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Comparing monolithic and membrane reactors in catalytic oxidation of propene and toluene in excess of oxygen

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ABSTRACT

The catalytic oxidation of propene has been studied as a model chemical reaction, in order to compare performances of a conventional monolithic reactor and a flow-through membrane reactor (contactor type [1]). These formers are different by their configurations but have the same catalytic system: Pt/Al_2O_3. The results report the catalytic performance of the two reactors in the catalytic oxidation of VOCs in excess of oxygen. In our operating conditions, the most efficient process is the flow-through catalytic membrane reactor.

1. Introduction

The destruction of VOCs is a great challenge and also of great industrial importance. Our aim is to investigate the catalytic oxidation of propene and toluene, as model chemical reactions, in order to compare performances of a conventional monolithic reactor and a flow-through membrane reactor (contactor type [1]). Both catalytic reactors are different in their configurations but have the same catalytic system: $Pt/\gamma\text{-}Al_2O_3$. Platinum supported on γ-alumina has been fully investigated in the literature and is described as the most efficient catalytic system in removal of VOCs, leading to the lowest operating temperature for the total conversion of VOCs [2,3,10,11]. Furthermore, this catalytic system can be easily implemented in both monolithic and ceramic membrane reactors. In a catalytic membrane reactor, the catalyst and the porous membrane can be combined in different ways depending on the required application [1,5] (extractor, distributor, and contactor). The catalytic membrane reactor (CMR) used in this study is in a flow-through contactor configuration (Fig. 1). In this case, the gas mixture of reactants is forced to go through the membrane, i.e. through the catalytic pores [1].

2. Experimental

2.1. Materials

Two $\gamma\text{-}Al_2O_3$ supported catalysts were used. A monolith coated with $\gamma\text{-}Al_2O_3$ precursor (Alfa Aesar) and a $\gamma\text{-}Al_2O_3$ top layered membrane (Pall-Exekia). Ceramic monoliths (Corning S.A.) made from synthetic cordierite (2 MgO, 2 Al_2O_3, 5 SiO_2) have been used to prepare a batch of monoliths (2 cm length and diameter). These ones exhibited a regular structure of small parallel square channels of 1 mm aside and a cellular density of 400 CPSI. The monolith washcoating procedure was performed as previously described by Villegas [4]. We have used a $\gamma\text{-}Al_2O_3$ powder (3 μm average particle sizes, Alfa Aesar, 99.97%) for the washcoat preparation. The procedure was performed in order to obtain 15 wt.% of $\gamma\text{-}Al_2O_3$. The ceramic membrane was a commercial, asymmetric porous, tubular support (length 15 cm, enamelled on 1 cm on both sides) provided by Pall-Exekia (Fig. 2). It is composed of three macroporous layers of $\alpha\text{-}Al_2O_3$, exhibiting an average pore diameter from 0.2 to 12 μm and thickness from 30 μm to 1.5 mm, increasing from the inside to the outside part. The mesoporous top-layer was made of $\gamma\text{-}Al_2O_3$ (3 μm thickness, 5 nm average pore diameter).

2.2. Pt impregnation

For each material (monolith or membrane), the Pt impregnation protocole was optimising in a previous work and the catalytic activity of platinum powders have been well described previously by Benard et al. [10]. Whatever the precursor salt and the condition

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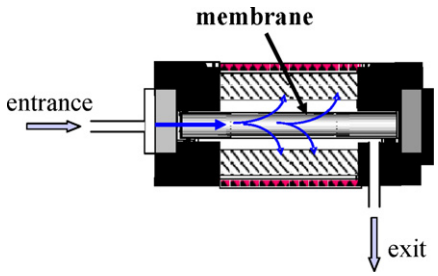

Fig. 1. Catalytic membrane reactor in the flow-through contactor configuration.

of activation treatments, the catalytic activities of the Pt/γ-Al_2O_3 are similar. Pt was introduced on γ-Al_2O_3 washcoat of monoliths by wet impregnation of $Pt(NH_3)_4(OH)_2$. After Pt impregnation, each monolith was dried at room temperature and atmospheric pressure during 24 h, followed by a drying step in a micro-wave [4] oven operating at 200 W for 1 h. The catalysts were calcined in flowing oxygen (3.6 L h^{-1}) at 773 K for 2 h, with a temperature ramp of 1 °C min^{-1}, prior to activity measurements. Pt impregnation of the γ-Al_2O_3 mesoporous top-layer of the ceramic membrane was performed by ionic exchange with a H_2PtCl_6 solution followed by a HNO_3 washing in order to remove chlorine [6,7]. Impregnated membranes were calcined at 473 K under N_2 and reduced at the same temperature under H_2.

2.3. Characterizations of catalytic systems

Chemical analysis was performed by ICP in order to determine the concentration of Pt in each catalytic system.

The Pt dispersion was determined by H_2 chemisorption in a static volumetric apparatus. Transmission electron microscopie (JEOL 2010) was performed on each sample in order to observe platinum phase dispersion and to evaluate the particle sizes. Prior to TEM observations, Pt/Al_2O_3 samples were prepared by a replica extraction of the γ-Al_2O_3 layer [8,9]. Specific surface areas were measured on complete, and crushed monoliths by N_2 adsorption–desorption at 77 K, using a TRISTAR 3000 apparatus. The samples were previously treated at 673 K under vacuum (2×10^{-3} Pa) for 2 h. Gasesous permeabilities of N_2 through the ceramic membrane were measured at room temperature (Uzio et al. [6]). The gas was introduced inside the tube and the flow permeating outside the tube was measured by a bubble flowmeter. In our conditions, the inner pressure was varied while the differential pressure across the tube was maintained at 20 mbar. The difference of pressure between the entrance and the exit of both reactors was measured under He and under reactive mixture using a Keller PD/23 (Serv'Instrumenation) pressure sensor.

2.4. Catalytic testing

The catalytic activity measurements were carried out at atmospheric pressure in a tubular fixed-bed (monolithic reactor) or in a flow-through membrane reactor. The catalytic testing apparatus has been well described previously by Benard et al. [10]. The reactive mixture was composed of 1000 ppmv of C_3H_6 or C_7H_8, 9% O_2 and balance He. The total gas flow rate was varied from 35 to 145 mL min^{-1}. Reactants and products were analysed by gas chromatography as well as using IR analyser for CO_2.

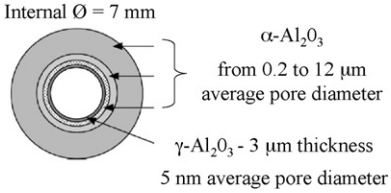

Fig. 2. Schematic cross-section of the tubular ceramic membrane structure used in this work.

Table 1
Characteristics and catalytic performances of both catalytic reactors at a total gas flow rate of 120 mL min^{-1}.

	Catalytic reactor	
	Monolithic	Membrane
Mass of γ-Al_2O_3 (g)	0.438	0.026
Pt loading (mg)	1	1
Pt dispersion (%)	5	5
T.O.F. of C_3H_6 oxidation at 115 °C (s^{-1})	43	300
T.O.F. of C_7H_8 oxidation at 150 °C (s^{-1})	41	240

3. Results

3.1. Preparation and characterization of catalytic systems

Characteristics of both catalytic systems are reported in Table 1. The washcoating procedure performed for the preparation of monolithic systems allowed us to washcoat about 400 mg of Al_2O_3 on cordierite structures with good reproducibility. Specific surface areas of γ-Al_2O_3 washcoats before and after Pt impregnation were quite similar to the value of the surface area of the alumina powder used as a precusor (80 m^2/g). Concerning the ceramic membrane, Uzio et al. [6] have reported that the value of the specific surface area of the γ-Al_2O_3 powder (Pall-Exekia) used as precursor of the mesoporous top-layer was 223 m^2/g. This value decreased by 150 m^2/g due to the sintering of γ-Al_2O_3 particles during the thermal treatment for the preparation of such ceramic membrane [11]. They also have reported that the platinum deposition does not result in further modifications of the membrane textural properties [6]. Chemical analyses of Pt have shown that the same amount (1 mg) has been introduced in both catalytic systems. N_2 permeability measurements carried out with the ceramic membrane have shown that the value remained almost unchanged before and after Pt deposition (4.9 µmol/s/Pa/m^2). Figs. 3 and 4 show TEM micrographs of the catalytic membrane and monolith, respectively. Both catalytic systems exhibit large particles as well as numerous smaller ones. This bimodal distribution of Pt particles and above all the presence of large particles (>20 nm) result in a low averaged low value of Pt dispersion (5%), confirmed by both microscopy and H_2 chemisorption. In the case of the ceramic membrane, Pt particles with an average diameter below 5 nm are mainly located in the mesoporous γ-Al_2O_3 top-layer, as reported by Uzio et al. [12], but larger ones (~100 nm) have also been formed outside of the mesoporous layer. The formation of these large particles is likely due to the high Pt loading introduced, compared to the relatively small amount of γ-Al_2O_3 (26 mg). Nevertheless, Uzio et al. [6] have reported that the slow diffusion of platinum precursors in the exchange solution within the pores of the membrane may also give rise to some large metallic particles on the surface of the membrane. The bimodal distribution of Pt particles exhibited by the monolithic system is assumed to be due to the micro-wave treatment after Pt impregnation. Indeed, Villegas et al. [4], have observed the formation of large Ni particles (from 10 to 20 nm) after impregnation on a γ-alumina support, followed by a micro-wave drying step. Fig. 5 shows the evolution of the pressure drop inside the membrane reactor under inert conditions (He flow), and in our operationg conditions for propene

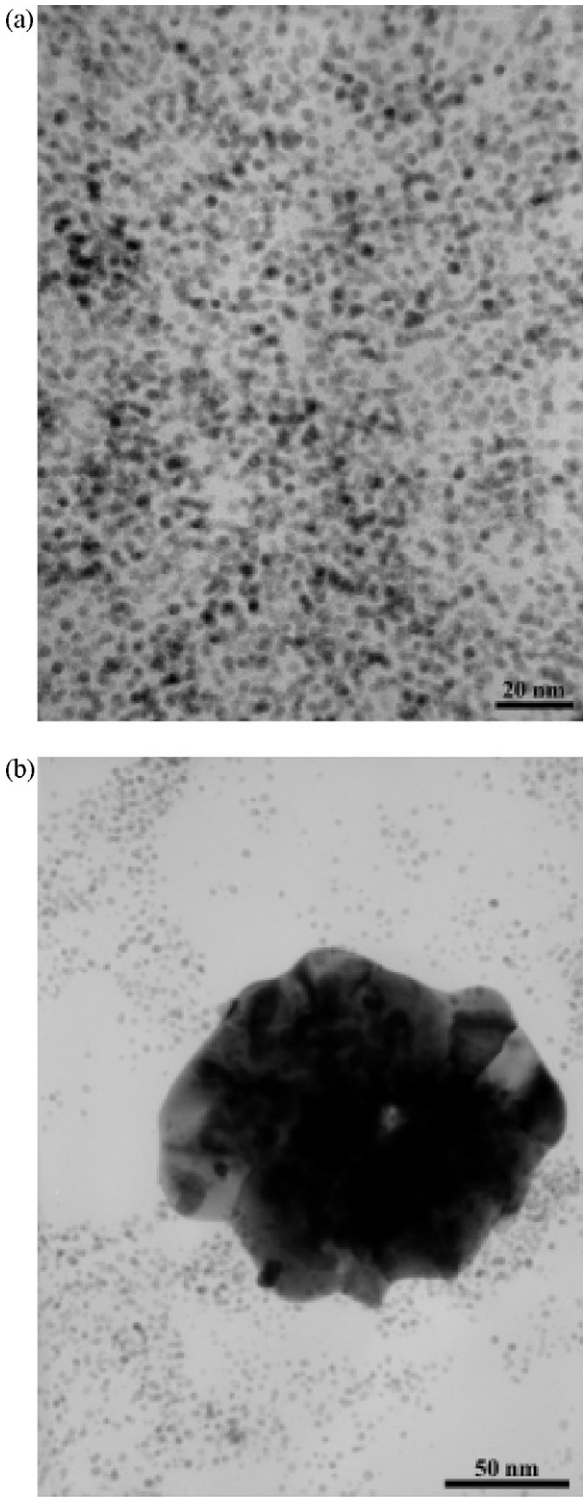

Fig. 3. (a) TEM micrograph of Pt particles inside the mesoporous γ-Al_2O_3 top-layer of the membrane and (b) TEM micrograph of Pt particles outside the mesoporous layer of the membrane.

oxidation. The relation between the difference of pressure and the total gas flow rate is linear regardless in the composition of the flow. However, the pressure difference measured under reactive mixture is slightly higher. In the overall gas flow rate range of this study, the pressure difference observed goes from 6 to 26 mbar. No pressure difference was observed in the monolithic reactor.

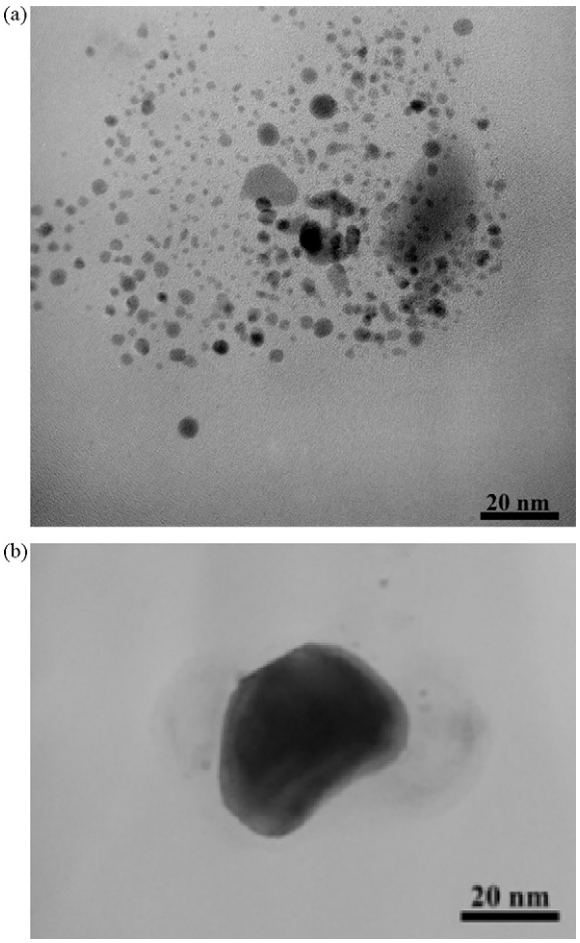

Fig. 4. TEM micrographs of Pt particles deposited on the γ-Al_2O_3 washcoat of the monolith.

3.2. Catalytic results

Preliminary studies performed on powdered catalysts for propene combustion have shown that the different characteristics of alumina support (pore size, specific surface area, etc.) have no influence on catalytic properties since the catalytic process only occurs on Pt metallic particles [10]. Therefore, kinetic studies have highlighted that during propene oxidation on Pt supported on γ-Al_2O_3, the reaction mechanism seems to be governed by a competition of adsorption between propene and O_2 at the platinum surface, according to a Langmuir–Hinshelwood mechanism

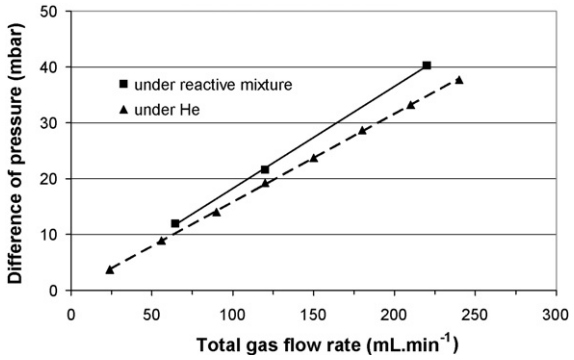

Fig. 5. Difference of pressure measured in the membrane reactor versus the total gas flow rate (■, under reactive mixture: 1000 ppm C_3H_6–9% O_2–He balance; ▲, under He).

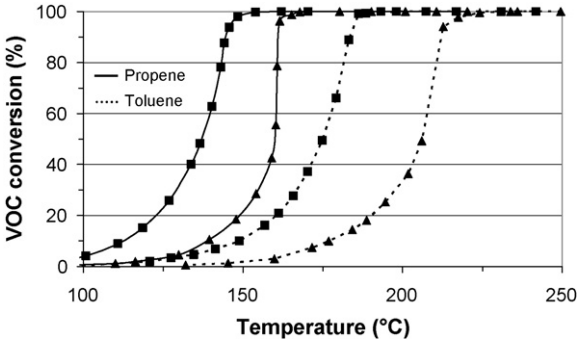

Fig. 6. VOC conversion versus temperature. Flow rate (120 mL min^{-1}) (■, membrane reactor, ▲, monolithic reactor).

[5]. Nevertheless, the alumina support provides the surface for the metallic phase dispersion, which has a great influence on VOC total oxidation. It has been largely reported in the literature that large Pt particles are more active in propene and toluene total oxidation [10,13–15]. Benard et al. [16] and Denton et al. [18] have shown that Pt supported on oxide catalysts, the Pt–O bond strength is lower for larger Pt particles, which favors adsorption of other reactants, and above all, gives rise to more reactive adsorbed oxygenated species. Thus, even though characteristics and amount of alumina support are different in both reactors, Pt dispersions are similar, and catalytic performances of those reactors can be compared according to the catalyst geometry. Fig. 6 depicts propene and toluene conversion variation versus temperature for a total gas flow rate of 120 mL min^{-1}. The general behaviour of the Pt/γ-Al_2O_3 based catalysts is in good agreement with that reported in the literature. However, temperatures of VOC complete oxidation reached with the flow-through catalytic membrane reactor (CMR) are lower (150 °C for propene and 185 °C for toluene) than those obtained with the monolithic reactor. Catalytic performances of both catalytic systems, in terms of turn over frequencies (T.O.F.), are reported in Table 1. The performance of the flow-through membrane reactor during propene and toluene oxidation, under operating conditions, was about seven times better compared to the conventional monolithic reactor. We have also studied the influence of the total gas flow rate variation on catalytic performances. Fig. 7 compares the values of T.O.F for propene oxidation calculated at 115 °C for both reactors, at different total gas flow rates. These values are also reported in Table 2. The performance of the monolithic reactor varies slightly in the overall range of total gas flow rate (from 30 to 40 × 10^4 s^{-1}), except for the highest rate (145 mL min^{-1}) where the T.O.F. value decreased significantly (12.5 × 10^4 s^{-1}).

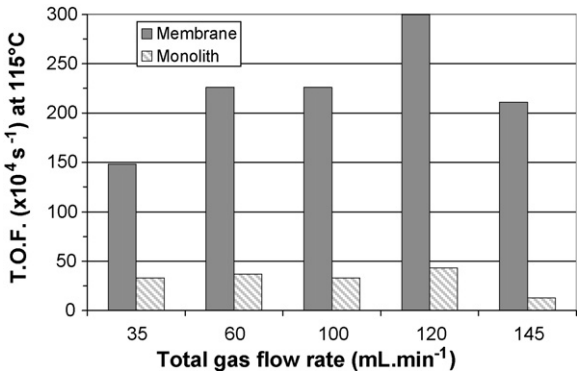

Fig. 7. T.O.F of C_3H_6 oxidation at 115 °C versus total gas flow rate for both membrane and monolithic reactor.

Table 2
T.O.F. values (10^4 s^{-1}) of propene oxidation at 115 °C for both catalytic reactors at different total gas flow rates.

Total gas flow rate (mL min^{-1})	35	60	100	120	145
Monolith reactor	33	37	33	43	12.5
Membrane reactor	148	226	226	300	211
T.O.F.$_{MEM}$/T.O.F.$_{MON}$	4.5	6	7	7	17

T.O.F. is calculated as follows:

$$\text{Turn over frequency } (s^{-1}) = r\frac{100M_{Pt}}{Pt \text{ dispersion}}$$

with

$$r \text{ (mol VOC s}^{-1}\text{ g}^{-1} \text{ of Pt)} = Q\frac{1}{V_{mol}}\frac{273}{T_{exp}}\frac{[VOC]_0}{10^6}\frac{1}{m_{cata}}\frac{X_{VOC}}{\%_{Pt}}$$

In the above equations, r is the intrinsic rate of VOC transformation, Q is the total gas flow rate (L s^{-1}), V_{mol} = 22.4 L mol^{-1}, $[VOC]_0$ initial VOC concentration (ppm), X_{VOC} is the VOC conversion (%), T_{exp} = temperature at the instant t (K), m is the catalyst mass (g), $\%_{Pt}$ is the loading of Pt in the catalyst (%) and M_{Pt} is the molecular weight of the platinum (195.08 g mol^{-1}).

We have also studied the influence of the total gas flow rate variation on catalytic performances. Fig. 7 compares the values of T.O.F for propene oxidation calculated at 115 °C for both reactors, at different total gas flow rates. These values are reported in Table 2. The performances of the monolithic reactor varied slightly in the overall range of total gas flow rate (from 30 to 40 × 10^4 s^{-1}), except for the highest rate (145 mL min^{-1}) where the T.O.F. value decreased significantly (12.5 × 10^4 s^{-1}). Concerning the membrane reactor, the variation of T.O.F. values passed through a maximum followed by a decrease at higher flow rates. Nevertheless, at a high flow rate of 145 mL min^{-1}, the membrane reactor was still much more active than the monolith reactor. As reported in Table 2, the catalytic activity of the membrane reactor is 17 times higher than the one of the monolithic reactor. At lower gas flow rate, the performance of the membrane reactor was also higher than the monolith reactor, even though the T.O.F. membrane/T.O.F. monolith ratio was lower (4.5 to 7 × 10^4 s^{-1}).

4. Discussion

The higher efficiency of the flow-through CMR configuration is likely due to the forced flow of the reactants through the catalytic pores themselves (cf. Fig. 8), where the active sites are located. Furthermore, Uzio et al. [6] have shown that due to the mean pore size of the mesoporous top-layer, and as confirmed by permeability measurements, the reactants diffusion in such membranes is controlled by a Knudsen flow process. This transport mechanism increases the average collision number between reactants and active sites [17]. In addition the influence of the differential pressure inside the membrane reactor was determined. The difference of pressure observed between the entrance and the exit of the membrane is low enough to be considered as negligible; as a con-

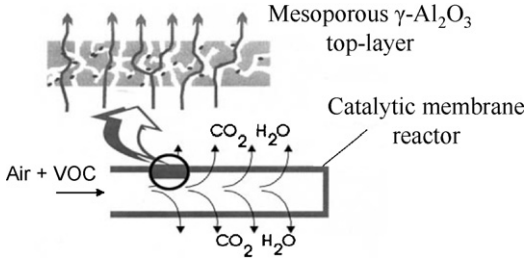

Fig. 8. Schematic transport of reactants in a flow-through membrane reactor.

Table 3
Knudsen effective diffusivity of propene and toluene.

	Propene	Toluene
D_{ke} at 50 °C (m^2/s)	4.5×10^{-9}	2.05×10^{-9}
D_{ke} at 250 °C (m^2/s)	6×10^{-9}	2.8×10^{-9}

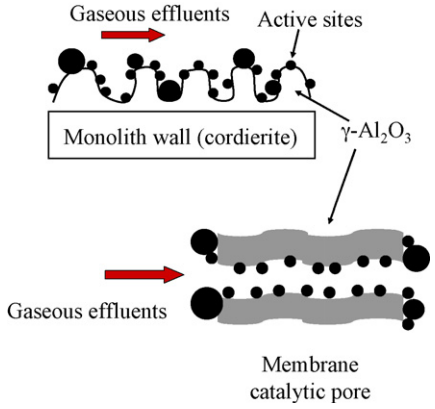

Fig. 9. Schematic comparison of the transport of reactants in both monolithic and membrane reactors.

sequence we cannot consider this parameter to explain the higher efficiency of the membrane for VOC's removal. We have evaluated the diffusivity of propene and toluene in the membrane reactor. The values of effective diffusivity of Knudsen were calculated for both molecules in the overall range of temperature of the study (from 50 to 250 °C) and are reported in Table 3.

D_{ke} is calculated as follows : $D_{ke} = \frac{2}{3}\frac{\varepsilon}{\tau}\bar{r}\bar{v}$ with $\bar{v} = \left(\frac{8RT}{\pi M}\right)^{0.5}$

In the above equations, ε is the porosity (25%), τ the tortuosity (1.2) of the γ-Al_2O_3 layer [6], $r = 3 \times 10^{-9}$ m; $M_{C3H6} = 42$ g/mol, $M_{C7H8} = 92$ g/mol, R is the ideal gas constant (8.314 J K^{-1} mol^{-1}), and T temperature in K.

The Knudsen effective diffusivity (D_{ke}) of propene is about two times higher than the D_{ke} of toluene, which means that propene diffuses better in the membrane reactor. This observation correlates the higher activity in the membrane reactor for propene oxidation compared to toluene oxidation. Thus the higher required temperature for the total oxidation of toluene in such a reactor is due to a slower diffusion rate.

The study of performances, according to the total gas flow rate, confirms the assumption that the efficiency of contact between gaseous reactants and active sites is higher in the membrane, since it exhibits a high T.O.F. value even at the highest flow rate (cf. Table 2). Fig. 9 is a schematic comparison of the transport of reactants through both membrane and monolithic reactors. This is also confirmed by considering the gas flow in both reactors. In the case of the monolith reactor, the reactants transport is also governed by Knudsen diffusion if we assume that the overall flow passes through the mesopores. However, unlike the membrane reactor Knudsen diffusion is not the only reactants transport occurring in the monolith. By the way, some active sites located in pores (cf. Fig. 9) of the alumina layer are less accessible to reactants in the monolithic reactor. Consequently, it is assumed that the reactivity of the reactants will be lower for alumina layer. Thus a flow-through configuration of a membrane reactor, operating in the Knudsen diffusion regime, will provide an intimate contact between VOC and O_2 molecules and active sites. These results are in accordance with those reported by Pina et al. [17] for toluene oxidation. In the same way, Coronas and Santamaria [5] have discussed that such membranes would be expected to give high contact efficiency in the reaction of diluted streams, such as those commonly encountered in VOC removal.

5. Conclusions

These results on propene and toluene combustion showed that the catalytic membrane reactor performed better than the conventional monolithic reactor in term of efficiency. This confirms that the membrane reactor is a promising alternative for the combustion of VOCs. The flow-through membrane reactor may lead to decreased light-off and total VOC combustion temperature in addition to a lower overall Pt loading.

Acknowledgements

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