M., Rev. Chim.(Bucureși), 57 nr. 12, 2006, p 1205

Manuscript received: 21.02.2008