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# A COMBINED SELECTIVE ADSORPTION AND OZONATION PROCESS FOR VOCs REMOVAL FROM AIR

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A new hybrid process combining adsorption and ozonation is examined as an alternative treatment for Volatile Organic Compounds (VOC). The physical adsorption of ozone was clarified on a ZSM-5 zeolite. Oxidation of two industrial solvents was achieved on two zeolites and followed with temperature profiles and sub-products detection. Total regeneration of the fixed bed was achieved with a complete mineralization of organic compounds. Detection and identification of sub-products traces allowed us to suspect oxidation reactive species. A mass balance on oxygen showed that all the inlet ozone was used for organic compounds oxidation. A selective oxidation was achieved, allowing the separation and the recovery of minor compound.

On examine un nouveau procédé hybride combinant l'adsorption et l'ozonation comme traitement alternatif pour les composés organiques volatils (VOC). L'adsorption physique de l'ozone sur une zéolite ZSM-5 est clarifiée. On a oxydé deux solvants industriels sur deux zéolites, puis on a établi les profils de température et détecté les sous-produits. La régénération totale du lit fixe a été atteinte avec complète minéralisation des composés organiques. La détection et l'identification de traces de sous-produits permettent de suspecter la présence d'espèces réactives à l'oxydation. Un bilan de matière sur l'oxygène a montré que tout l'oxygène introduit est utilisé pour l'oxydation des composés organiques. On a réalisé une oxydation sélective, qui permet la séparation et la récupération de composés mineurs.

**Keywords:** adsorption, ozone, VOC, high-silica zeolites (HSZ)

## INTRODUCTION

Volatile Organic Compounds (VOC) are considered major air pollutants resulting largely from solvent waste of industrial processes. Thus, the purification of effluents is of great interest for chemical engineering, and one of the main techniques available toward dilute polluted air streams is adsorption onto a porous material, such as activated charcoal or hydrophobic zeolites (Le Cloirec, 1998). Besides a large adsorption capacity, high-silica zeolites (HSZ) exhibit notably a very low dependence on effluent humidity, a chemical and thermal stability up to 1000°C and are non-flammable (Otten et al., 1992). Moreover, HSZ show an interesting selective adsorption behaviour that can often be qualitatively described using a distillation analogy (Clause et al., 1998; Meininghaus and Prins, 2000) and quantitatively predicted using thermodynamics models (Valenzuela and Myers, 1989; Garrot et al., 2002; Monneyron et al., 2003a). The adsorption process is usually conducted in two steps, since the saturated material requires regeneration (Ruthven, 1984). Aiming at restoring the adsorption capacities with as little damage as

possible to the original pore structure, activated carbon is usually regenerated via pressure or thermal desorption leading to a secondary effluent to be treated. In addition, the carbonaceous structure of activated carbon makes oxidative techniques unsuitable for its regeneration, as shown by Dusenbury and Cannon (1996) and Masuda et al. (2001) when highlighting the scavenger effect of activated carbon toward gaseous ozone.

In parallel, advanced oxidation processes were investigated as direct methods of gas treatment (Shen and Ku, 1999), for which mineral supports such as zeolites can provide a good environment for heterogeneous photocatalysis (Yoneyama and Torimoto, 2000; Monneyron et al., 2003b), for ozonation (Zlotopol'sky and Smolenskaya, 1996) and in a recent study for Vacuum-UV photolysis using an excimer lamp (Monneyron et al., 2003c). This latest study showed the synergetic effect of UV photolysis and ozone produced from ambient oxygen.

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Aiming at oxidizing VOC adsorbed on zeolite, a preliminary study clarified the reactivity of ozone on two HSZ, a de-aluminated faujasite Y (Fau Y) and a silicalite (Sil Z). Two different phenomena occurred: ozone decomposition on Fau Y silanol groups induced by the de-alumination step; and physical adsorption in silicalite porosity (Monneyron et al., 2003d). Furthermore, the adsorption properties of HSZ—in terms of capacity and selectivity toward a solvent mixture—were not significantly modified by the contact with gaseous ozone.

In this study, a hybrid process combining adsorption and oxidation by an ozonated air stream of two different VOC (toluene and butan-2-one) was conducted on two HSZ, investigating adsorbent regeneration, sub-products identification, and oxidation mass balances.

## EXPERIMENTAL SECTION

### Adsorbents

Two commercial HSZ, supplied in pellets form, were used in this work, a de-aluminated faujasite Y (Frichtner-Schmittler et al., 1990) and a silicalite ZSM-5 (Olson et al., 1980). The supplier kept undisclosed the chemical nature of the clay binder together with details of de-alumination technique. The main characteristics of adsorbents are given in Table 1. Prior to experimentation, the zeolites were heated at 500 K overnight, and kept in a desiccator to prevent ambient humidity to interfere with experiments.

### Adsorbates

Volatile organic compounds studied were butan-2-one (99.5%) and toluene (99 + %). They were chosen as model compounds of daily used industrial solvents, having very different chemical structure and physical properties. Moreover, these compounds exhibit very weak reactivity with ozone in gaseous phase: their kinetic constant is about  $10^{-20} \text{ cm}^3 \cdot \text{molec}^{-1} \cdot \text{s}^{-1}$  (Atkinson and Carter, 1984). The main properties of the pure compounds are summarized in Table 2.

Type (Symbol)	Faujasite (Fau Y)	ZSM-5 (Sil Z)
Crystalline framework	$\alpha$ -cages	Interconnected channels
Pore internal diameter (nm)	1.3	(0.57 * 0.51) and 0.54
$\text{SiO}_2/\text{Al}_2\text{O}_3$ (mol mol <sup>-1</sup> )	360	1880
Active porous volume (cm <sup>3</sup> g <sup>-1</sup> )	0.24	0.18
$\text{Na}_2\text{O}$ (wt. %)	0.02	< 0.01
Clay binder content (%)	25	20
Pellet diameter (mm)	3.0	1.5

Properties Symbol	Butan-2-one MEK	Toluene TOL
Formula	$\text{C}_4\text{H}_8\text{O}$	$\text{C}_7\text{H}_8$
Molar volume 25°C (cm <sup>3</sup> mol <sup>-1</sup> )	90.14	107.51
Vapour pressure at 25°C (kPa)	12.60	3.79
Kinetic diameter (nm)	0.52	0.58

### Adsorption—Ozonation Experimental Set-Up

A schematic representation of the fixed bed experimental set-up is given in Figure 1. 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 VOC polluted air stream obtained via a bubbler was diluted with dry air to reach a typical industrial air stream concentration of 1 to 5 g.m<sup>-3</sup>.

The ozonated air stream was obtained from a commercial ozone generator (model 5LO from Trailgaz), and since the ozone production is function of air pressure (70 kPa), flow (0.25 m<sup>3</sup>.h<sup>-1</sup>), and power applied, the ozone inlet mass concentration was reproduced with an uncertainty of  $\pm 0.5 \text{ g.m}^{-3}$ . At the inlet, outlet and every 5 cm, an intermediate gaseous sample could be taken and sent either to a BMT ozone analyzer to determine ozone concentration, or to a GC-MS for VOC quantification, oxidation organic sub-products identification, and mineralization products (CO<sub>2</sub>, H<sub>2</sub>O) detection. 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  $\mu\text{m}$  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 vapour, giving a very precise concentration especially in the low concentration range (< 0.01 g.m<sup>-3</sup>). Both methods gave similar results, with a typical difference smaller than 5%. Experimental conditions are summarized in Table 3.

## RESULTS AND DISCUSSION

### Ozone Physical Adsorption on ZSM-5

In a previous study, the interactions of gaseous ozone and hydrophobic zeolites at ambient temperature were characterized (Monneyron et al., 2003d), indicating that in the case of a ZSM-5 type zeolite, consecutive adsorption and decomposition phases occurred. Here, different experimental conditions have been tested in order to clarify the successive phenomena. The evolution of ozone concentration at the outlet of the bed is shown on Figure 2,

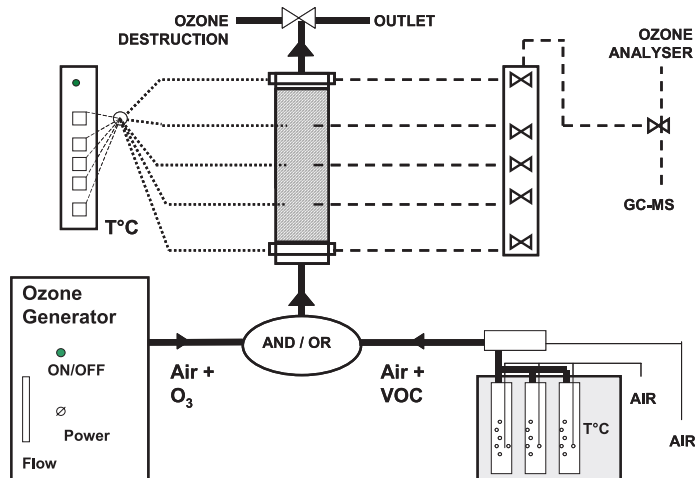


Figure 1. Adsorption/ozonation experimental set-up

when an ozonated air stream was sent on new Sil Z, which has not been in contact either with ozone or VOC.

For the three lowest concentrations, classical breakthrough curves were obtained, whereas at 18 g/m<sup>3</sup> concentration, the breakthrough is followed by a decrease of ozone concentration down to 0 and remain nil constantly. This particular behaviour was also observed in the previous study for a higher concentration (27 g/m<sup>3</sup>). Using these profiles, the corresponding adsorbed amounts were calculated or estimated when decomposition occurred before complete adsorption ([O<sub>3</sub>] = 18 g/m<sup>3</sup>), and the results are reported in Figure 3 as a typical adsorption isotherm, although the adsorption did not occurred in real isothermal conditions since temperature profiles were observed. Langmuir approach was used to fit experimental data, Equation (1), with the corresponding parameters  $b = 0.35 \text{ m}^3/\text{g}$  and  $Q_m = 20.2 \text{ mmol/g}$ , highlighting the favourable adsorption of ozone on ZSM-5 type hydrophobic zeolite.

$$Q = \frac{bQ_m C}{1 + bC} \quad (1)$$

This graph gives interesting information to explain the decomposition of ozone at high concentrations. Indeed, for concentration greater than 10 g/m<sup>3</sup>, the adsorbed amount per unit mass and thus the local ozone concentration are stable, indicating that it is not the only critical parameter that influences ozone decomposition. In addition, during the adsorption phase, the temperature increase in the bed is directly proportional to ozone inlet concentration. In these experimental conditions, this temperature increase is 1.8 K m<sup>3</sup>/gO<sub>3</sub>, representing the equilibrium of heat production and diffusion in the

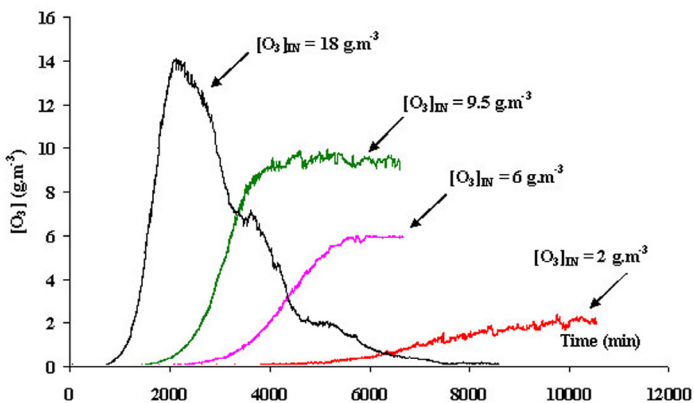


Figure 2. Ozone concentration profiles at reactor outlet during ozone adsorption at 298 K (gas velocity  $U = 0.01 \text{ m/s}$ )

Table 3. Experimental conditions for dynamic adsorption/ozonation		
	Fau Y	Sil Z
Bulk density (kg/L)	0.42	0.66
Adsorbent mass (g)	150-400	200-600
Temperature (K)	298	
VOC polluted air flow (Nm <sup>3</sup> .h <sup>-1</sup> )	5	
VOC air stream velocity (m.s <sup>-1</sup> )	0.275	
Air relative humidity (%)	0 except when specified	
Ozonated air flow (Nm <sup>3</sup> .h <sup>-1</sup> )	0.25	
O <sub>3</sub> concentration (g.m <sup>-3</sup> )	0-30	

micropores—the heat generated by adsorption enthalpy being, in a first approximation, proportional to the adsorbed quantity per unit of time—and the intergranular convective flux that can be considered identical for similar hydrodynamic conditions. Therefore, the ozone decomposition can be regarded as a thermo catalytic effect controlled by local ozone concentration and temperature at the micropore scale. The specific influence of surface chemistry of solids (crystalline defects, extra network aluminum clusters) has to be considered in addition to local temperature since gaseous ozone is stable up to 250°C (Dhandapani and Oyama, 1997). A specific study of local intracrystalline temperature estimation is now being conducted.

### Dynamic Adsorption of Organic Compounds on High Silica Zeolites

The first part of the process consists in a partial saturation of adsorbent due to air stream treatment. Here, the main objective being to exhibit the feasibility and to study the mechanisms of oxidation, as a regeneration method, the complete saturation of zeolites was obtained. As an example of specific adsorption behaviour, breakthrough curves of TOL on both zeolites are shown in Figure 4, where the relative outlet concentration is reported toward the gaseous volume per unit mass of pure adsorbent. 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 wider mass-transfer zone is observed, representative of lower affinities of VOC than toward ZSM-5.

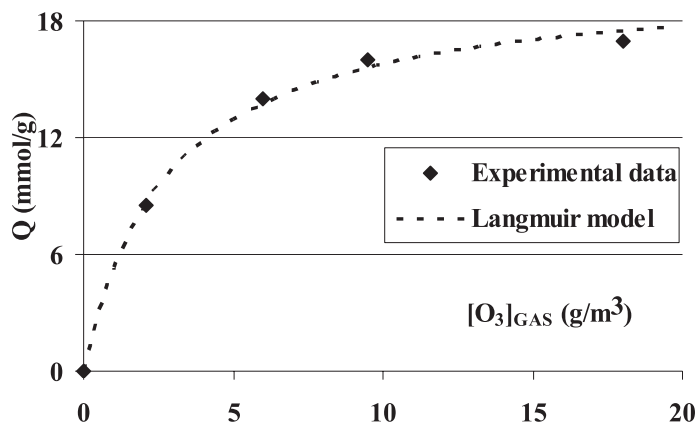


Figure 3. Adsorption isotherm of ozone on Sil Z at 298 K

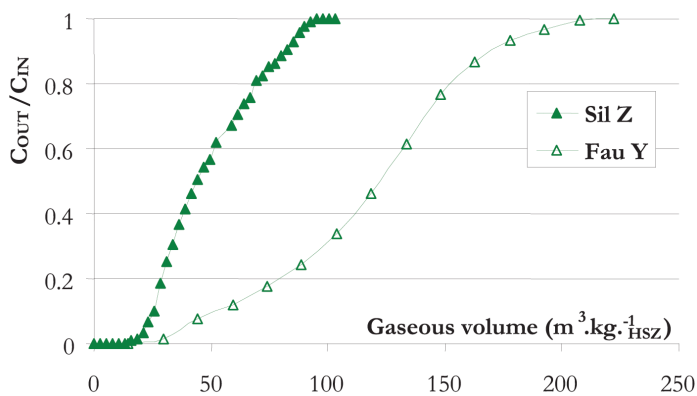
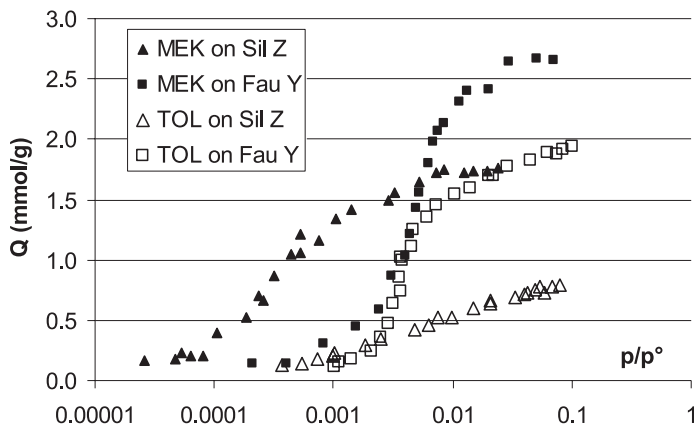
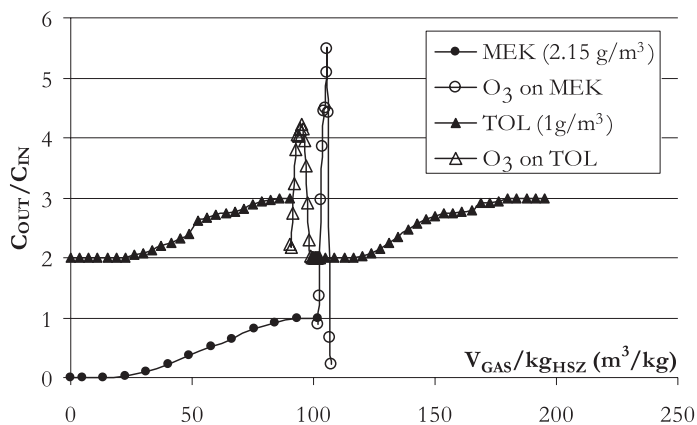


Figure 4. Breakthrough curves of toluene on a 10 cm bed of both zeolite ( $C_{IN} = 1 \text{ g/m}^3$  – linear velocity  $U = 0.275 \text{ m/s}$ )



**Figure 5.** Adsorption isotherms of TOL and MEK on Sil Z and Fau Y at 298 K



**Figure 6.** VOC concentration profiles during a discontinuous adsorption/ozonation cycle of Sil Z

These different behaviours confirmed the investigations of adsorption equilibrium properties. Adsorption properties of the two zeolites are very different, as shown in Figure 5: Sil Z presents a type I isotherm, considered as favourable adsorption, whereas a type V isotherm is observed for Fau Y, indicating unfavourable adsorption at very low pressure.

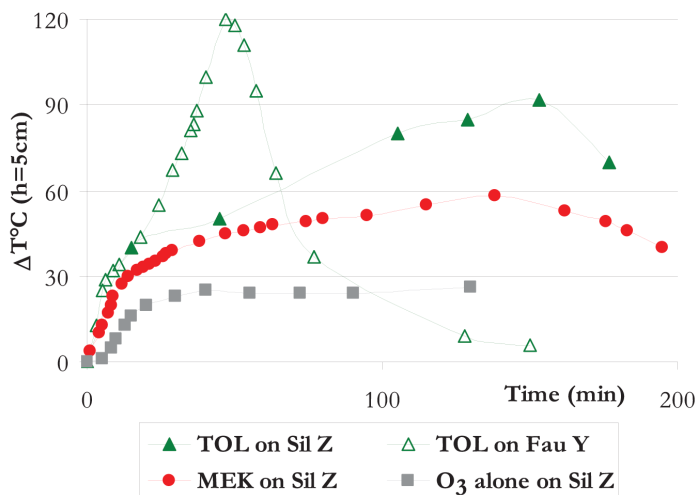
In addition, the dynamic adsorbed amounts at complete saturation were calculated using the classic integration of breakthrough curves using:

$$Q = \frac{U \cdot S \cdot C_{IN}}{m} \int_0^{\infty} \left(1 - \frac{C_{OUT}(t)}{C_{IN}}\right) dt \quad (2)$$

with  $U$ , superficial velocity (m/s),  $S$ , column section ( $m^2$ ),  $m$ , mass of adsorbent, and  $C_{IN}$  inlet concentration of VOC (10.85 mol/L for TOL and 29.82 mol/L for MEK). The results obtained for TOL  $\{0.54 \text{ mol/kg}_{SilZ} \text{ and } 1.41 \text{ mol/kg}_{FauY}\}$  and butan-2-one  $\{1.50 \text{ mol/kg}_{SilZ}\}$  are in good agreement with a previous study carried out using a volumetric method  $\{0.53 \text{ mol/kg}_{SilZ} \text{ and } 1.48 \text{ mol/kg}_{FauY} \text{ for TOL and } 1.68 \text{ mol/kg}_{SilZ} \text{ for MEK}\}$  (Monneyron et al., 2003a).

### Ozonation of Adsorbate Phase— Adsorbent Regeneration

When a complete saturation with VOC of the fixed bed was obtained, its regeneration was conducted by oxidation using preferentially an ozonated dry air stream at the high  $18 \text{ g/m}^3$  concentration, injected at the bottom of the bed, while the outlet

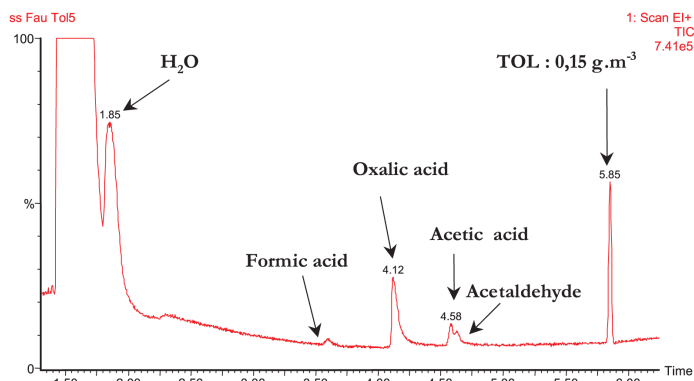


**Figure 7.** Temperature profiles inside the bed during ozonation at  $18 \text{ g/m}^3$  of pure and VOC saturated zeolite

concentration of ozone and organic compounds were determined. For both zeolites and both VOC, a highly exothermic oxidation took place, leading to organic sub-products and a strong increase of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  content in the exit air. Oxidation was evaluated in terms of thermal effect and mass balance on VOC and on ozone. Figure 6 presents an example of concentration profiles of VOC at the outlet of the reactor during two distinct discontinuous adsorption/ozonation cycles on Sil Z, leading to a regeneration of adsorption capacities greater than 95%, calculated by determining the difference in the adsorption in the first and second cycles (the TOL  $C_{out}/C_{in}$  origin has been displaced for better clarity).

After the adsorption breakthrough curve of VOC a high increase of VOC concentration is observed, which can be linked to a thermodesorption induced by the exothermic effect of oxidation. Indeed, during ozonation of adsorbed VOCs, the temperature increases observed in both cases are much larger than the one found for the decomposition of single ozone ( $30^\circ\text{C}$  for  $18 \text{ g}_{\text{O}_3}\cdot\text{m}^{-3}$ ), and have reached  $120^\circ\text{C}$  as shown on Figure 7. According to this point, a significant oxidation of adsorbed compounds can be deduced and, as ozone is sent to the bottom of the bed, oxidation reaction occurs in the lower part of the reactor before moving up. Therefore, some desorption of the adsorbed compound occurred because the bed was totally saturated before its ozonation. Indeed, to detect and identify generated sub-products, it was decided to start from a fully saturated bed. From an industrial perspective, the bed would only be partially saturated, before being cleaned and the thermal desorbed VOCs would be adsorbed in the bed zone free of adsorbate or would be recycled during the ozonation phase.

The difference in thermal elevation for the two zeolites (Sil Z and Fau Y) during the oxidation of TOL can be explained by two factors related to the crystalline structure: first Fau Y is more porous ( $0.3$  versus  $0.19 \text{ cm}^3/\text{g}$  for Sil Z); leading to a greater VOC amount adsorbed which can accelerate the oxidation kinetics. In addition, the Fau Y structure is characterized by larger pore diameters ( $13 \text{ \AA}$  versus  $5\text{-}6 \text{ \AA}$  for Sil Z), which facilitates the diffusion of species—VOC, ozone and sub-products. Moreover, on Sil Z, the thermal increase is smaller for MEK than for TOL, due to an incomplete oxidation and the formation of a quite stable sub-product, and to a higher desorption (45% of adsorbed amount versus 25% for TOL).



**Figure 8.** GC-MS chromatogram obtained during the ozonation of adsorbed toluene on Fau Y

In order to evaluate the consumption of ozone of such a process, a mass balance on oxygen was carried out, and is presented in Table 4 for the silicalite. Taking the uncertainties on VOC concentration into account (5%) and of partial oxidation, especially for MEK, this rough calculation of the balance shows that all the ozone that has been sent was used to oxidize organic compounds. This supports the experimental observation that no ozone was coming out of the adsorbent bed.

Moreover, the same treatment on Fau Y was less efficient as the regeneration rate of the bed was only 75%. This probably comes from the reactivity difference of these zeolites in contact with ozone (Monneyron et al., 2003d), and more specifically, from the place where the ozone decomposition takes place. On Fau Y, ozone is immediately decomposed before adsorption, producing short-life-time oxidative radicals on the zeolite surface which leads to the oxidation of VOCs only at the crystals external surface and a time limitation by intracrystalline diffusion. 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. Investigating petrochemical catalysts, Hutchings et al. (1987) found the same difference between ZSM-5 and Fau Y based coked catalyst: ZSM-5 material was very well regenerated with an  $O_2/O_3$  mixture whereas Fau Y material was only regenerated on surface, leaving deep coke. This phenomenon led us to suspect oxidation to be a radical-based mechanism. This was investigated via sub-products identifications.

### In Situ Ozonation Mechanisms

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 the selected ion recording (SIR) method. In Figure 8, a chromatogram obtained during ozonation of TOL on Fau Y is presented with the highest concentrations observed. The initial toluene concentration is indicated on the right side of the figure, in order to give a qualitative idea of the amounts of the sub-products formed.

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

A lot of reactive products can be found in the zeolite bed, in contact with ozonated air: ozone degradation products, oxygen and hydroxyl radicals in presence of humidity. It is, therefore, difficult to conclude about specific species and about mechanisms involved in their formation. Partially degradation of toluene was studied by Sekiguchi et al. (2003) using an ozone degradation catalyst ( $MnO_2$  deposited on a mixed support  $TiO_2/SiO_2$ ), with different hygrometries. Mineralization 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%. This phenomenon emphasizes the specificity of catalysts. Akubuiro (1993) worked on MEK degradation mechanism on activated carbon and proposed a hydroperoxide to be a first intermediate product from ambient oxygen, prior to the appearance of 2,3-butanedione, before acetaldehyde and acetic acid.

According to the works of Leichsenring et al. (1996) concerning dioxins and furans catalytic oxidation on hydrophobic zeolites, and Büchel et al. (2001) about mesoporous MCM-synthesis surfactant removal using ozone, 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 probably not the only one.

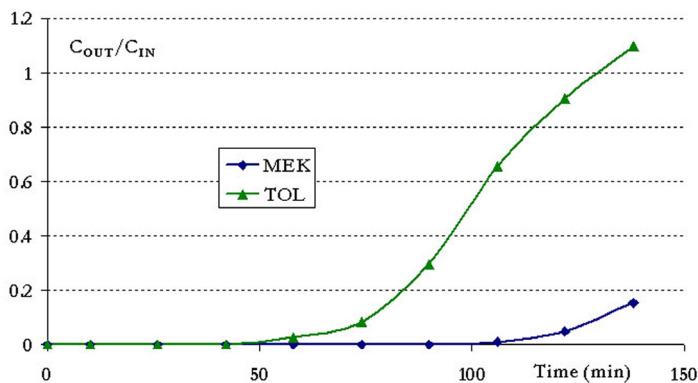
In this experimental study, an acceleration of the degradation of adsorbed compounds in the presence of water has also been observed. When using an 80% relative humidity ozonated air flow instead of a dry (0% RH) flow, an almost immediate increase of temperature of 30°C was noticed, whereas no heat was produced when a pure zeolite (without any VOC adsorbed) is ozonated, indicating that water is responsible for an acceleration of oxidation but is not sufficient to induce ozone decomposition. Competition between water and ozone molecules is suspected on ozone decomposition sites.

### Selective Oxidation on HSZ

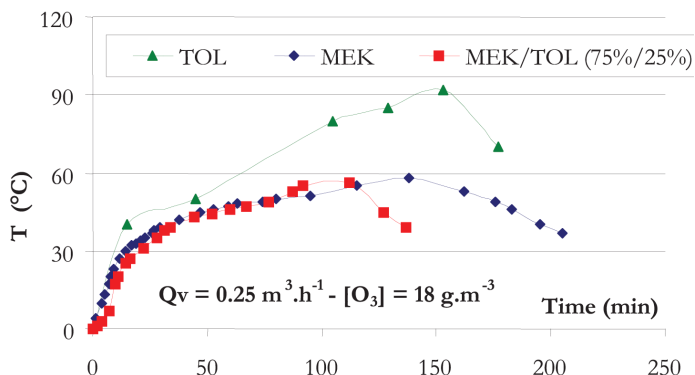
This adsorption/ozonation process can be interesting to treat multi-component effluents in a selective way. A previous study on zeolites selectivity (Monneyron et al., 2003a) showed that MEK/TOL mixture could be selectively treated. Zeolite bed is used as a purification filter, adsorbing MEK, while TOL, the minor compound, can be recovered. Breakthrough curves of both components are given in Figure 9, for a mixture rich in MEK ( $X_{MEK} = 75\%$  and  $X_{TOL} = 25\%$ ), on Sil Z. Ozone was sent before saturation, with  $C_{O_3} = 18\text{ g.m}^{-3}$  and adsorbed MEK was degraded. Sub-products detected were 2,3-butanedione and acetic acid, as for pure adsorbed MEK ozonation. Temperature profiles in the bed were followed and are reported in Figure 10 at a 5 cm height point. The temperature increase is similar to the one obtained for single MEK, except that the decrease starts

**Table 4.** VOC oxidation mass balance on Sil Z

VOC	Amount adsorbed (g)	Amount non desorbed (g)	Amount of $O_3$ sent (g)	Experimental stoichiometry ( $mol_{O_3}/mol_{VOC}$ )	Theoretical mineralization stoichiometry ( $mol_{O_3}/mol_{COV}$ )
MEC	15	8.2 (55%)	18 (4h)	3.30	3.66
TOL	8	6.0 (75%)	18 (4h)	5.75	6.00



**Figure 9.** Breakthrough curves of MEK/TOL mixture (75%–25%) on Sil Z ( $p_{TOT} = 100$  Pa)



**Figure 10.** Comparison of temperature increase profiles at 5 cm height: ozonation of an adsorbed mixture MEK/TOL and ozonation of pure adsorbed components

earlier because of a lower adsorbed amount of MEK than for pure VOC ozonation.

## HYBRID PROCESS ADSORPTION/SELECTIVE OXIDATION ANALYSIS

Experimental feasibility was studied for a sequential process: adsorption on a fixed bed of single or binary VOC air stream until saturation and regeneration by an ozonated air. Oxidation on both zeolites was evaluated in terms of associated thermal effect, main product and ozone mass balance. For both zeolites (Fau Y and Sil Z) and both VOC (MEK and TOL), a highly exothermic reaction took place in the reactor leading to organic sub-products formation and a high concentration of water and carbon dioxide, while no residual ozone was detected. Moreover, there was no or very little ozone lost via side-effect decomposition/deactivation mechanisms. A good efficiency of bed regeneration was found (95%) without any optimization of the process, highlighting the interest and potentialities of this hybrid process. In term of exploitation cost, the main part of it comes from the regeneration of the adsorbent phase and, thus, of the ozone consumption. This can be 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  $1 \text{ g.m}^{-3}$  of dioxane in a  $1000 \text{ m}^3.\text{h}^{-1}$  air stream is estimated at approximately 2,7 Euro/h, for a conventional corona discharge generator of ozone, costing about 1,5 Euro/ $\text{kg}_{\text{O}_3}$  produced (Manero and Monneyron, 2005). Some works showed that ozone generation with better efficiency is possible, using zeolite as concentrator of ozone (Izumi et al., 2001), giving basis for an optimization of the process.

## CONCLUSION

An experimental set-up, based on adsorption and ozonation, was examined as an alternative hybrid treatment for Volatile Organic Compounds (butan-2-one and toluene). Two commercial high silica zeolites (Faujasite Y and Silicalite Z) were used as adsorbent for dilute polluted air stream treatment. The first part of this study consisted in clarifying the physical adsorption of ozone on ZSM-5 zeolite, and a thermocatalytic decomposition was figured out from high ozone local concentration and high crystallite temperature. Then, the oxidation of the two industrial solvents and total regeneration of the fixed bed were achieved on both zeolites with a complete mineralization of organic compounds. Detection and identification of sub-products traces allowed us to identify a radical-based oxidation mechanism and a critical role of water for hydroxyl radicals local concentration. A mass balance on oxygen showed that all the inlet ozone was used for organic compounds oxidation. At last, a selective oxidation was achieved, allowing the separation and the recovery of minor compound. This study points out the interest and potentialities of this hybrid process. Further understanding of local catalytic behaviour and heat and mass transfer is required.

## ACKNOWLEDGMENTS

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## NOMENCLATURE

b	Langmuir parameter ( $\text{m}^3/\text{g}$ )
C	VOC concentration in air ( $\text{g.m}^{-3}$ )
m	mass of adsorbent (g)
$p_{TOT}$	gas phase total partial pressure induced by VOC concentration (Pa)
Q	amount adsorbed ( $\text{mol kg}^{-1}$ )
$Q_m$	Langmuir parameter ( $\text{mmol/g}$ )
$Q_v$	volumetric air flow ( $\text{m}^3.\text{h}^{-1}$ )
S	column section ( $\text{m}^2$ )
T	temperature (K)
U	linear velocity ( $\text{m.s}^{-1}$ )
V	gaseous volume ( $\text{m}^3$ )
$\xi_i$	molar fraction of component <i>i</i> in inlet gas

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