Organic pollution selective degradation by adsorption on high silica zeolites and regeneration by ozone

M-H Manero[*1], P.Monneyron[2], S.Mathé[1]

[1] Institut National des Sciences Appliquées, Laboratoire d'Ingénierie des Procédés de l'Environnement, 135, avenue de Rangueil, 31077 Toulouse, France, manero@insa-toulouse.fr

[2] Ecole Nationale Supérieure des Arts et Métiers, Laboratoire Transferts Ecoulements Fluides et Energétique, Esplanades des Arts et Métiers, 33405 Talence, France.

Abstract

This study concerns the treatment of industrial airstreams polluted with volatile organic compounds (VOCs), and focuses on highlighting the experimental feasibility of a new hybrid process combining VOC adsorption on hydrophobic zeolites and regeneration by an ozonated airstream in a single reactor.

A preliminary study of high-silica zeolites has shown the different kinds of interactions between gaseous ozone and two mineral zeolitic adsorbents, a faujasite Y (FauY) and a ZSM-5 type silicalite (SilZ), and the conservation of the solids adsorption properties (capacities and selectivity) after their contact with ozone.

Here, results concerning the contact of gaseous ozone and zeolites saturated with adsorbed VOC are presented. Using temperature measurements inside the fixed bed, oxidation of two models VOC, methyl ethyl ketone (MEK) and toluene (TOL), was observed on both zeolites. Adsorbents were fully regenerated, and the adsorption capacities of the zeolites after their contact with ozone were not affected when used in a discontinuous adsorption / oxidation mode.

In addition, the adsorbed VOC were totally mineralized. Detection and identification of oxidation sub-products traces using mass spectrometer - gas chromatography (formic, oxalic, acetic acids, and acetaldehyde for TOL and 2,3-butanedione and acetic acid for MEK) makes possible the indentification of oxidative species. Moreover, a mass balance on oxygen showed that all the produced ozone was used for organic compounds oxidation. There was no or very little ozone lost via side-effect decomposition/deactivation mechanisms.

At last, using the zeolites selectivity determined in a previous study toward a binary MEK-TOL mixture, the adsorption / ozonation cyclic process enables the recovery of the minor compound and the selective oxidation of the other component.

The great interest of this new process is clearly highlighted, and the technology transfer to industrial operating plants is now studied.

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[*] Corresponding author :manero@insa-toulouse.fr

Introduction

The removal of volatile organic compounds (VOCs) in gaseous airstreams is one of the most important challenges of our society because of their implication in photochemical pollution and global climate change. One of the most used techniques to remove VOCs is adsorption on granular activated carbon (GAC) (David Cooper, 2002). In this case, the saturated fixed bed is usually regenerated by steam while the polluted gas is continuously treated in a parallel adsorber. An alternative process was studied to treat VOCs by adsorption: the AD-OZ process. This system allows the adsorption of VOCs and the regeneration of the adsorbent in a single reactor, using new materials such as alumino-silicate molecular sieve. These mineral adsorbents permit operating conditions for which activated carbon is inappropriate due to its inflammability and adsorption capacity dependence on effluent relative humidity. Apart from hydrophobicity, High Silica Zeolites (HSZ) offers notably a thermal and chemical stability, a high steric selectivity and a complete regeneration at low temperatures (Otten, 1992).

In this paper, experimental feasibility of this new hybrid process is studied. Two commercial hydrophobic zeolites were used as adsorbents: a dealuminated faujasite Y (Fau Y) and a ZSM-5 type silicalite (Sil Z). In a previous study (Monneyron, 2003) we studied the reactivity of these two zeolites in contact with ozonated air. Different kinds of behaviours took place, according to the nature of the adsorbent. In case of Fau Y, no physical adsorption occurred but a total degradation of ozone. In the contrary, ozone was adsorbed on Sil Z until a certain local concentration, before being degraded. Adsorption equilibrium measurements showed that the contact of ozonated air with hydrophobic zeolites had no effect on its adsorption properties: capacities in single component isotherms and selectivity towards VOC binary mixtures are kept. After having characterized interactions between gaseous ozone and zeolites, the feasibility of hybrid process VOCs adsorption / regeneration by ozonated air was evaluated. In a first part , dynamic adsorption of VOCs is presented on the Fau Y and Sil Z. Then, the compounds degradation is studied following the temperature changes inside the fixed bed and the composition of outlet phase.

I-   Methods and Materials

Adsorbents

Two commercial HSZ supplied in pellets form, were used in this work, a desaluminated faujasite Y and a silicalite ZSM-5. The supplier kept undisclosed the chemical nature of the clay binder together with details of desalumination technique. The main characteristics of adsorbents are given in table 1. Prior to experimentation, the zeolites were heated at 500K overnight, and kept in a desiccator to prevent ambient humidity to interfere with experiments.

Type (Symbol)	Faujasite (Fau Y)	ZSM-5 (Sil Z)
Crystalline framework	α-cages	Interconnected channels
Pore internal diameter (Å)	13	(5.7 * 5.1) and 5.4
SiO_2/Al_2O_3 (mol mol^{-1})	360	1880
Active porous volume (cm^3 g^{-1})	0.24	0.18
Na_2O (wt%)	0.02	< 0.01
Clay binder content (%)	25	20
Pellet diameter (mm)	3.0	1.5

Table 1. Main characteristics of zeolites.

Adsorbates

Volatile organic compounds studied were methyl ethyl ketone (MEK, 99.5%) and toluene (TOL, 99+%). They were chosen as model compounds of daily used industrial solvents having very different chemical structure and physical properties. Moreover, these compounds were chosen for their very weak reactivity with ozone in gaseous phase : their velocity constant is about 10^{-20} cm^3.molec^{-1}.s^{-1}.The main properties of the pure compounds are summarized in table 2.

Properties	Methyl ethyl ketone	toluene
Symbol	MEK	TOL
Formula	C_4H_8O	C_7H_8
Molar volume 25°C (cm^3 mol^{-1})	90.14	107.51
Vapour pressure at 25°C (kPa)	12.60	3.79
Dipolar moment (D)	2.78	0.375

Kinetic diameter (Å)	5.2	5.8

Table 2. Main properties of adsorbates.

Adsorption - Ozonation experimental set-up

A schematic representation of the fixed bed experimental set-up is given in Figure I. The column containing the adsorbent was 20 cm high and 8 cm in internal diameter. The different air streams could be injected at the bottom of the reactor alternatively or simultaneously. The air / VOC mixture obtained via a bubbler was diluted with dry air to reach a typical industrial air stream concentration of 1 to 5 g.m^{-3}.
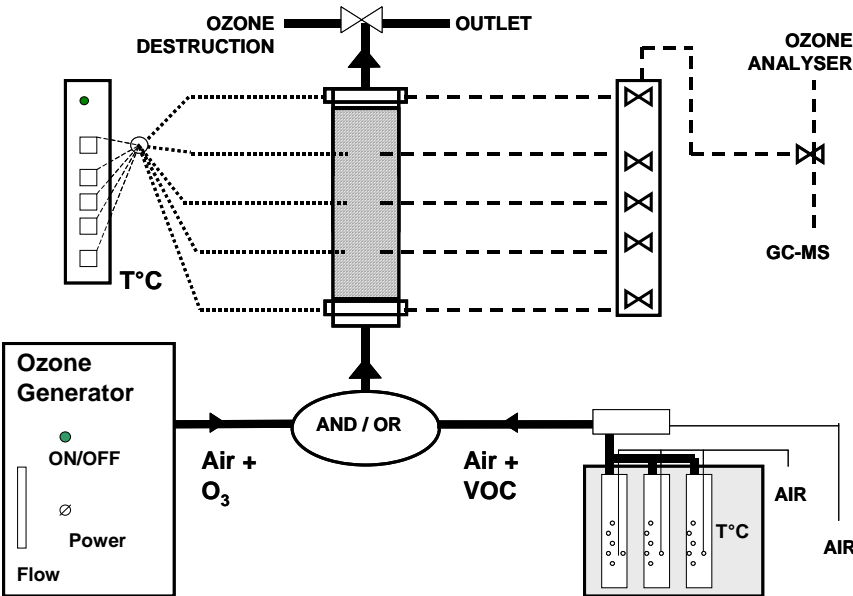

Figure I. Adsorption / Ozonation experimental set-up

The air/ozone mixture was obtained from a commercial ozone generator and since the ozone production is function of air pressure (0.7 bar), flow (0.25 m^3.h^{-1}), and power applied, the ozone inlet concentration was reproduced with an uncertainty of $\pm$ 0.5 g.m^{-3}. At the inlet, outlet and every 5 cm, an intermediate gaseous sample could be taken and sent either to an ozone analyzer to determine ozone concentration, or to a GC-MS for VOC quantification, oxidation organic sub-products identification, and mineralization products (CO_2, H_2O) concentration profiles observation. The gas chromatograph capillary column used for separation was a CP-Select 624 CB with a WCOT fused silica stationary phase impregnated

with a 1.4 μm thick film. Electronic Ionization mode at 70 eV was used in the mass spectrometer source.

The selected ion recording (SIR) technique was used coupled with GC-MS to detect and quantify model compounds alone or in oxidation products mixtures. Calibration of SIR response was carried out either using the automated bubbling VOC generation system and/or with a manual gas injection of VOC vapor, giving a very precise concentration especially in the low concentration range (< 0.01 g.m^{-3}). Both methods gave similar results, with a typical difference smaller than 5%. Experimental conditions are summarized in Table 3.

	Fau Y	Sil Z
Bulk density (kg/L)	0.42	0.66
Adsorbent mass (g)	150 - 400	200 - 600
Temperature (K)	298	
Air / VOC flow (m^3.h^{-1})	5	
Air / VOC superficial velocity (m.s^{-1})	0.275	
Air relative humidity (%)	0 except when specified	
Air / O$_3$ flow (m^3.h^{-1})	0.25	
O$_3$ concentration (g.m^{-3})	0 - 30	

Table 3. Experimental conditions for dynamic adsorption / ozonation.

II - Results and Discussion

II-1   Dynamic Adsorption of Organic compounds on high silica zeolites

Breakthrough curves of TOL on both zeolites are shown in Figure II. The steep concentration profile for adsorption on Sil Z is significant of a quite rapid mass transfer and representative of a good affinity between adsorbent and adsorbate. On Fau Y, a wide mass-transfer zone is showed towards the extended curve, representative of worse affinities than on ZSM-5. These different behaviours can be explained when looking at equilibrium properties. Adsorption properties of the two zeolites are very different, as shown in Figure III: Sil Z is a type I isotherm, considered as favourable adsorption whereas Fau Y is a type V isotherm, less positive.
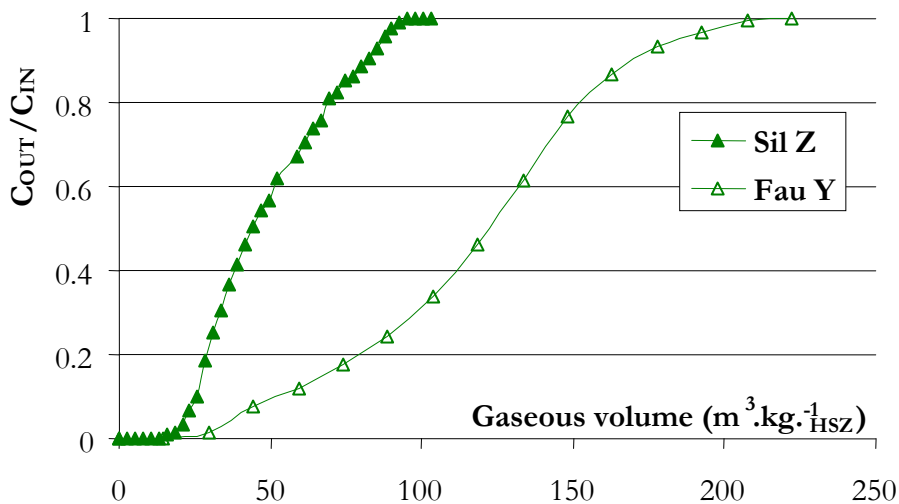
Figure II – Breakthrough curves of toluene on a 10 cm bed of both zeolite ($C_{IN} = 1$ g.m^{-3} – linear velocity U = 0.275 m.s^{-1})
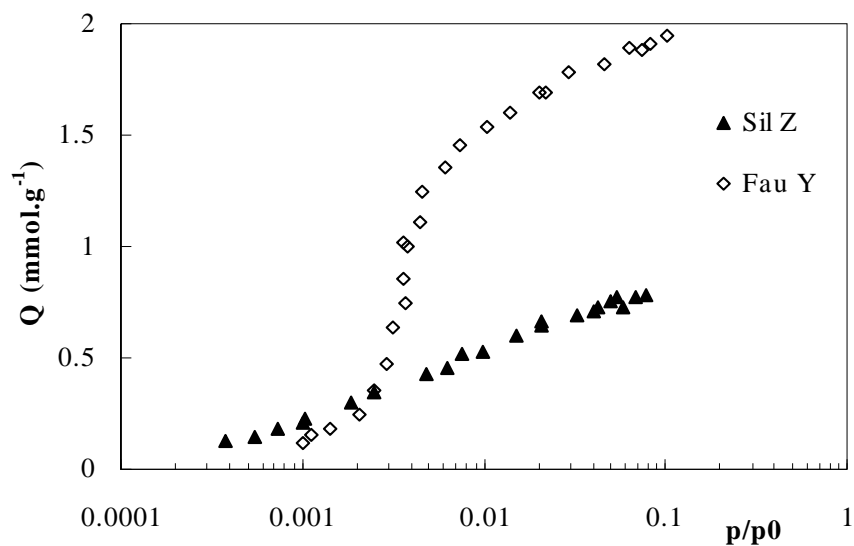

Figure III. Adsorption isotherms of TOL on Sil Z and Fau Y at 298 K.

II-2 Ozonation of adsorbate phase

When the fixed bed is saturated with VOCs, regeneration is made by oxidation thanks to an ozonated dry air stream sent at the bottom of the reactor : 18 $g_{O3}.m^{-3}$, 0.25 $m^3.h^{-1}$. VOCs degradation was proved on both zeolites by the sub-products detection and by a strong increase of CO_2 and H_2O in the exit air. Moreover, a big heat production was measured inside the bed.

Thermic effect

During ozonation of adsorbed VOCs, an increase of temperature of several tens of Celsius degrees was observed in the bottom of the bed. As ozone is sent at the bottom of the bed, oxidation reaction occurs in the lower part of the reactor before moving. Therefore, the desorption of the adsorbed compound is realized, as it is shown on Figure IV for a sequential operation: adsorption of MEK on Sil Z then oxidation by ozone.
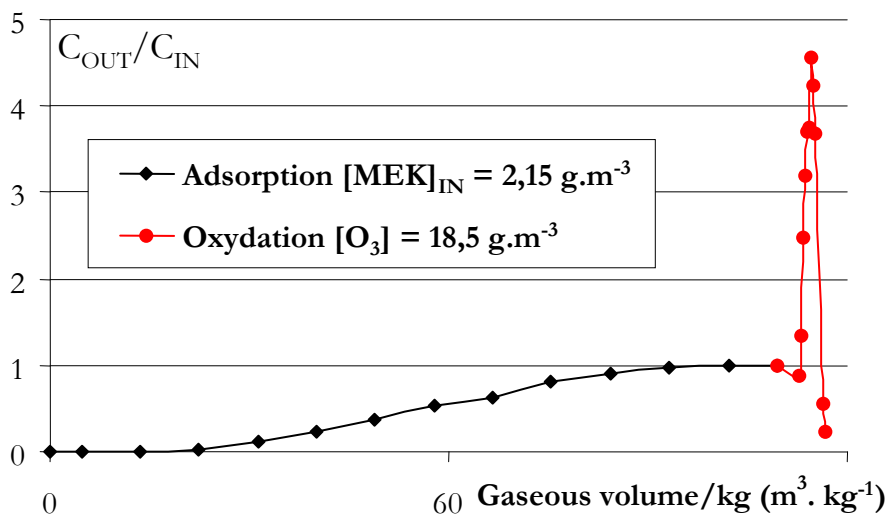

Figure IV – MEK concentration in outlet gas during sequential treatment adsorption/ ozonation on Sil Z

The amount of desorbed MEK can be determined. This non degraded quantity represents 25% of total adsorbed amount during the bed saturation step of Sil Z. Similar phenomena was

found with TOL on Sil Z. Thermodesorption was much more important on Fau Y, probably because of greater adsorbed amounts leading to greater heat production, as it can be seen on Figure V for TOL. Besides, diffusion of adsorbed species is faster in Fau Y than in Sil Z because of the larger pores of the first.
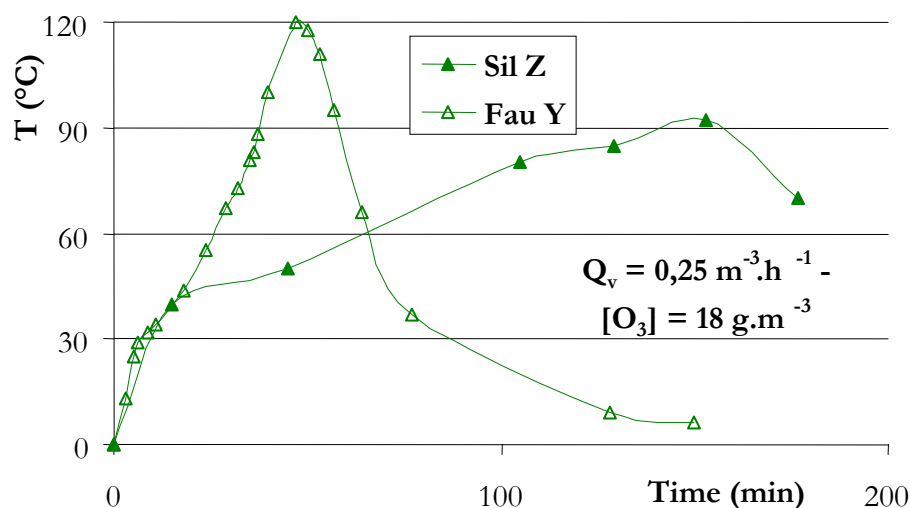

Figure V – Comparison of temperature profiles at 5 cm height during ozonation of hydrophobic zeolites partially saturated of TOL

Temperature increasing observed in both cases are much greater than those found for the decomposition of single ozone (30 °C for 18 $g_{O3}.m^{-3}$). According to this point, a significant oxidation of adsorbed compounds can be deduced. This important thermodesorption occurred because the bed was totally saturated before its ozonation. Indeed, to detect and identify formed sub-products, we have chosen to start from a fully saturated bed. In an industrial perspective, the bed would be only partially saturated, before being cleaned and the thermal desorbed VOCs would be adsorbed in the free adsorbate zone of the bed or would be recycled during the ozonation phase.

Ozonation products

Total Ionic Current (TIC) acquisition method was used to obtain the chromatograms.

During adsorbed toluene oxidation, oxalic acid, acetic acid, formic acid and acetaldehyde were detected for both ozonation, on Fau Y and on Sil Z. All these products were found at trace state whereas very high amounts of CO_2 and H_2O were observed with SIR method. On Figure VI, a chromatogram obtained during ozonation of TOL on Fau Y is presented with highest concentrations observed. The initial toluene concentration is indicated on the right side of the figure, to give a qualitative idea of the amounts of the formed sub-products.

During adsorbed MEK oxidation by ozonated air, only two sub-products were detected :2,3-butanedione and acetic acid.
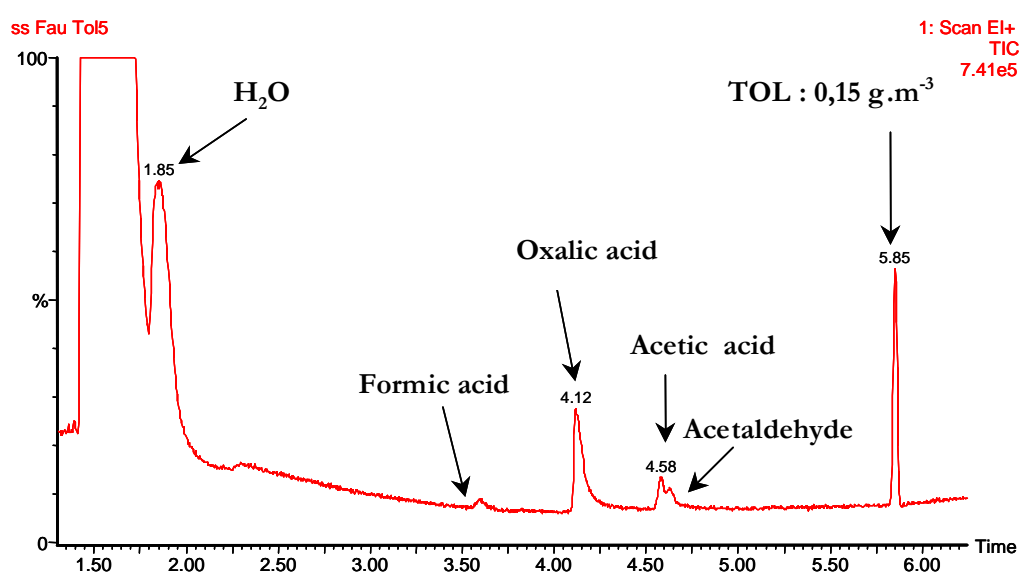

Figure VI- Chromatogram obtained during the ozonation of adsorbed toluene on Fau Y

Oxidative species

A lot of reactive products can be found in the zeolite bed, in contact with ozonated air: ozone degradation products, hydroxyl radicals in presence of humidity … It is therefore difficult to conclude about determined species and about mechanisms involved in their formation. Partially degradation of toluene was studied by Sekiguchi and al. (2003) using an ozone degradation catalyst (MnO_2 deposed on a mixt support TiO_2/SiO_2), with different hygrometries. Mineralisation rates determined from CO_2 trapping were reported at 66%. Active oxidants could not be clearly identified by the authors but they observed that hydroxyl

radical concentration was not amplified when increasing the humidity rate from 10% to 80%. Akubuiro (1992) or Wagner (1993) worked on MEK degradation mechanism on activated carbon and proposed a hydroperoxyde as a first intermediate product, then the appearance of 2,3-butanedione before acetaldehyde and acetic acid.

According to Leichsenring (1996) and Büchel (2000) works, water has a great influence on oxidation of adsorbed VOCs. Higher rates of mineralization are reached in presence of water and more hydroxyl radicals were trapped. These results suggest that hydroxyl radicals are one of the most important oxidative specie but certainly not the only one.

In our experimental studies, we also observed an acceleration of the degradation of adsorbed compounds in presence of water. For an 80% humid flow, an almost immediate increase of temperature of 30°C was noticed, whereas no heat was produced when a non saturated zeolite is ozonated.

II-3 Hybrid process adsorption / selective oxidation

Experimental feasibility was studied for a sequential process: adsorption on a fixed bed of TOL or MEK until saturation and regeneration by an ozonated air. Operating conditions are detailed in Table 3.

For both zeolites and both VOC, a highly exothermic reaction takes place in the reactor leading to organic sub-products formation and a high concentration of water and carbon dioxide, while no residual ozone is detected. Moreover, a mass balance on oxygen showed that all the produced ozone was used for organic compounds oxidation. There was no or very little ozone lost via side-effect decomposition/deactivation mechanisms.

Oxidation on both zeolites was evaluated in terms of associated thermal effect, main product and ozone mass balance. Figure VII shows an example of VOC concentration profile in outlet during discontinuous adsorption – ozonation cycle of TOL and MEK on Sil Z. A good efficiency of bed regeneration is found (96%) without any optimization.
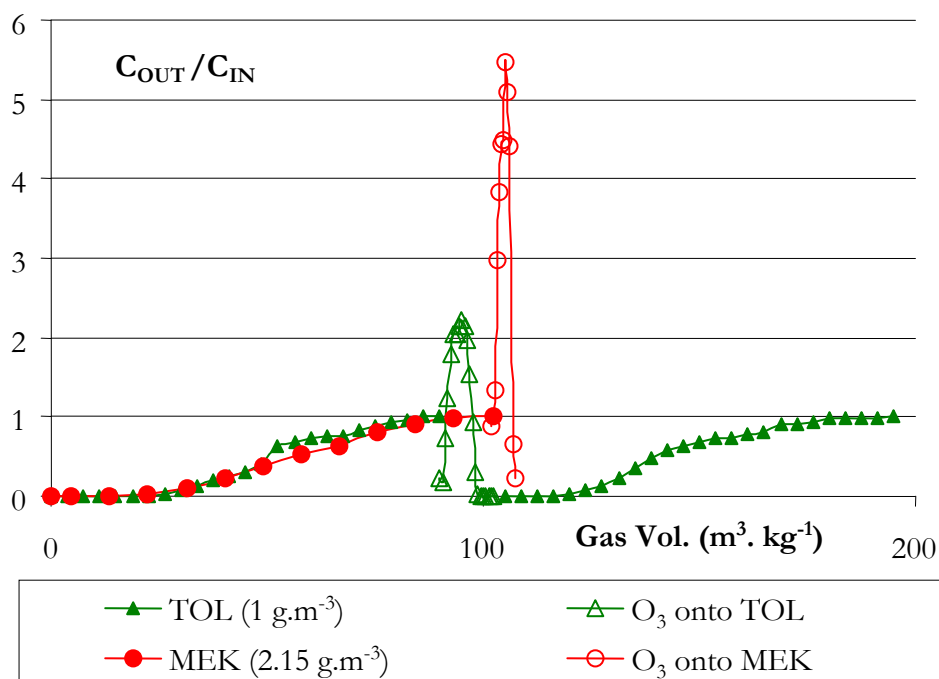
Figure VII. VOC concentration profile during discontinuous adsorption – ozonation cycle on Sil Z (C_{O_3} = 18 g.m^{-3})

Moreover, a same treatment on Fau Y was less efficient as the regeneration rate of the bed was only of 75%. This probably comes from the reactivity difference of these zeolites in contact with ozone (Monneyron 2003). On Fau-Y, ozone is immediately decomposed before adsorption, producing oxidative species on the zeolite surface which leads only to the oxidation of VOCs adsorbed on surface. On the other hand, ozone is adsorbed in Sil-Z pores before being decomposed. In this case, oxidative species degrade VOCs which are adsorbed in the porous volume. Hutchings (1987) found the same difference between ZSM-5 and Fau-Y based catalyst : ZSM-5 material was very well regenerated with a mixture O_2/O_3 whereas Fau-Y material was only regenerated on surface, leaving deep coke.

In term of process, interest and potentialities of this hybrid process were shown. In term of exploitation cost, the main part of it comes from the regeneration phase of the adsorbent and thus of the ozone consumption. This one is deduced from the mass balance of the theoretical reaction of oxidation and thus depends on molecular composition of the VOC. For instance, a removal of 1g.m^{-3} of dioxane in 1000 m^3.h^{-1} of air is estimated to approximately 2,7 € per hour, for a conventional corona discharge generator of ozone, costing about 1,5 €/kg $O_{3\ produced}$

(Manero and Monneyron, 2005). Some works pointed that ozone generation with better energetical performances is possible, using zeolite as concentrator of ozone (Izumi et al., 2001), giving basis for an optimisation of the process.

II-8 Selective oxidation

The AD-OZ process can be interesting to treat multicomponent effluents in a selective way. A previous study on zeolites selectivity (Monneyron, 2003) showed that MEK/TOL mixture could be selectively treated. Zeolite bed is used as a purificative filter, adsorbing MEK while TOL, the minor compound, can be recovered. Breakthrough curves of both components are given in Figure VIII, for a mixture rich in MEK (Z_{MEK} = 75 % and Z_{TOL} = 25%), on Sil Z. Ozone was sent before saturation, with $C_{O_3} = 18$ g.m^{-3} and adsorbed MEK was degraded. Sub-products detected were 2,3-butanedione and acetic acid, as for pure adsorbed MEK ozonation. Temperature changes in the bed were followed and are reported in Figure IX at a 5 cm height point (from the bottom). The temperature raising is quite the same as the one obtained for single MEK, except that the beginning of the decrease starts earlier because of a lower adsorbed amount than for pure MEK ozonation.
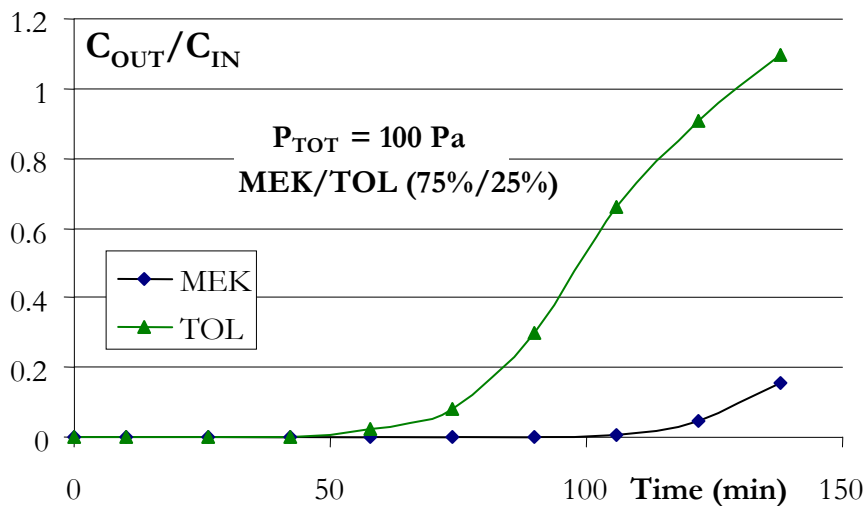

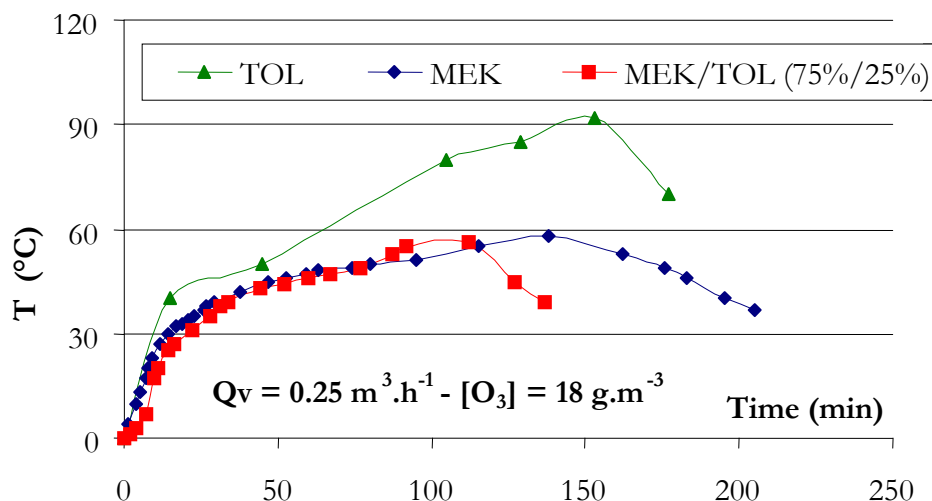Figure VIII- Breakthrough curves of MEK/TOL mixture (75%-25%) on Sil Z

Figure IX- Comparison of temperature profiles at 5 cm height : ozonation of an adsorbed mixture MEK/TOL and ozonation of pure adsorbed components

Acknowledgment

Nomenclature

C_i concentration of i in air (g.m^{-3})
p   gas phase total pressure induced by VOC concentration (Pa)
p_0 vapor pressure (Pa)
Q   amount adsorbed (mol kg^{-1})
Q_v volumetric air flow (m^3.h^{-1})
T   temperature (K)
U   linear velocity (m.s^{-1})
Z_i initial molar percentage of component i

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