

## 1. PUBLISHABLE SUMMARY

Oxygenated compounds are added to gasoline in order to improve fuel combustion efficiency and to lower exhaust emissions of CO and hydrocarbons. MTBE is the most important fuel oxygenate used worldwide. MTBE is considered as a unique contaminant due to its ability to move readily throughout various environmental compartments and to its resistance to degradation. The contamination of water supplies by MTBE and other fuel oxygenates is a problem of increasing concern. Some high gasoline polluted sites have been identified in Europe in the last years, particularly in Germany. In that sense, the main scientific objective of the present project is the assessment of wet peroxide oxidation (WPO) of fuel oxygenates using innovative catalysts. This purpose was achieved by using Fe-Zeolites as catalysts and combining their properties to adsorb fuel oxygenates and to catalyze Fenton-like reactions. The main project objectives were: (Obj. 1) synthesis and/or selection of new Fe-zeolites, (Obj. 2) characterization of the catalysts, (Obj. 3) catalytic activity tests under different conditions, (Obj. 4) studies on the mechanisms of reaction and (Obj. 5) optimization of the catalyst and the design of the treatment process.

Up to 8 different zeolites with different structures (ZSM5, Beta and Y) and hydrophobicity (determined by higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio) have been selected as support for iron which has been introduced by a liquid ion exchange method and subsequent calcination step (Obj. 1). All these catalysts have been characterized in terms of particle size, Fe leaching, BET analysis (porosity analysis), XRD analysis (determination of zeolite structure variation), X-ray fluorescence (elemental analysis) and UV-Vis/DRS spectrometry (determination of Fe species) (Obj. 2). Different tests have been done with selected Fe-zeolites that include: catalytic activity for  $\text{H}_2\text{O}_2$  decomposition, influence of different parameters on the catalytic behavior such as contaminant concentration,  $\text{H}_2\text{O}_2$  concentration, catalyst concentration, pH, test with different contaminants such as MTBE, ETBE, BTX, trichloroethylene, perchloroethylene, dichloroacetic acid, Triton X-100, phenol and imidacloprid, tests using  $\text{O}_3$  as oxidizing agent and tests under UV conditions and dark conditions (Obj. 3). Furthermore, studies were done to aim at the elucidation of the type of reactive species involved in the heterogeneous Fenton reaction using Fe-containing zeolites. Electron paramagnetic resonance (EPR) measurements using dimethyl pyrroline-N-oxide (DMPO) as spin trap, epoxidation experiments and kinetic deuterium isotope effect (KDIE) studies for methanol oxidation were carried out (Obj. 4). Batch and column experiments were done in order to determine the best operational configuration for the process (Obj. 5). Two treatment modes were tested in order to use this catalyst in a column treatment unit. In continuous mode  $\text{H}_2\text{O}_2$  is continuously fed to the contaminated water stream which enters the column. In intermittent mode, the contaminants are removed from the water primarily by means of adsorption on the Fe-zeolite combined with intermittent regeneration of the spent adsorbent by flushing with a  $\text{H}_2\text{O}_2$  solution.

The results of this study suggested that hydrophobic zeolites, i.e. those with a high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, and smaller pore size (ZSM5 structure) show the best adsorption properties for MTBE. Their regeneration by different advanced oxidation processes (AOP) was studied: 1) Fenton treatment using  $\text{H}_2\text{O}_2$  with dissolved iron salts and 2) heterogeneous Fenton-like oxidation with Fe immobilized on the zeolites. The first were ineffective to regenerate loaded zeolites. On the other hand, heterogeneous catalysis using Fe species immobilized by liquid ion exchange on the zeolite was more effective. Although these hydrophobic zeolites have less acidic sites which are important for the anchoring of the Fe catalyst, it was possible to obtain sufficiently active catalysts. Hydrophobic Fe-zeolites are promising adsorbents/catalysts for the removal of MTBE from water since they allow the combination of highly efficient adsorption and oxidative degradation by  $\text{H}_2\text{O}_2$ . In contrast to the homogeneous catalysis by dissolved iron ions, these heterogeneous catalysts work at near neutral pH and can be easily reused. These catalysts have a good stability and low Fe leaching as our batch and column experiments have shown. The best configuration for MTBE treatment is the so-called intermittent mode because the removal efficiency is increased and the

$\text{H}_2\text{O}_2$  consumption is reduced. With this configuration it is possible to remove MTBE from groundwater by adsorption and reuse the adsorbent several times. The process has been tested in different lab columns loaded with a hydrophobic zeolite ZSM5 with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 236$  that previously was treated to incorporate the iron with a liquid ion exchange method. In the column tests synthetic and real contaminated groundwater from Leuna, Germany was applied.

On the other hand mechanistic studies were conducted. Electron paramagnetic resonance (EPR) measurements in WPO with Fe-zeolites using dimethyl pyrroline-N-oxide (DMPO) as spin trap were carried out for WPO with Fe-zeolites and the formation of the complex DMPO-OH was observed which is often ascribed to a reaction with  $\text{OH}^-$ . Significant differences were found for the kinetic deuterium isotope effect (KDIE) for methanol oxidation between the heterogeneous Fenton-like reaction and genuine  $\text{OH}^-$  reactions initiated by homogeneous Fenton reaction which indicates that other oxidant species additionally to  $\text{OH}^-$  were involved. In addition, Fe-zeolites catalyze the epoxidation of cyclohexene by  $\text{H}_2\text{O}_2$ . This type of reaction suggests the participation of a high valent oxoiron complex (ferryl).

On the other hand, a part of the experimental results of this project have been used to elucidate mechanisms of biological degradation by evaluating isotopic fractionation of Fenton-like degradation of fuel oxygenates. This work was done in cooperation with another Marie Curie IEF fellow (Dr. Rosell) working the Department of Isotope Biogeochemistry of the host institution.

Moreover new lines of research were started and focused on the use of solar UV light to enhance the reaction rate. Positive effects were found in the mineralization degrees of contaminants in water when the Fenton-like process was done under UV (natural and solar) radiation. The project has started to be extended to other materials such as natural zeolites, and mesoporous materials, which could be interesting alternative supports in specific applications of the WPO.

As a conclusion Fe-zeolites can be used in the treatment of contaminated effluents by a combination of adsorption and oxidation promoted by Fenton-like reactions. The concentration of the target pollutants in the vicinity of the catalytic active centres, where the oxidants species are produced, increase the degradation efficiency and let to work in a wide range of conditions including wide pH range (important drawback in homogenous Fenton reaction). Furthermore the reuse of the heterogeneous catalyst, with low leaching, is an advantage that makes it more attractive from an economical and process engineering point of view. The possibility of applying in the future this technology to treat contaminated water has a realistic chance and would of course have a real positive impact on our environment. This includes the application for groundwater remediation in case of contamination with fuel oxygenates where this approach could replace other less energy and cost efficient technologies (stripping and activated carbon adsorption). However, the obtained results are also promising in terms of an application in the field of treatment of industrial wastewater.