Voc abatement

Performance of different ceramic membranes in a catalytic membrane reactor

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The catalytic combustion of Volatile Organic Compounds (VOC) was carried out using catalytic membrane reactor (CMR). Membranes formed of thin layers of titania, zirconia, γ-alumina and zeolite (ZSM-5) were used for catalyst (Pt) deposition. The light-off temperatures obtained by using toluene or propane as model molecules for VOC, were compared. Results showed that the performance of the membranes was a function of layer characteristics. It was given an activity order in terms of turnover number (TON). For the catalytic combustion reaction the membranes with platinum deposited onto the titania selective layer performed satisfactorily.

Through the 1990's, there has been a renewed scientifically-based and economically beneficial approach to solve environmental problems. Regulatory compliance is frequently the driving force behind emission control technology developments. In particular Volatile Organic Compound removal requires an efficient technology capable to comply with the more and more strict regulatory requirements where the current and traditional technology falls [1].

Catalytic combustion is perhaps the most promising technology to control VOC emissions due to lower energy and material costs with respect to thermal combustion and to its flexibility compared with other means of VOC removal by physical method [2, 3].

In this contest the catalytic membrane reactor, which over the past has been mostly used for biological transformations in industrial processes, could become an effective alternative for the abatement of Volatile Organic Compounds (VOC), an important class of pollutants released by many big (e.g. chemical process industry, food processing) and small (e.g. production of paints, cleaning agents, solvents etc.) industries. Ceramic membranes are the basis of this novel technology thanks to their peculiar characteristics: they suit to high temperature operations, they have also intrinsic catalytic activity and often serve as a support for the catalyst.

In a previous paper [4] we reported the preliminary results of the catalytic combustion of toluene, varying the operating conditions (oxygen concentration, residence time), on a catalytic membrane reactor. In literature [5, 6] the performance of γ-alumina/Pt or perovskite membranes in the catalytic combustion at low concentration of VOC are available.

In this paper the catalytic combustion of toluene and propane is carried out by using membranes with different layers (titania, zirconia, γ-alumina or ZSM-5) to support the catalyst; the membranes were used in two different ways with respect to the contact between the gaseous stream and the catalytic layer (monolith-like or flow-trough configurations). So the effect of different morphological and structural properties of the membranes on the catalytic performance is investigated. At least a first attempt to scale-up the reactor was done using a multichannels membrane.

Experimental

Membranes and catalytic membranes preparation

Ceramic membranes made of three α-Al_2O_3 macroporous layers as support of an inner mesoporous layer of TiO_2, ZrO_2 (supplied by Schumacher, Germany) or γ-Al_2O_3 (supplied by SCT/US Filter, France) were used. A zeolite membrane was also prepared in our labs by coating the inner TiO_2 surface membrane with a layer of ZSM-5 via the hydrothermal process [7]. Single channel membrane tubes had an internal diameter of about 6.7 mm and a thickness of 2 mm, while the multichannel was a monolith composed of 19 channels with diameter of 3.4 mm.

The membranes were impregnated with an opportune precursor in order to deposit the combustion catalyst, platinum. Table I lists the various types of membrane, labelled for commodity reason with a letter, along with the catalyst precursor. The catalyst was deposited onto the M, A, G, membranes by the ion exchange technique with a solution of H_2PtCl_6 and onto the Z membrane with a solution of $Pt(NH_3)_4Cl_2$ since the

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Table I - Catalytic membrane used

Membrane	Type	Pore diameter (nm)	Catalytic system	Precursor
M	Multichannel	5	Pt/TiO_2	H_2PtCl_6
A	Single channel	5	Pt/TiO_2	H_2PtCl_6
B	Single channel	10	Pt/ZrO_2	Pt/mesitylene
G	Single channel	5	Pt/γ-Al_2O_3	H_2PtCl_6
Z	Single channel	<1	Pt/TiO_2/ZSM-5	$Pt(NH_3)_4Cl_2$

Table II - Thickness and specific surface area of the skin layer

Membrane	Inner layer composition	Specific surface area (m^2/g)	Thickness (μm)
M	TiO_2	254 (1)	0.4-0.6
A	TiO_2	250 (1)	0.4-0.6
B	ZrO_2	57 (1)	3.5
G	γ-Al_2O_3	234 (1)	1.8-2.0
Z	TiO_2/ZSM-5	486 (2)	33

(1) Evaluated by the BET method; (2) Calculated by the Langmuir method

ZSM-5 is a cation exchanger. For the B membrane, platinum was deposited by the Metal Vapour Deposition method described elsewhere [8], as zirconia shows the lowest specific surface area than other membranes.

Catalytic membranes characterization

The distribution of the deposited Pt along the cross-section of the membrane was evaluated by a scanning electron microscope (SEM, Leica Stereoscan 440) equipped with a microprobe for X-ray analysis (Link System 860 Analyser LTD). The catalyst loading was evaluated by ICP, Inductively Coupled Plasma (ICP-AES; JY 24). For this aim a membrane sample was subjected to a chemical attack with aqua regia followed, in the case of the zeolite membrane, by a further attack with HF.

Platinum particles' size distribution was determined by a transmission electron microscope (TEM, Jeol Jem 2000 EX/T). Samples for TEM observations were prepared using two different methods, depending on the type of membrane. In the mesoporous membranes case the thin layer was scratched from the α-alumina support and then reduced to powder to be dispersed onto a Lacey carbon-Cu grids (200 mesh) while in the Z microporous membrane instance the replica technique described in reference [9] was used.

Surface area and pore size distribution of the membranes were evaluated by N_2 adsorption-desorption measurements (Micromeritics ASAP 2010). Permeability tests, on the same pilot plant used for catalytic tests, with N_2 at different temperatures were carried out in order to establish the gas-flow regime.

Catalytic tests were carried out in continuous and in isothermal conditions, with a constant residence time of 2.5 s, by using the experimental set-up for gas-phase reactions reported in [4]. Air was used as oxygen supplier and as diluent. Toluene was feed up through the reactor by diluting with air an hydrocarbon saturated air stream. The air/hydrocarbon stream was fed up through the tube-side of the catalytic membrane in order to exploit two reactor operating modes of contact:

a) the gaseous stream went in and out trough the tube-side (monolith-like configuration);

b) the gaseous stream was forced through the catalytic membrane from the tube side to the shell-side (flow-trough configuration).

The effect of temperature and hydrocarbon (toluene or propane) concentration was investigated between 100-350 °C and 800-5,000 ppm, respectively.

Two gas chromatographs, equipped with FID and TCD respectively with Carbowax 20M and Porapack Q columns, were used to evaluate the hydrocarbon concentration.

Results and discussion

The values of specific surface area and thickness of the inner layer are shown in Table II. The skin layer of the A, B, G, M membranes was mesoporous (by the pore diameter distribution not shown) in agreement with the nominal pore diameter reported in Table I.

The shape of the adsorption/desorption isotherm for the zeolite membrane (Figure 1) revealed the microporous structure of the ZSM-5 deposited. Among the mesoporous membranes, the B membrane had the lowest value of specific surface area. The A and M membranes have a TiO_2 selective layer with thickness below 0.6 μm (Figure 2a) but, as clearly indicated by the micrograph shown in Figure 2b, this layer presents some defects.

Figure 3 shows the cross-section of the zeolite membrane. Two ZSM-5 layers corresponding to two successive hydrothermal deposition routes can be observed.

The results of EDX-analysis along the cross section of the membranes are shown in Figures 4 and 5. From Figure 4 it is clear that the Pt was mostly present onto the TiO_2 layer and the same result was found on the other mesoporous membranes; Figure 5 shows that in the Z membrane the Pt is present on TiO_2 layer and only a small amount onto the ZSM-5

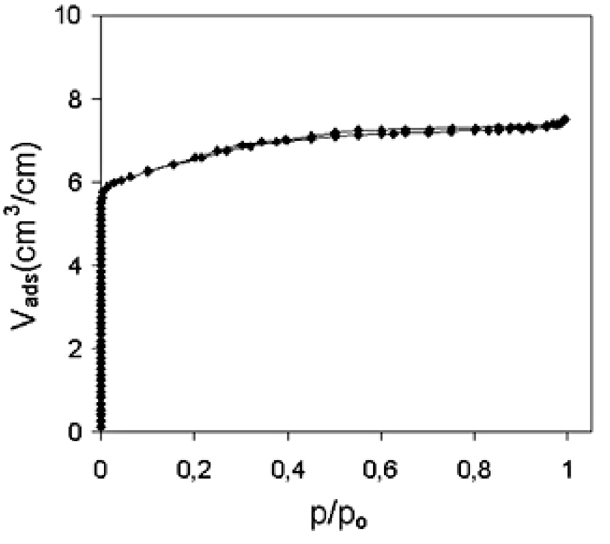

Figure 1 - N_2 adsorption/desorption isotherm of the zeolite membrane (Z). The adsorbed volume is referred to the unity of membrane length (cm)

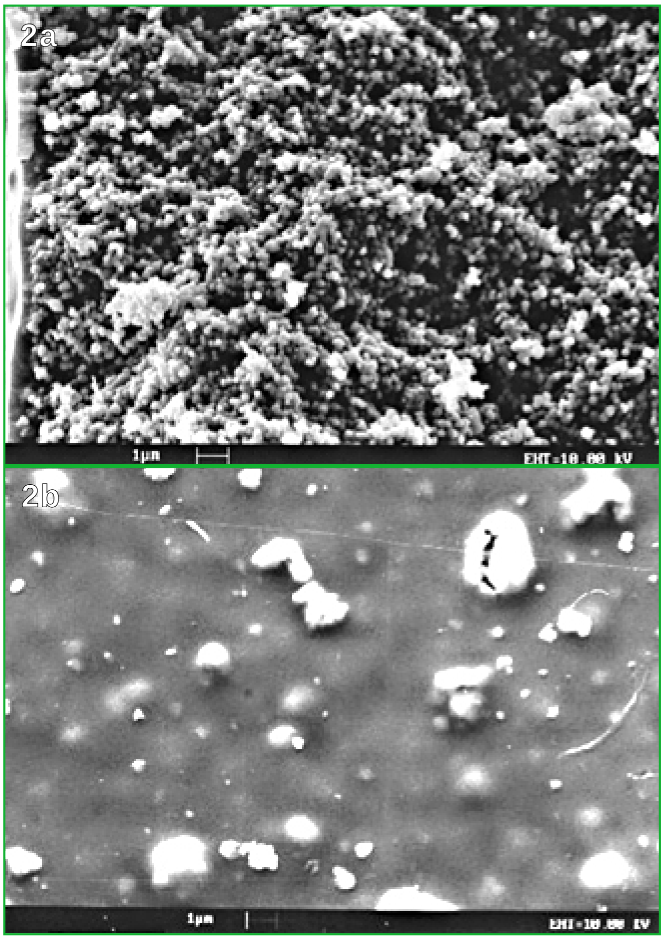

Figure 2 - SEM micrograph of the cross-section (2a; A membrane) and of the surface (2b; M membrane)

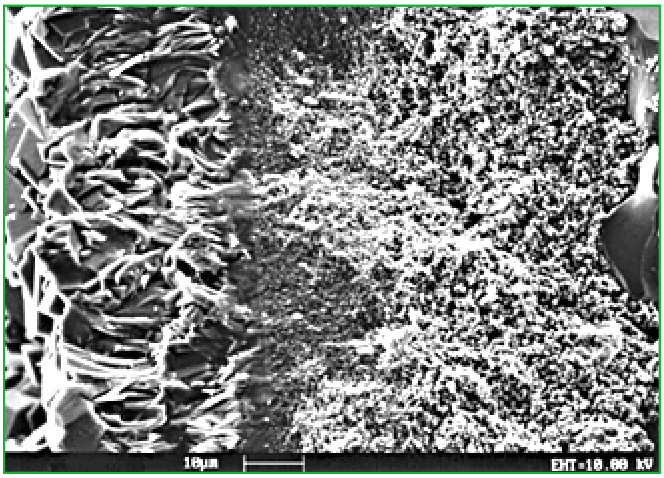

Figure 3 - SEM micrograph of the cross-section of the zeolite membrane (Z)

layer as well as on the α-alumina support.

In Figure 6 the N_2 permeance as a function of the average pressure for all the catalytic membranes is reported. The permeance values are obviously governed by skin layer characteristics. The Z membrane exhibits the lowest permeance while the A membrane is more permeable than the G one. The permeance of the Z, G, B, A membranes seems not dependent on the average pressure, in accordance with a Knudsen transport regime, while the positive slope observed for the M membrane indicates the presence of a slight viscous flow contribution probably due to the defects observed on the TiO_2 surface (see Figure 2b). Considering the microporous structure of the zeolite and its very high thickness, the permeance of the Z membrane appears high when compared with that of the G membrane. Most probably this fact is related to the presence of free spaces between the crystals of the ZSM-5 layer.

Table III - Characteristics of the platinum deposited on the membranes

Membrane type	*A*	*B*	*G*	*M*	*Z*
Pt loading (mg)	1.49	7.9	1.59	1.91	5.22
d_{VA} (nm)	2.5	3.3	2.8	3.0	2.6
D_M	45.5	33.9	40.4	37.4	43.1

Table III reports data on the total catalyst amount deposited on the membranes, the mean diameter of the platinum particles, d_{VA}, and the Pt dispersion, D_M. The amount of deposited Pt varied from membrane to membrane while the characteristics of the deposited platinum particles (d_{VA}, D_M) are similar.

The catalytic performance of the membranes is shown in Figure 7 in terms of toluene conversion as a function of temperature. The curves exhibited different shape and also the light-off temperature was different. From combustion tests carried out with membranes without catalyst it was observed a light-off temperature about 100 °C higher than the one derived from Figure 7. It means that in order to achieve higher conversion at lower temperature an active catalyst like platinum must be used. Platinum supported by TiO_2 layers (A) offers a better catalytic performance with a lower light-off temperature. In detail the TiO_2 membranes reached complete combustion already at temperature below 200 °C, probably titania gives some contribution to the combustion reaction [10,11]. The G membrane, working at a temperature range higher than the

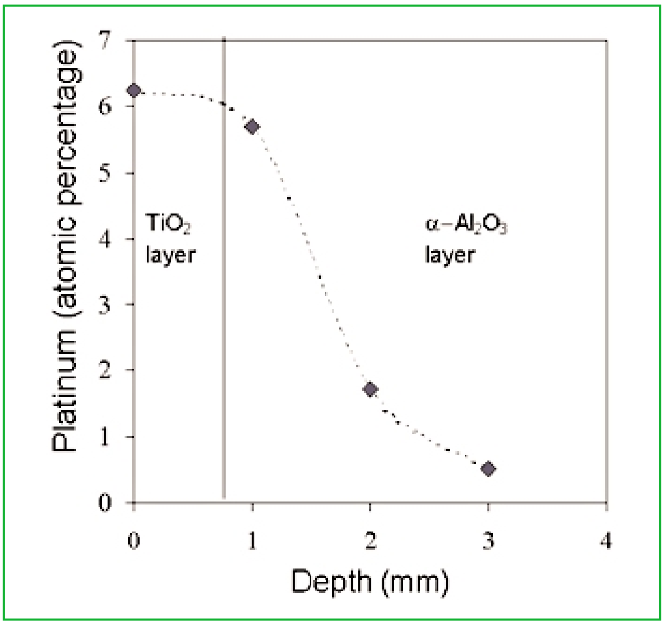

Figure 4 - Platinum distribution along the cross-section of the A membrane

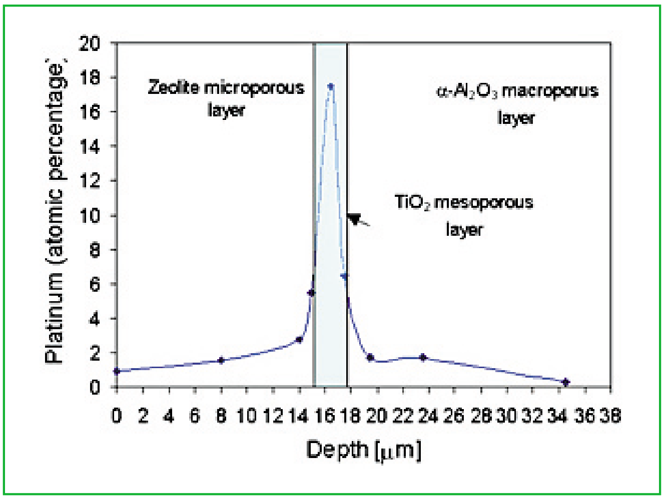

Figure 5 - Catalyst distribution along the cross-section of the Z membrane

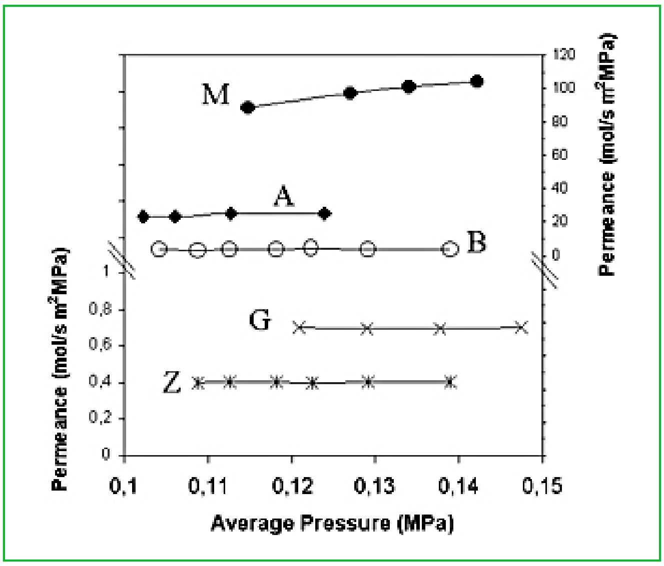

Figure 6 - N_2 permeance comparison among the different type of the membrane used

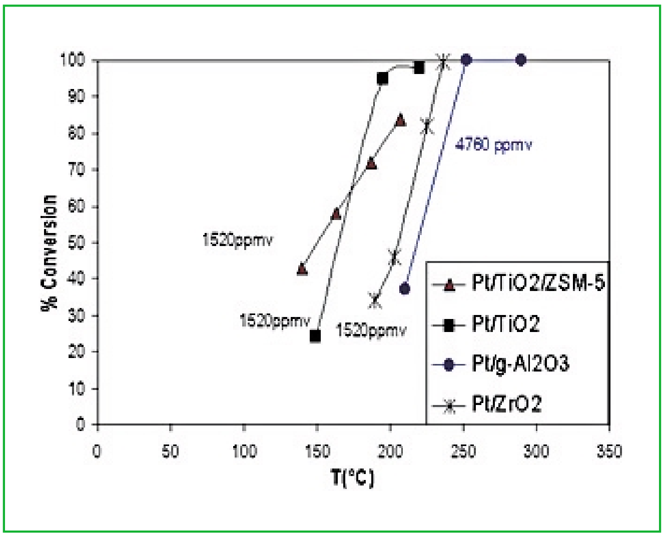

Figure 7 - Conversion as a function of the temperature for the membranes with different nature of the active layer

other membranes, could seem the worse system although the inlet hydrocarbon concentration was four times higher the in the other test. Nevertheless the literature [12] for the catalytic combustion over platinum reports a zeroth order kinetics with respect to aromatic hydrocarbons.

So the activity in terms of hydrocarbon converted moles per gram of platinum was calculated (e.g. at 200 °C). It was observed the following reactivity order:

Membrane (layer)	$A(TiO_2)>$	$G(\gamma\text{-}Al_2O_3)\geq$	$Z(ZSM\text{-}5/TiO_2)>$	$B(ZrO_2)$
TON (10^3 mol/sg)	6.60	1.75	1.60	0.55

The lower activity of the B membrane is due to a smaller specific surface area and to a lower metallic dispersion of the catalyst.

The performance of the multichannels membrane, M, and the single-channel membrane, A, shown in Figure 8 and compared with the one of the catalytic combustion of toluene and propane is considered. The M membrane shows a better behaviour and this is important because the multichannel tube is more suitable than monochannel ones for industrial applications. Furthermore, according to what reported in literature [13], the molecule of paraffin shows a light-off temperature higher than the aromatic one.

The effect of feed configuration was also investigated and between monolith-like or of flow-trough no appreciable differences configuration were observed in the case of the thin mesoporous layers. Obviously if a viscous contribution to the permeance was present the performance of flow-trough configuration was worse because of the easier slip of the hydrocarbon from the catalytic zone. These results are not in contrast with the ones reported in the literature [5] where the conversion obtained by flow-through configuration is higher than that of monolith-like configuration. However in this case the Pt/γ-alumina system was distributed along the entire porous membrane thickness (of about 2 mm) while our system is different because the Pt is present only in a thin inner layer (2μm).

The performance of the Zeolite membrane is reported in Figure 9. The feed configuration affects the reactor performance and as well as the type of hydrocarbon is concerned, propane shows a lower light-off temperature in the flow-through configuration while toluene shows a higher light-off temperature when monolith-like configuration is used.

The differences between the A and M membrane are mainly due to the different catalyst loading while the comparison of the catalytic performance between the A and M membrane seems to indicate an important role played by the different configuration. With respect to the other types of membranes, in the Z membrane the hydrocarbon conversion is controlled by mass transport phenomena and hence a different behaviour of the conversion as a function of the temperature should be expected. In addition a given role may be played by to the adsorbent characteristics of the zeolite with consequent increase of the local hydrocarbon concentration onto the surface of the active layer [14].

Furthermore it can be concluded that, for the catalytic combustion reaction, the membranes with platinum deposited onto the titania selective layer perform satisfactorily; in fact the toluene combustion is reached at temperature lower than 200 °C for each Pt/TiO_2 membrane.

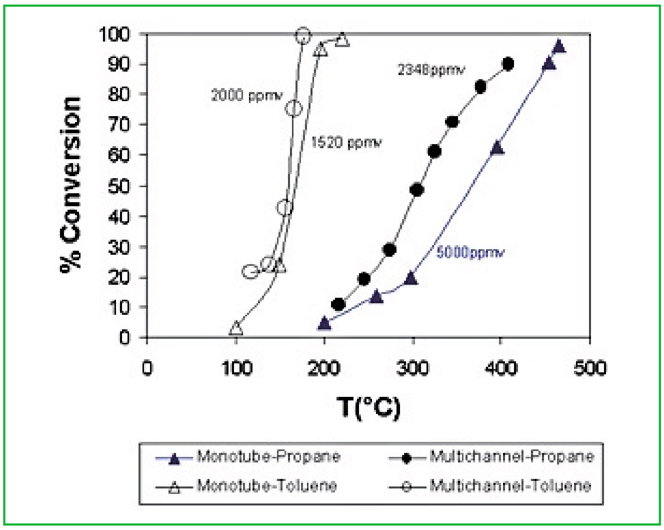

Figure 8 - Catalytic combustion of toluene and propane by using the monolith-like configuration for the monotube (A) and the multichannel (M) membrane

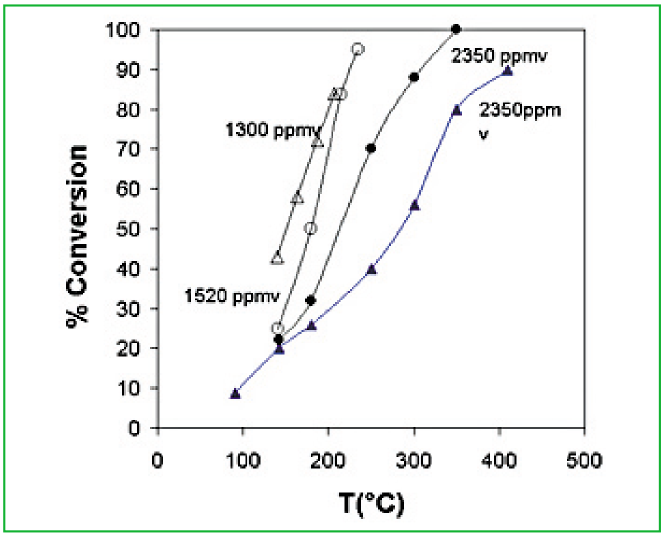

Figure 9 - Effect of the feed configurations, monolith-like (triangles) or flow-trough (circles), on the catalytic activity of the zeolite membrane on the combustion of toluene (open symbols) and propane (filled symbols)

Conclusions

The catalytic combustion of propane and toluene was studied by using various types of membranes and two different configurations. The best results were obtained with the Pt/TiO_2 system as the toluene combustion was reached at temperatures lower than 200°C.

The titania multichannel tube gives an higher productivity with respect to the single tube one; this should be considered if the membrane catalytic burner will be attractive for an industrial application. Furthermore, except for the zeolite membrane, prepared in laboratory, all the other ones were commercial membranes. The following scale-up, in order to verify field test performance of the system, could be realised without too many difficulties.

The exploitations on the zeolite membrane revealed the different performances of the reactor using the two configurations with regard to the type of hydrocarbon. Therefore the use of the catalytic membrane combustor has demonstrated a great flexibility of use and the possibility to follow a change in the nature of the hydrocarbon pollutants only by a change of the reactor configuration.

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