

## Remediation of Methyl Tert-Butyl Ether (MTBE) Contaminated Water by Using *In situ* Catalytic and Biological Combined Techniques

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**Abstract:** The hydrolysis reaction of Methyl Tert-Butyl Ether (MTBE) into biodegradable products was studied on as-synthesized and commercial H-MFI zeolites. The effect of synthesis procedure and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio was investigated. The results obtained were indicated that H-MFI zeolites were effective in MTBE hydrolysis and increasing of the Si/Al ratio promotes the hydrolysis reaction. The amount of produced TBA was always lower than what expected stoichiometrically. It is concluded that the missing amount of TBA can be a result of possible formation of an alkene. The capability of indigenous microorganism to biodegrade hydrolysis products in presence of zeolite was also studied. Microorganism was able to use products except TBA produced intermediate carbocation hasn't any adverse effects on the microbial activity.

**Keywords:** MTBE contamination, hydrolysis reaction, H-MFI, indigenous microorganism

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### INTRODUCTION

Methyl Tert-Butyl Ether (MTBE) has been introduced as a gasoline octane enhancer on the late 1970s to substitute lead tetraethyl. As a result of its low production cost and excellent blending characteristics, its production has been exponentially growing, reaching more than 33 million tons per year at present time<sup>[1,2]</sup>.

Widespread use of MTBE in gasoline, leaks of fuel underground and above ground fuel tanks, spill or accidental runoff, from petroleum facilities (including refineries, terminals, the pipelines and service stations) has introduced MTBE into the environment compartments, mostly into the ground water and surface water as a second most frequently detected contaminant<sup>[3]</sup>.

On the contrary with other gasoline components like BTEX compounds (Benzene, Toluene, Ethyl benzene and Xylenes), MTBE is less sorbed to soils and highly soluble in water mobile in ground water<sup>[2]</sup>. This, together with very slow or absence of natural attenuation and usually a long incubation time, which is necessary before the start of microbiological degradation, explain why ground water pollution with MTBE results in plume lengths that can reach several hundreds of meters, with reported cases of well above a kilometers<sup>[4-6]</sup>.

A modeling research has indicated that MTBE plume lengths will extend in the coming years hence significant numbers of MTBE release accidents may continue to reveal this contaminant as problematic source of contamination for the environment as of the year of 2010<sup>[7,8]</sup>.

Investigation conducted by a Blue Ribbon Panel of the USEPA, reported that MTBE concentration in approximately 1% of drinking water supplies exceeded 20 ppb<sup>[9]</sup>.

Because MTBE is a hazardous chemical and is generally unpleasant in taste and odor, The US EPA has issued a drinking water advisory of 20-40 ppb on the basis of taste and odor threshold (2.5 and 2.0 ppb, respectively<sup>[10,11]</sup> and the California Department of Health Services issued a maximum contaminant level of 5 ppb MTBE<sup>[12]</sup>.

Therefore, there is an urgent need to seek economically efficient and environmentally friendly approaches to treat MTBE contaminated water so far. several technologies have been proposed, some of which proven to be practical such as air stripping, which needs to have a large air streams contaminated with MTBE, that require further treatment; adsorption of MTBE on the carbon active or high silica zeolites that requires disposal of spent adsorbent; advanced oxidation by ozone, peroxides, ultrasound or combination, which may form dangerous products, such

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as aldehydes some proven to expensive and not yet ready to be deployed in this field like those techniques based on membranes<sup>[1,13]</sup>.

Controversial results have been reported regarding in situ bioremediation of MTBE. Biodegradation processes need dissolved oxygen and pure strain or adapted consortium<sup>[14-17]</sup>. Recently, MTBE catalytic conversion by solid catalysts was proposed. Hydrolysis of MTBE to biodegradable compounds expected to be catalyzed even at room temperature by acidic materials such as zeolites of MFI group (e.g., ZSM-5)<sup>[17-18]</sup>.

Zeolites are three-dimensional, crystalline inorganic compounds, which are built from  $AlO_4$  and  $SiO_4$  tetrahedra. ZSM-5 is a strong solid acid with a characteristic structure containing channels, which allow diffusion of molecules with appropriate size<sup>[19-21]</sup>.

Falconer *et al.*<sup>[22]</sup> were shown that all-silica zeolite is an effective sorbent for MTBE removal from contaminated waters. Hyman *et al.*<sup>[23]</sup> reported a MTBE acid-catalyzed hydrolysis reaction that generates Tert-Butyl Alcohol (TBA) and Methanol (MeOH) as products. Anderson *et al.*<sup>[24]</sup> were shown that mordenite and silicalite with high  $SiO_2/Al_2O_3$  ratios demonstrate superior sorption characteristics toward MTBE and TCE in comparison to activated carbon. Centi *et al.*<sup>[13]</sup> were evaluated different acidic zeolites and found those zeolites with a suitable pore structure (channel structure and pore opening), such as H-MFI and H-BEA zeolites were presented effective adsorption and catalytic characteristics toward MTBE at rates comparable to biodegradation by indigenous microorganisms. They suggest that these zeolites may be applied for in situ groundwater remediation and as a protection barrier for wells or leaking tanks. In addition to acting as adsorbents for MTBE and the products of its hydrolysis reaction, the used zeolites were also catalyzed the hydrolysis reaction of MTBE<sup>[13]</sup>. However, in this study, the detected amounts of TBA and MeOH were always lower than what expected to be resulted from MTBE conversion reaction. It is concluded that the missing amounts were due to the adsorption of MTBE and degradation products by the zeolites.

More recently, the authors<sup>[18]</sup> were evaluated hydrolysis behavior of synthesized H-ZSM-5 and Na-ZSM-5 of different  $SiO_2/Al_2O_3$  ratios with reference to the possibility of MTBE conversion to more biodegradable products. On that research, acidic form of ZSM-5 catalyst was more effective than a sodium form and the TBA product was always lower than the expected stoichiometric amount.

This study intends to report the experimental results of a research concerning with the catalytic behavior of as-synthesized ZSM-5 (synthesized at our

laboratory) and a commercial ZSM-5 (obtained from SUD-CHEMIE, Germany) zeolites in the conversion reaction of MTBE in water at room temperature and static condition. To evaluate the hydrolysis reaction in order to find missing amounts of MTBE and hydrolysis products a new mechanism is proposed. The capability of indigenous microorganism to biodegrade MTBE hydrolysis products was also investigated.

## MATERIALS AND METHODS

Commercial H-ZSM-5 zeolite was supplied by SUD-CHEMIE company (from Germany), with  $SiO_2/Al_2O_3 = 90$ , which was used without any further treatment (entitled as Z-SUD). An artificial ZSM-5 zeolite with  $SiO_2/Al_2O_3 = 50$  (entitled as Z-SYN) was synthesized in our laboratory according to a method reported by Stan Whittingham<sup>[25]</sup>.

Z-SYN was synthesized by crystallization of the prepared gel followed by calcination in an electrical furnace under nitrogen controlled atmosphere and converted to H-form (H-ZSM-5) by ion exchange treatment using 1M ammonium sulfate solution, followed by a thermal decomposition of ammonium ions at 380°C.

All of the used materials were analytical grade chemicals from Merck Company, Germany.

**Experimental:** In order to characterize Z-SYN, its chemical composition and crystallinity were determined. Si/Al ratio of the synthesized zeolites (Z-SYN) was measured by XRF technique, using a Philips PW 2404 instrument, which has a good correlation with expected ratios.

Crystalline structural of the sample was approved by X-ray diffraction technique using a Philips Xpert diffractometer (Cu  $K\alpha$  radiation at 40kV and 50 mA). The X-ray diffraction pattern reported in Fig. 1 shows a relatively pure crystalline phase, which was consistent with that of the MFI-type structure (ZSM-5 zeolites).

MFI catalysts were tested to evaluate their capability for MTBE degradation. Tests of MTBE catalytic conversion have been performed at static condition in 50 mL PE bottles fitted with a screw cap and a Teflon lined silicon septum. Typically 50 mL of the solution was in contact with 0.5 g of zeolite powder. The initial concentration of MTBE in aqueous solution was in the range of 740-3000 ppm, which is in the range of MTBE concentration in contaminated water within a distance of about 3-5 m far from a leaking underground fuel tank<sup>[13]</sup>. Concentrations of MTBE and its hydrolysis products were measured using a gas chromatograph (Philips PU-14100) equipped with a

Flame Ionization Detector (FID) and a 10% SE30 packed column (1.5 m, 0.4 mm ID). The temperature of GC column, injector and detector were adjusted isothermally at 50, 180 and 200°C respectively. Nitrogen gas (20 mL min<sup>-1</sup>) was used as the carrier gas. Measurement was done using one micro liter portions of liquid phase, which was taken from gas-tight reaction vessels with a micro syringe.

In order to perform biodegradation tests, 300 mL of supernatant urban activated sludge was added to 1l of mineral medium, fully flushed with air for 30 min, MTBE was then added at the concentration of 400 mg L<sup>-1</sup>, which has not any inhibitory effects on the MTBE biodegradation<sup>[14]</sup>.

Experiments were conducted in 115 mL poly ethylene bottles fitted with a butyl rubber septum. In each bottles, 25 mL of above mentioned solution was added. A headspace of 90 ml was guaranteed sufficient air for aerobic degradation. After inoculation, three sets of duplicate bottles were amended with above mentioned mixture and incubated with: 1) 25 mg zeolite, 2) 25 mg zeolite and 1% NaCN as control 3) without adding of zeolite. All bottles were shaken at 150 rpm in a dark environment and at room temperature (25±0.5°C). A gas chromatograph device was used to measure the concentrations of MTB and hydrolysis products by analyzing samples of bottles head space at different time.

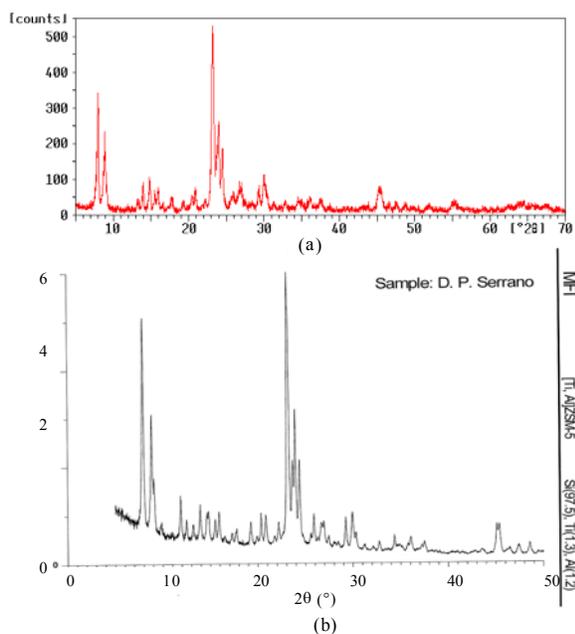


Fig. 1: X-ray diffraction pattern of MFI-type zeolites (a): Synthesized pattern; (b): Standard pattern

## RESULTS AND DISCUSSION

Results obtained from a typical hydrolysis reaction of MTBE to lighter molecules, which is catalyzed by 0.5 g of zeolite powder in a solution contains 740 ppm of MTBE at room temperature is shown in Fig. 2. Blank sample in the absence of zeolite is also illustrated, which is pointed out that no changes is observed due to possible biodegradation, photochemical conversion, adsorption on the wall and diffusion from septum of the reaction vessel.

By adding zeolite powder, a fast decrease of the MTBE concentration was observed at the beginning few hours, while, no simultaneous parallel formation of other molecules of reaction products were detected. This can be considered as a result of adsorption of MTBE molecules onto the zeolite surface. After a few hours, a change in the slope of decreasing curve of MTBE concentration is observed with a parallel increasing of the formation of TBA and MeOH molecules. This evidence clearly confirms that hydrolysis reaction of MTBE takes place. According to the obtained results, the amount of produced MeOH molecules is nearly equal to the theoretically expected amount, while, the detected TBA is always lower than stoichiometric amount. We concluded that the missing amount of TBA can be a result of possible formation of new product.

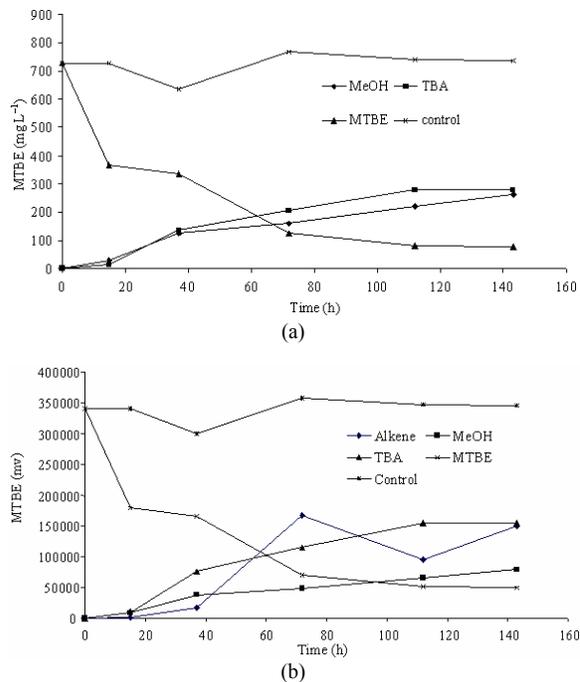


Fig. 2: Behavior of ZSM-5 zeolite in the conversion of MTBE in water solution containing an initial concentration 740 ppm MTBE (a): (mg), (b): mean peak area (mv)

Ether molecules are comparatively unreactive compounds. The ether linkages just can cleavage at very severe conditions (e.g., in the presence of concentrated acids at high temperatures). Cleavage of the ether bond of MTBE undergoes to an alcohol (MeOH) and a stable tertiary carbocation. Like free radicals, the carbocation is an exceedingly reactive particle to complete the octet of carbon atom. It takes a pair of electrons to complete the octet sphere; therefore, the carbocation is extremely powerful Lewis acid. To do this, it may 1) combines with a nucleophile following a SN1 reaction mechanism to produce a stable TBA molecule, 2) following an E1 reaction to eliminate a proton and produces an alkene molecule (i.e. iso-butene or 2-butene), or 3) rearranging to more stable carbocations. Reaction mechanism deeply depends on the experimental conditions<sup>[26]</sup>.

Analysis of the headspace gases were carried out by a gas chromatography instrument equipped with a mass quadrupole detector and DB1, DB5, CP Sili5 columns. Results were unsuitable and the used setup couldn't identify the products possibly because of detector saturation phenomena resulting from the presence of water molecules as well as unsuitable columns. Simultaneous injection of a sample portion along with isobutene undergoes to a double peaks at the position, where unknown peak was observed.

Qualitative identification test was done on a sample using bromation reaction in which alkene compound was identified. Unknown compound was suggested to be isobutene or isobutene oligomers<sup>[27]</sup>. Comparative result is presented as a mean peak area. Summarized results in Fig. 3 are showing the catalytic behavior of zeolites in different concentration of MTBE after 100 hrs of reaction.

Changing the Si/Al ratio can modulate acidity and hydrophobic properties of zeolites<sup>[13, 19]</sup>. Both of the used zeolites showed good catalytic activities toward MTBE hydrolysis reaction, but Z-SUD showed rapid decreasing of initial MTBE concentration as well as a higher rate of MeOH formation. It is expected that MTBE hydrolysis rate increases with increasing of the number of acidic sites as a result of higher Si/Al ratio, because of higher hydrophilic character, an easier back-diffusion of the hydrolysis products from the zeolite pores into the aqueous phase can be take place.

Therefore, in higher Al content, adsorption of the hydrolysis products blocks the hydrolytic activity. Therefore after the initial activity, the residual activity was determined by the rate of desorption of reaction products. Despite of abovementioned reason, it should be noted that the amount of produced TBA in the presence of Z-SYN is lower than Z-SUD, while the amount of produced Alkene is higher, which is in contradiction of what was expected from Si/Al content.

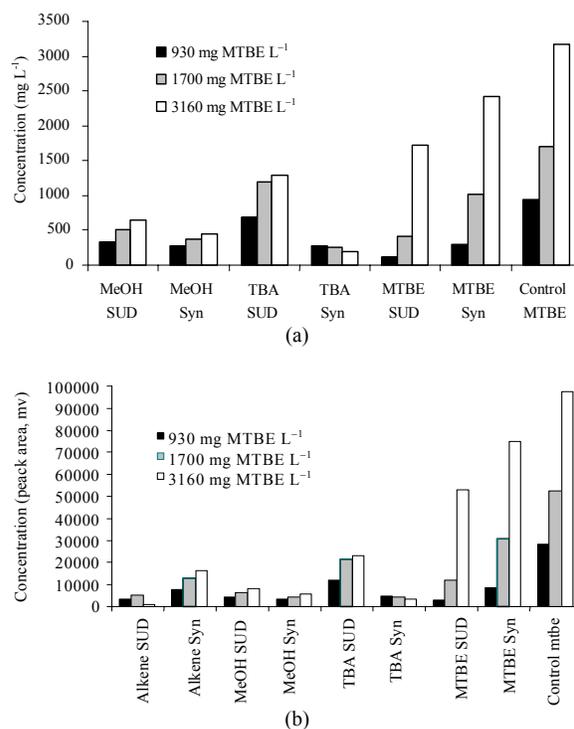


Fig. 3: Comparison of the behavior of two different zeolites in the r.t. conversion of MTBE in different concentration by according to (mg L<sup>-1</sup>) (a) and (b) mean peak area (mv)

Zeolites hydrophobicity can be evaluated as a result of several parameters such as Si/Al ratio in Zeolites frame work, cation present in zeolite structure, synthesis method, structural defects and post-synthesis modification<sup>[19,20]</sup>. It seems that different catalytic behavior of the investigated catalysts (i.e., type and amounts of the reaction products), can be attributed to the differences in synthesis methods, probable structural defects and post-synthesis treatment of the catalysts.

Results of the effect of MTBE initial concentration on the catalytic efficiency of two catalysts with the different Si/Al ratio is shown in Fig. 4. Residual concentration of MTBE was measured in the liquid phase.

Comparative results of different tests on the combined MTBE catalytic conversion and biodegradation reaction are shown in Fig. 5.

Based on the obtained results, indigenous microbial strains could not make any degradation alone, while addition of zeolite to the reactor vessel leads to a rapid decreasing of MTBE at initial times (up to 30 h) without producing any products, which is possibly as a result of adsorption of MTBE on the zeolite surface.

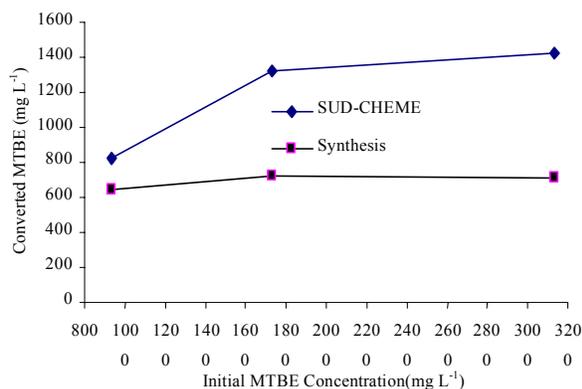


Fig. 4: Effect of MTBE initial concentration on catalytic activity of the used zeolites

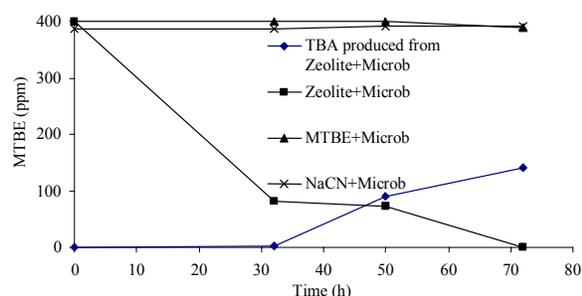


Fig. 5: Comparison results of MTBE degradation experiment by combination catalytic conversion and biodegradation by indigenous microbial strain

By passing the time (>30 h) TBA molecules formed as a result of MTBE catalytic conversion. A mixture of microorganism, NaCN and MTBE was used as blank.

Normally, MTBE catalytic conversion reaction results amounts of hydrolysis products (e.g., TBA, MeOH and Alkenes), while according to the results obtained in these tests, the only detected products was TBA. It can be concluded that the disappeared products (MeOH and Alkenes), can be used by the indigenous microorganism in activated sludge. The intermediate carbocation produced in catalytic conversion path has not any adverse effects on the microbial activity.

### CONCLUSION

Based on the results obtained at the research, the zeolite catalysts can be used for degradation of MTBE in contaminated water streams. The different catalytic behavior of the investigated catalysts (i.e., type and amounts of the reaction products), can be attributed to the differences in synthesis methods, probable

structural defects and post-synthesis treatment of the catalysts. According to these preliminary results, zeolites can be used to make Permeable Passive Barriers (PBR), which is a potential way for MTBE conversion to more biodegradable compounds<sup>[13]</sup>. The produced TBA molecules, which show high resistance to biodegradation reaction, will be left unchanged. It can be suggested that the TBA source in underground water may be as a result of MTBE hydrolysis reaction. TBA is common MTBE hydrolysis and biodegradation product. As regards that MTBE biodegradation reaction has to be conducted by specific strain in an aerobic condition, which such a condition isn't available in underground water, therefore, TBA can not be formed as a result of MTBE biodegradation<sup>[8]</sup>. It seems that, aluminosilicate compounds in the earth layers can catalyze the MTBE hydrolysis reaction in a long term period. Most of the hydrolysis products are biodegradable compounds by indigenous microorganisms in an anaerobic condition, but TBA needs to specific strain, which is not accessible easily. Then TBA in underground waters may have hydrolysis source.

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