ELSEVIER

Catalysis Today 75 (2002) 69–76

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Catalytic conversion of MTBE to biodegradable chemicals in contaminated water

G. Centi, A. Grande, S. Perathoner*

Department of Industrial Chemistry and Engineering of Materials, University of Messina, Salita Sperone 31, 98166 Messina, Italy

Abstract

The behavior of different acid zeolites in the hydrolysis at room temperature of methyl *tert*-butyl ether (MTBE) was studied with reference to the possibility of its conversion to more biodegradable products in underground water contaminated by MTBE. The effect of the structure of the zeolite and SiO_2/Al_2O_3 ratio was analyzed. The results indicate that acid H-MFI and H-BEA zeolites are effective in both adsorption and hydrolysis of MTBE and may be applied for both in situ underground water remediation and as protection barrier for wells or leaking tanks. However, other zeolites (mordenite and faujasite) result completely inactive. Furthermore, contrary to what was expected, the increase of the Si/Al ratio promotes the reactivity which is determined by the resistance to diffusion of MTBE in the pores of zeolites and the resistance of back-diffusion of the reaction products. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: MTBE contamination; Catalytic adsorbents; H-MFI; H-BEA

1. Introduction

MTBE (methyl *tert*-butyl ether), a widely used gasoline additive has increasingly been detected in both ground water and surface water [1]. Use of MTBE as a gasoline additive began in the late 1970s to maintain adequate octane rating during the phase-out of alkyl lead additives. Its use has been exponentially growing reaching a value of over 10^4 millions kg per year today.

MTBE, like chlorinated solvent compounds, has been found to persist in ground water. MTBE water contamination derives from leaking of underground fuel tanks and pipelines, tank overfilling and faulty construction at gas stations [1]. Gasoline components like BTX (benzene, toluene and xylenes) are characterized from good biodegradability and low water solubility. Therefore, contamination by released gasoline is fast mitigated by natural processes and a low migration index is observed. On the contrary, MTBE is very soluble in water and therefore very mobile in ground water system [2]. Furthermore, it is very resistant to biodegradation and usually a long incubation time is necessary before the start of microbiological degradation [3]. MTBE plumes extending kilometer scale distances in the subsurface have been detected [1,2,4]. The September 1999 US Report of the “Blue Ribbon Panel on Oxygenates in Gasoline” stated that 5–10% of US community drinking water show detectable concentrations of MTBE. The suggested MTBE remediation “action level” is 10–20 μg/l, but several wells were found to show concentrations above these limits [5,6]. MTBE is a suspected carcinogenic agent, but also gives a very unpleasant taste to drinking water when present also in very low amounts.

Models on MTBE diffusion [1,4] pointed out that, although banned from gasoline pool, community water supply wells may be affected by significant

---

* Corresponding author. Tel.: +39-90-393134; fax: +39-90-391518.
E-mail address: perathon@unime.it (S. Perathoner).

PII: S0920-5861(02)00046-9

concentrations of MTBE over the next 10 years [5,6]. Furthermore, the use of other gasoline additives will require very large investments.

Therefore, there is an urgent need to find technically and economically feasible solutions to prevent MTBE contamination as well as remediate water contaminated by MTBE. Several technologies have been proposed, some of which proven to be practical such as air stripping (which need, however, a secondary treatment to eliminate MTBE from the stripping air), advanced oxidation (based on ozone or peroxides, but which may form dangerous products such as aldehydes) and activated carbon (which need periodic regeneration), and some proven to be expensive, like those based on membranes [7]. Controversial results have been reported on in situ bioremediation [7,8]. Phytoremediation has been also proposed [9] as well as a number of other less conventional techniques such as sonolytic destruction [10]. However, no attention was given at all at the possible use of solid catalysts.

The hydrolysis of MTBE to *t*-butyl alcohol (TBA) and methanol is expected to be catalyzed even at room temperature by acid materials such as zeolites. The advantage of this conversion is that TBA shows a higher biodegradability than MTBE and especially a large reduction in the induction time necessary for adaptation of the microorganisms and the starting of the microbial activity in MTBE degradation [3].

Zeolites, due to their microporous structure, would be effective in adsorbing released gasoline. Furthermore, having a hydrophilic character, this material would be more effective in adsorbing MTBE than other gasoline components. Barriers based on microporous materials and zeolites have been suggested as an effective way to prevent diffusion of leaked gasoline from underground tanks by making a layer around the underground tank or around wells. It would be thus worthwhile to study the behavior of zeolites in the conversion of MTBE in aqueous solution under conditions of interest for the above mentioned cases.

The scope of the work reported here is the analysis of the behavior of different zeolites in the conversion of MTBE in water at room temperature, in order to evaluate whether or not zeolites may be a potential solution for remediation of contaminated water and/or protect contamination of underground wells.

2. Experimental

Different commercial zeolites have been tested in MTBE conversion. The selection has been made taking into consideration the possibility to check the role of Si/Al ratio and the zeolite structure. For comparison, the behavior of a zeolite in the sodium form has been also checked. Table 1 summarizes the characteristics of the zeolites used. The acid form of the zeolites has been obtained by calcination of the ammonium form.

Tests of MTBE conversion have been made usually in static conditions in a batch-type reactor, in order to better simulate the behavior in the case of in situ conversion, although tests stirring the solution have been also sometimes made. The volume of the solution was typically 50 ml with an aqueous solution to zeolite volume ratio in the 30–70 range (0.5 g zeolite). The tests were made using the zeolite in the form of powder as commercialized without pretreatment. The MTBE initial concentration was changed in the 1000–4000 ppm range, in order to simulate the expected concentration of MTBE in water within a distance of about 3–5 m from a leaking underground fuel tank (LUFT) [5].

The analysis of MTBE was made by gas chromatography with a mass quadrupole detector (Trace

Table 1
Characteristics of the zeolite used in MTBE conversion

Zeolite code	Type	Primary crystal length (μm)	Surface area (m^2/g)	SiO_2/Al_2O_3	Producer
H-MFI-25	H-ZSM-5	1–3	450	25	Alsi-Penta
H-BEA-25	H-beta	0.2–1.0	680	25	Zeolyst
H-MFI-80	H-ZSM-5	1–3	425	80	Zeolyst
H-MOR-15	H-mordenite	0.2–1.2	480	15	Alsi-Penta
HY-30	H-faujasite	1–3	780	30	Zeolyst
Na-MFI-25	Na-ZSM-5	1–3	430	25	Alsi-Penta

from Thermoquest). A CP Porabond Q Fused Silica (25 m × 0.32 mm) column with the following temperature programmed ramp was used: 70 °C (5 min), then heating up to 115 °C with a rate of 10 °C/min, isotherm at 115 °C (8 min), and finally heating with a rate of 10 °C/min up to 200 °C, temperature which is hold for further 10 min. MTBE, TBA and methanol (MeOH) concentrations were determined following the intensity of the signal at the mass 73 (MTBA), 59 (TBA) and 31 (MeOH), after checking linearity of the response in the target concentration range. Mass acquiring was started after 5.5 min to avoid saturation effects of detector by water.

3. Results and discussion

Reported in Fig. 1 is a typical behavior obtained in the conversion at r.t. (22 °C) of MTBE after addition of 0.5 g zeolite (volume solution to volume zeolite ratio of 72) to a solution containing 2000 ppm MTBE. For comparison, the behavior in the absence of zeolite is also indicated which point out that no change in the concentration of MTBE is observed due to either possible absorption on the wall of the reactor or photochemical conversion.

The start of the aerobic MTBE degradation activity by microorganisms, as reported by Bradley et al. [3] is also indicated as reference data. It should be noted that the tested microorganisms [3] were indigenous to the stream-bed sediments at two gasoline-contaminated ground water US sites and thus already have been adapted to gasoline-contaminated water, showing therefore a 1–2 order of magnitude higher activity than the usual microorganisms present in the environment. Furthermore, tests were made with oxygen-saturated solutions, while typical oxygen concentration in underground water is lower. In anaerobic conditions mineralization activity was negligible. The indicative start of microbiological activity reported in Fig. 1 is thus the most optimistic expected scenario.

After addition of the zeolite, a fast decrease of the concentration is observed which may be related to the adsorption of MTBE, because no parallel formation of products of reactions (TBA and MeOH) was detected. After few hours, a change in the slope of decrease of MTBE concentration is noted with a parallel increase in the formation of TBA and MeOH. This clearly

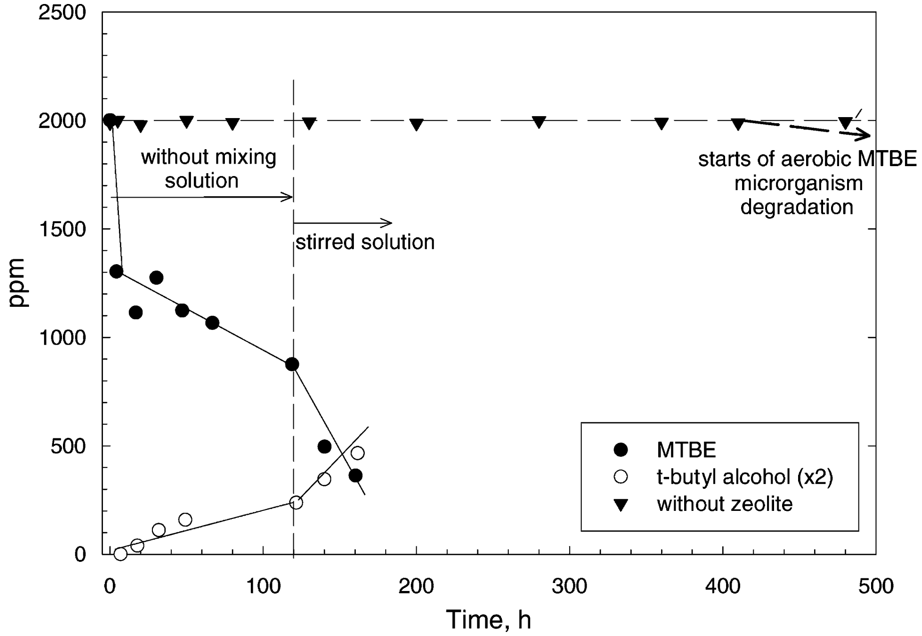

Fig. 1. Behavior of H-MFI-25 zeolite in the r.t. conversion of MTBE in the presence and absence of mixing of the aqueous solution containing an initial concentration of 2000 ppm MTBE.

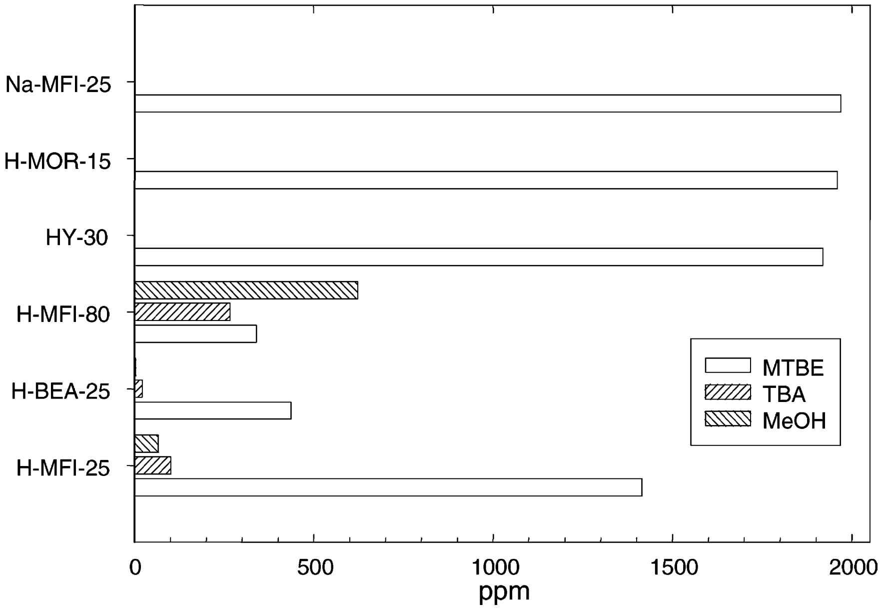

Fig. 2. Comparison of the behavior of different zeolites in the r.t. conversion of MTBE after 120 h of reaction.

evidences that hydrolysis of MTBE occurs. However, note that the amount of TBA detected (as well as of MeOH) is lower than the change of concentration of MTBE, due to the adsorption of MTBE in the zeolite as well as probably of the products of reaction.

The amount of MTBE and of equivalent products of reaction, which remain adsorbed on the zeolite in 100 h, is around 23 mmol/g, e.g. about 1 mmol/m^2 of external zeolite surface. This amount would be equivalent to 20–50 times the value expected for a monolayer (depending on the surface estimated to be occupied from one adsorbed MTBE molecule) on the external surface only of the zeolites. This clearly indicates that the adsorption should occur within the zeolite cavities.

The rate of reaction is largely dominated from the diffusion of MTBE to the zeolite (external diffusion). In fact, the stirring of the solution (in Fig. 1 after about 120 h) leads to a fast increase in the rate of disappearance of MTBE and a parallel increase in the rate of formation of by-products. Tests using larger zeolites particles suggested that the internal diffusion of MTBE within the zeolite is not limiting the reaction rate, at least under static conditions of reaction.

Summarized in Fig. 2 is the behavior of different zeolites after 120 h (absence of stirring, r.t., 0.5 g zeolite). The nature of the zeolite, the Si/Al ratio and the acidity has a considerable influence on the activity. While BEA and MFI zeolites show a good activity, but which considerably depend on the Si/Al ratio as shown by the comparison of the two samples with MFI structure, Y and mordenite zeolites are completely inactive. The amount of formed products of reaction (TBA and MeOH) is always lower than the expected amount obtained from MTBE conversion, although their detection in the aqueous phase increases with the decrease of the Si/Al ratio (compare H-MFI-80 with H-MFI-25 and H-BEA-25). The missing amount is due both to MTBE and the alcohols adsorption in the zeolites. IR characterization of the zeolite after reaction confirms the presence of relevant amounts of the three compounds in the zeolite and the analysis of TOC (total organic carbon) on the solid (zeolite) confirms that the amount of MTBE and products missing from solution was remained adsorbed on the zeolite.

The comparison of the results obtained with zeolites in the acid and sodium form (H-MFI-25 and Na-MFI-25) shows that the acidity has a critical role. Worth noting is that nearly no change in the concentration of MTBE is observed in the case of sodium form. Being the pore volume, surface area and crystal

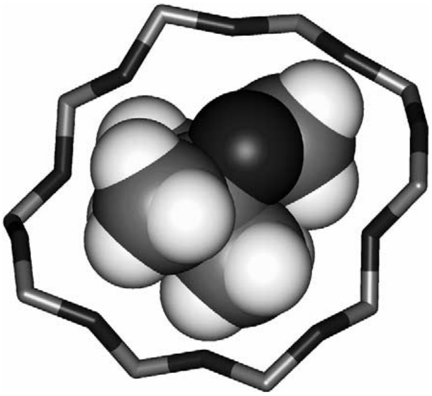

Fig. 3. Simulation of the dimensions of MTBE with respect to the 10-ring pore opening along the 0 1 0 direction of MFI zeolite.

dimensions similar to acid form, this result is surprising. The kinetic diameter of MTBE is compatible with the pore opening of MFI zeolites as shown in the simulation in Fig. 3 which reports the comparison of the dimensions of MTBE with respect to the 10-ring pore opening along the 0 1 0 direction. However, in water solution, the solvent hydration sphere makes larger the kinetic diameter of MTBE with respect to pore opening, and, therefore, the possibility of diffusion inside the zeolite would be probably determined by the competition between loss of hydration molecules and formation of bonds inside the pore structure of the zeolite.

As a consequence of this interpretation, both the pore structure and the hydrophilic/hydrophobic character of the zeolite are the factors which determine the effective possibility of diffusion of solvated MTBE into the pores of zeolites. In agreement with this interpretation, data reported in Fig. 2 show a very relevant role of the zeolite structure on the conversion of MTBE, as well a role of the Si/Al ratio which goes in the opposite direction of what was expected. In fact, one could expect that activity in MTBE conversion increases with the increase of the number of acid sites, while H-MFI-80 shows a rate of reaction significantly higher than H-MFI-25. On the other hand, beta-zeolite, which has a larger pore opening than MFI (12-atom ring—6.6 Å × 6.7 Å vs. 10-atom ring—5.3 Å × 5.6 Å in MFI) shows a much higher activity than H-MFI-25, notwithstanding the similar Si/Al ratio. Faujasite (HY-30) has also a 12-atom ring (7.4 Å × 7.4 Å), but smaller cavities for the access to supercages. Mordenite (H-MOR-15) has also a 12-atom ring (6.5 Å × 7.0 Å), but an 8-atom ring (2.6 Å × 5.7 Å) along the [0 0 1] direction connects the 12-ring channels. Taking into consideration the above discussion regarding effective kinetic diameter of MTBE in solution, it is thus reasonable that MTBE does not convert on mordenite and faujasite zeolites.

Reported in Fig. 4a is the residual concentration of MTBE measured in the liquid phase and in Fig. 4b, the TBA formation as a function of time for the H-MFI and H-BEA zeolites. It could be observed that while for both H-MFI-25 and H-BEA-25 the concentration of MTBE slowly decreases for times longer than about 20 h, after the initial fast conversion (initial concentration is about 2000 ppm), a much more relevant decrease is noted in the same range in the case of the zeolite with the higher Si/Al ratio. In terms of formation of reaction products (Fig. 4b), a similar formation of TBA is noted for H-BEA-25 and H-MFI-25, notwithstanding the higher conversion of MTBE of the former zeolite (see Fig. 4a). On the contrary, H-MFI-80 shows a much higher formation of TBA. Similar results were obtained in the case of MeOH formation. These data indicate that in the case of the samples having the lowest Si/Al ratio, the largest part of the alcohols formed remains adsorbed in the zeolite, while in the zeolite with the lowest Al content (H-MFI-80) and therefore most hydrophobic character, an easier back-diffusion of the alcohols to the bulk of the solution occurs. Reasonably, the adsorption of the alcohol blocks the hydrolytic activity and therefore after the initial fast activity of more acidic samples, their residual activity is determined by the rate of desorption of the alcohols.

The effect of the concentration of MTBE is summarized in Fig. 5 for H-MFI-80 sample. Comparable data were obtained for the other samples. Increasing the MTBE initial concentration from about 2000 to 4000 ppm the moles of MTBE converted increase, but not linearly. It could be also observed, that the rate of increase in conversion as a function of reaction time decreases on increasing initial concentration of MTBE, in agreement with the higher formation of alcohols (products of reaction), which rate of back-diffusion from the zeolite pores determines the rate of MTBE reaction as discussed above.

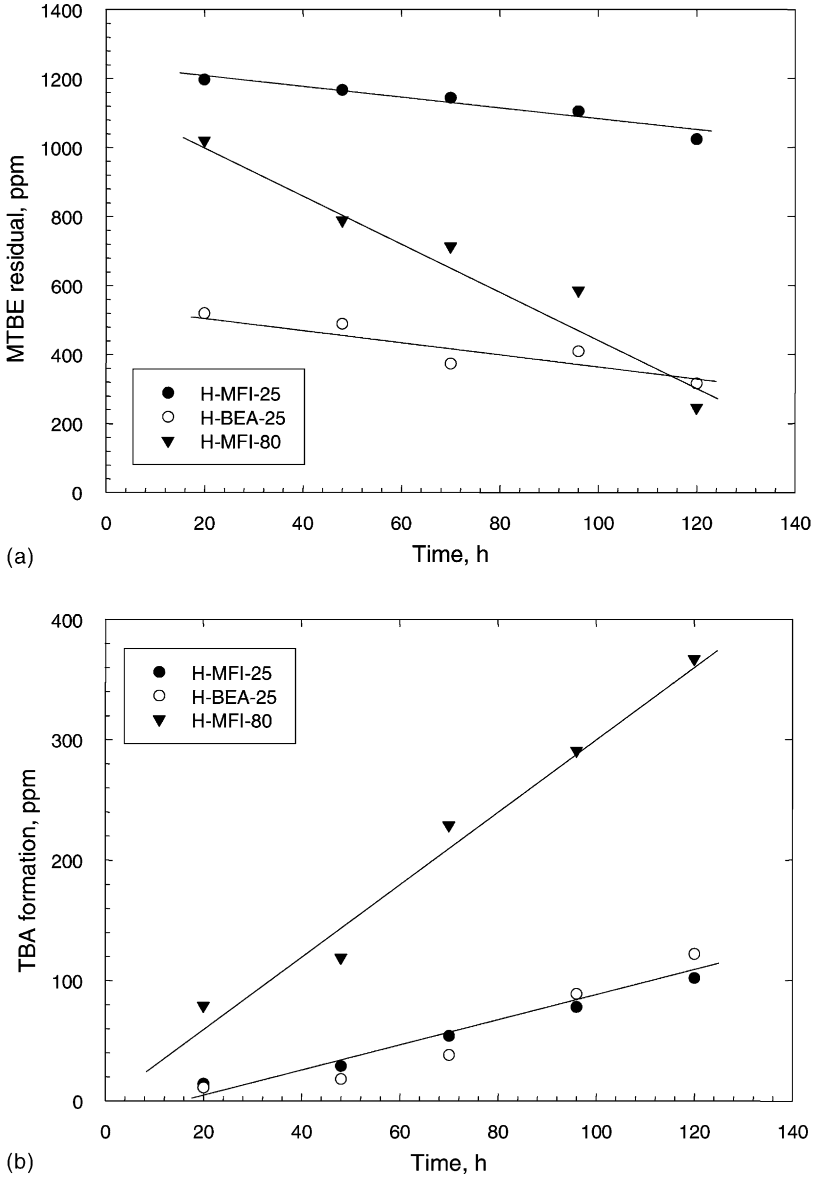

Fig. 4. Dependence of the residual MTBE concentration in the liquid phase (a) and of the TBA formation (b) from the time of reaction for H-MFI-25, H-BEA-25 and H-MFI-80 zeolites. Initial concentration of MTBE = 1936 ppm.

The effect of MTBE initial concentration on the formation of the reaction products is not very pronounced, but it could be observed that while MeOH is detected in solution in larger amounts than TBA in tests starting from a solution containing 2000 ppm MTBE, the opposite order is found using a higher concentration of MTBE. In both cases, the products of reaction in solution take into account only of one-third or less of the moles of MTBE converted, the difference remaining adsorbed in the zeolite. The unbalance increase decreasing the time of reaction in the 40–120 h range (Fig. 5), in agreement with the

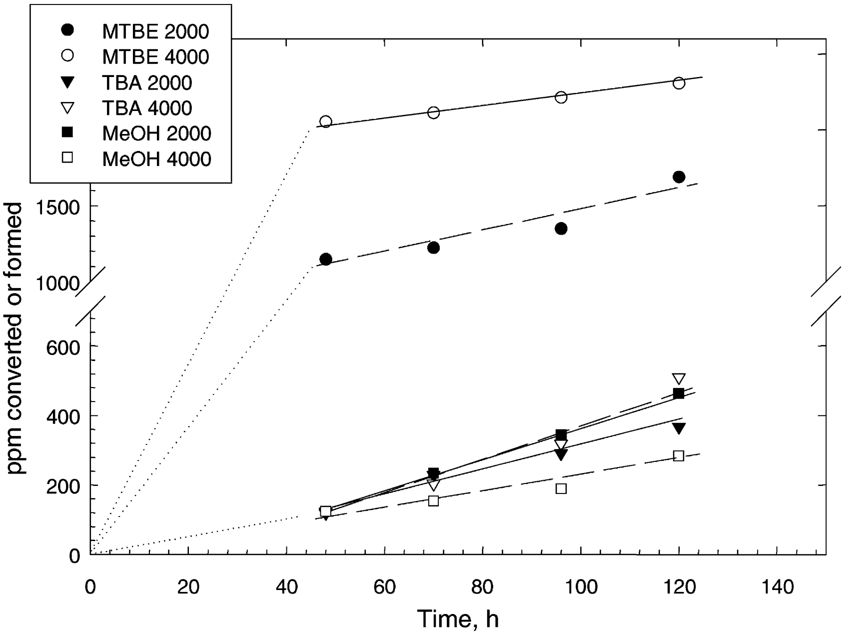

Fig. 5. Effect of the initial concentration of MTBE (about 2000 or 4000 ppm) on the ppm of MTBE converted or the ppm of TBA and MeOH formed on H-MFI-80 zeolite.

hypothesis that the catalytic behavior in these conditions is determined by the rate of back-diffusion of the alcohols from the zeolite pores.

4. Conclusions

Acid zeolites with suitable pore structure (channel structure and pore opening) like H-MFI and H-BEA could be applied as catalytic adsorbents for in situ remediation of water contaminated by MTBE, and as active barriers to prevent contamination of underground wells. These zeolites effectively catalyze the hydrolysis of MTBE to TBA and MeOH which could be fast biodegraded by indigenous microorganisms, besides to act as adsorbents for both MTBE and the products of reaction.

The structure of the zeolite has a pronounced effect on the catalytic behavior. While H-MFI and H-BEA show a good activity, especially the latter, mordenite and faujasite are completely inactive. Also MFI zeolite in the sodium form results completely inactive, including towards MTBE adsorption. The effect is interpreted in terms of effective kinetic diameter of MTBE in solution, taking into account also the hydration sphere.

The Si/Al ratio is also a critical parameter, but contrary to what expected, the behavior is promoted increasing the Si/Al ratio. This effect is interpreted in terms of a change in the hydrophobic/hydrophilic character of the pore walls of the zeolite which favors the rate of MTBE diffusion inside the pore structure as well as the rate of back-diffusion of the products of reaction. The largest part of the latter remains in the zeolite and slowly back diffuses to the aqueous solution, a positive aspect regarding the consecutive biodegradation.

It should be also noted that microorganism films have been observed to effectively growth onto heterogeneous supports such as zeolites and carbon. Therefore, zeolites used as protective in situ barrier for gasoline tanks or to protect underground wells would behave as adsorbent to prevent fast migration of MTBE, as a catalyst to catalyze transformation of MTBE to more biodegradable products, as a sink for a controlled release of the products of MTBE conversion (TBA and MeOH, with the latter which could act as nutrient for the microorganisms) and finally as a support for the growing of the degradation microorganisms.

Although clearly further studies would be necessary, present data indicate that acid zeolites such as H-MFI and H-BEA with a high Si/Al ratio may be an effective new possibility for in situ remediation of water contaminated by MTBE or as active barrier to prevent water contamination.

References

[1] R. Johnson, J. Pankow, D. Bender, C. Price, J. Zagorski, Environ. Sci. Technol. 34 (2000) 210A.

[2] L.S. Dernbach, Environ. Sci. Technol. 34 (2000) 516A.

[3] P.M. Bradley, J.E. Landmeyer, F.H. Chapelle, Environ. Sci. Technol. 33 (1999) 1877.

[4] S.E. Power, D. Rice, B. Dooher, P.J.J. Alvarez, Environ. Sci. Technol. 35 (2001) 24A.

[5] M.D. Einarson, D.M. Mackay, Environ. Sci. Technol. 35 (2001) 67A.

[6] D.P. Lince, L.R. Wilson, G.A. Carlson, A. Bucciferro, Environ. Sci. Technol. 35 (2001) 1050.

[7] MTBE Blue Ribbon Panel Meeting, Environmental Protection Agency, Sacramento, CA, March 1999, http://www.epa.gov/OMS/consumer/fuels/oxypanel/sacdraft.pdf.

[8] MTBE Fact Sheets, EPA510-F-97-014 and EPA510-F-97-015, Environmental Protection Agency, 1998.

[9] M.S. Hang, W.F. Farmayan, I.J. Dortch, C.Y. Chiang, S.K. Mcmillan, J.L. Schnoor, Environ. Sci. Technol. 35 (2001) 1231.

[10] J.W. Kang, M.R. Hoffmann, Environ. Sci. Technol. 32 (1997) 3194.