Novel and Sustainable Catalytic Ruthenium-Doped Glass Foam for Thermocatalytic Oxidation of Volatile Organic Compounds: An Experimental and Modeling Study

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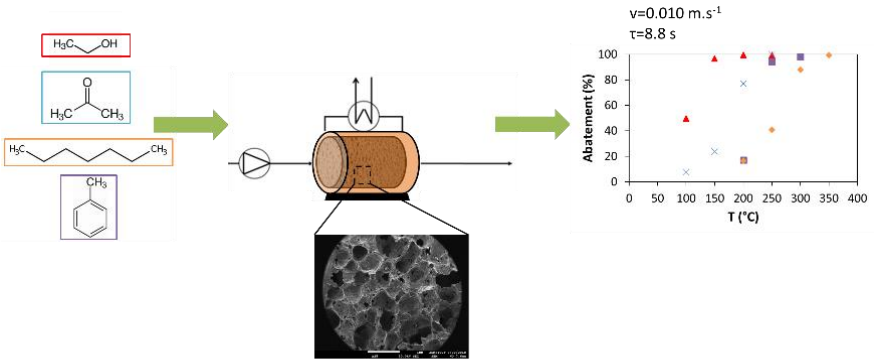

ABSTRACT

An open cell foam catalyst consisting of a glass foam support impregnated with zerovalent ruthenium nanoparticles (aiming to 0.1 wt%) without washcoating was used for the first time to remove several Volatile Organic Compounds (VOCs) by thermocatalytic oxidation. At initial concentrations between 1 $g.m^{-3}$ and 2 $g.m^{-3}$ and temperatures ranging from 100°C to 350°C, up to 100% of removal was achieved for the four VOCs tested. The ease of abatement of the VOCs with temperature had the following order: ethanol > acetone > toluene > heptane. The removal of ethanol was then modelled considering mass transfer limitation, temperature dependency and by-product formation. Full mineralization of ethanol can be achieved with a 30 cm length reactor at 150°C and 0.010 $m.s^{-1}$. While the tortuous foam achieved efficient mass transfer, the process was still limited by this phenomenon highlighting that the efficiency of the catalyst could be improved at higher gas velocities.

1. INTRODUCTION

Nowadays, air quality is a subject of major concern for human health and environment, and a special attention has to be paid towards Volatile Organic Compounds (VOCs). Many studies have highlighted their detrimental effects [1-3] and these compounds are present in many household products and are used in various industrial processes. For instance, they are responsible for eye and throat irritation, headaches and they are suspected to cause cancer in animals and humans.[4]

Various processes have already been designed and optimized to remove VOCs, based on physical, chemical or biological treatments.[5] The choice of the most efficient and less expensive process is not easy and mainly depends on the concentration, the volume and the type of VOCs. There are two main groups of treatments based on either recovery or destruction, each presenting advantages and drawbacks. The use of oxidative processes seems to be currently one of the most efficient solution with some processes already developed at the industrial scale. Actually, thermal oxidation (fume incinerators) is efficient to remove a large variety of VOCs at high concentrations and flowrates but still requires high temperatures around 1,000 °C, rendering this process energy-consuming.[5] To overcome this issue, catalysts have been developed and used to decrease the operating temperature down to 200-400 °C and reduce the energy requirement. The catalysts used are usually honeycomb structures with parallel channels coated with catalytic species (noble metals or metal oxides) [6-7-8] by different methods such as sol-gel deposition, impregnation or electrophoretic deposition.[9] Many studies focused on the influence of the catalytic species to the removal of various VOCs such as toluene,[10-11] benzene,[12-13] formaldehyde,[14] or ethanol.[15] However, these types of fixed bed catalysts suffer from several drawbacks: (i) the cost of some catalytic species and coating and (ii) the diffusional limitations. Some studies are still dedicated to overcome these issues and among the innovative solutions, the use of tortuous open-cell foams, composed of

interconnected net pores, to face with mass transfer limitations is very promising [16-17] and their structured shape can be easily integrated into already existing reactors. Ceramic and metallic foams were synthesized and characterized for some years. Even if pressure drops are higher with these catalysts compared to parallel channels, high mass transfer [18-22] and thermal [23] rates are achieved. However, there are only few applications of structure foams as support for catalytic oxidation of VOCs [24-26] and their widespread industrial use is limited by high costs of raw products and/or high operating costs for their synthesis. Nevertheless, recently, glass foams synthesized from recycled glass at milder conditions than other foams (temperature of 800-900°C against synthesis in many steps at more than 1,300°C for ceramic materials) were doped with zerovalent metal nanoparticles (aiming to 0.1 wt% metal) by a wet impregnation methodology in neat water at room temperature without washcoat layer, rendering these materials eco-friendly and cheaper than other foams.[27-28] Owing to their very small size in the range of 2-5 nm, the metal active nanospecies present high active surface area, and thus potentially affording relevant surface reactivities. These materials, well-characterized in terms of structure, pressure drops and surface charge, have proved to be relevant for the removal of ozone from air at room temperature.[28]

In this study, these glass foams impregnated with ruthenium nanoparticles were investigated for the first time for the removal of several VOCs (ethanol, acetone, toluene and heptane) from air by thermocatalytic oxidation at temperatures ranging from 100 to 350°C. The first part of the paper will show the potential of catalytic glass foams for the abatement of these VOCs. In the second part, the influence of the operating conditions will be assessed to improve the efficiency of the catalyst. Finally, modeling and predictive simulations of the process will allow to consider upscaling in order to evaluate and compare large scale process performances.

2. MATERIAL AND METHODS

2.1. Synthesis of the catalytic glass foam

The synthesis and characterization of various catalytic glass foams were already detailed.[27-28] In this study, only one catalyst was used for all the experiments. Its synthesis and characterization are explained in **Supplementary material S1**.

Only thermal characterizations were added compared to the previous paper dealing with the characterization of catalytic glass foams.[28] Differential thermal and gravimetric analyses (DTA–TGA) were carried out on TA Instruments Model SDT 2960 equipment. Measurements were done under synthetic air and a 10 $K.min^{-1}$ heating rate. The dilation of the glass foam at high temperature was evaluated with a Rheotronic parallel-plate viscometer (from Theta-US). A glass foam sample of 1.65 cm diameter was used with an applied load of 200 g. The temperature of the analysis ranged between room temperature and 700°C.

2.2. Thermocatalytic oxidation setup

The thermocatalytic oxidation setup consisted of a continuous fixed-bed reactor fed with air polluted with a VOC at the desired concentration (**Figure 1**). A 40 L Tedlar® bag was filled at steady state with oxygen and then a liquid VOC was vaporized in it to reach the desired concentration. Then, the polluted air was pumped from the Tedlar bag using a membrane pump, specifically designed by KNF (Germany) for this application, to the glass foam catalyst (reactor) inserted in an oven whose temperature was controlled between 100°C and 400°C. The accuracy of the oven temperature was 10°C. The temperature of the oven reached the desired value before starting the experiments about the removal of VOCs. The gas flow-rate (at room temperature) was controlled with a flow-meter (Brooks R-15-C) and it ranged between 6.6 $L.h^{-1}$ and 21.9 $L.h^{-1}$. According to the size of the catalyst (16 mm diameter and

94 mm length), the gas velocity varied between 0.010 $m.s^{-1}$ and 0.032 $m.s^{-1}$ and the gas hourly space velocity (GHSV) between 288 h^{-1} and 1236 h^{-1}.

Gas samples were withdrawn with a gas-tight syringe at the inlet and outlet of the reactor. All experiments were performed during at least one hour in order to ensure steady state conditions (it was checked by taking several samples during the experiments and after some minutes the outlet concentration was constant) and no catalyst deactivation was observed.

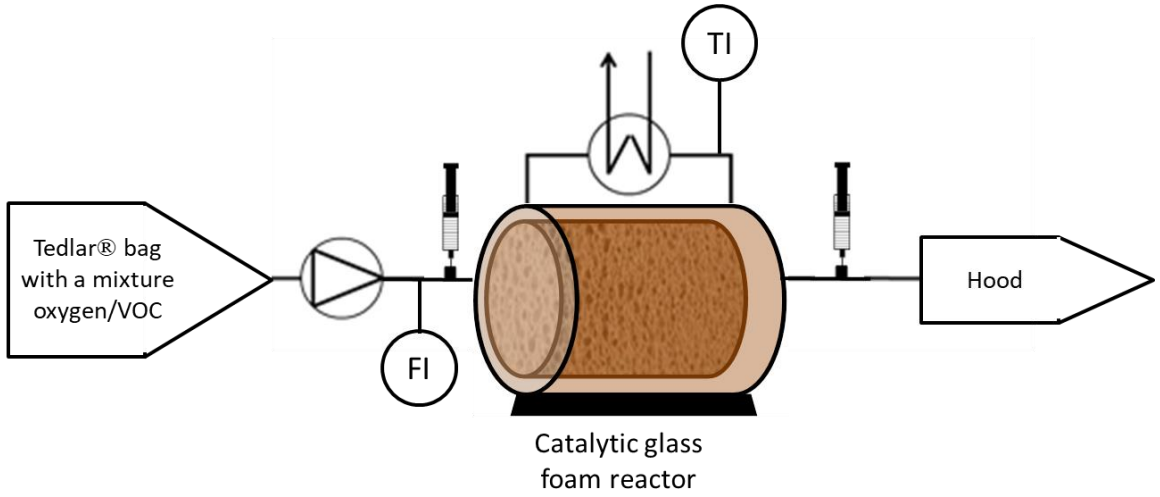

Figure 1. Layout of the setup for thermocatalytic oxidation of VOCs with a catalytic glass foam – TI: Temperature Indicator – FI: Flowrate indicator

2.3. VOCs and analyses

The removal of four VOCs (ethanol, acetone, toluene and heptane) was tested through a thermocatalytic oxidation process. These compounds were chosen since they belong to different families of chemicals and they are identified as detrimental for human health and environment.[6] **Table 1** gives the inlet concentrations implemented. Except for ethanol whose concentration was varied between 0.2 $g.m^{-3}$ and 1.0 $g.m^{-3}$, the inlet concentrations were kept constant at 1.0 gm^{-3} (toluene, heptane) or 2.0 $g.m^{-3}$ (acetone). These values were chosen in order to deal with industrial air treatment where such high concentrations can be measured.

The VOCs concentrations were quantified by Gas Chromatography (GC). The GC apparatus (Agilent 6890N) was equipped with a DB-624 column (30 m × 0.53 mm) and a Flame Ionisation Detector. The injector was heated at 150°C and the detector at 250°C. The gas vector was H_2. Depending on the VOC analyzed, the oven of the GC was heated at different temperatures. The accuracy on the concentration was ±2%. **Table 1** gives the temperature of the oven and the retention time for all the VOCs tested.

The removal efficiency (Eff, %) and rate of reaction (r, $g.m^{-3}.s^{-1}$) were calculated according to the inlet and outlet concentrations, and residence time (equation (1) and equation (2), respectively).

$$\text{Eff} = \frac{[\text{VOC}]_{\text{inlet}} - [\text{VOC}]_{\text{outlet}}}{[\text{VOC}]_{\text{inlet}}} \times 100 \quad (1)$$

$$\text{r} = \frac{[\text{VOC}]_{\text{inlet}} - [\text{VOC}]_{\text{outlet}}}{\tau} \quad (2)$$

With $[\text{VOC}]_{\text{inlet}}$ the VOC concentration at the inlet of the reactor ($g.m^{-3}$), $[\text{VOC}]_{\text{outlet}}$ the VOC concentration at the outlet of the reactor ($g.m^{-3}$) and τ the empty tube residence time (s).

The Turn-Over Frequency (TOF, h^{-1}) was determined with equation (3).

$$\text{TOF} = \frac{\dot{n}_{\text{EtOH oxidized}}}{n_{\text{Ru}}} \quad (3)$$

With $\dot{n}_{\text{EtOH oxidized}}$ the number of moles of ethanol oxidized per time unit calculated with equation (4) ($mol.h^{-1}$) and n_{Ru} the number of moles of ruthenium on the glass foam determined with equation (5) assuming that the ruthenium loading was 0.1 wt.% (mol).

$$\dot{n}_{\text{EtOH oxidized}} = Q \times \text{Eff} \times [\text{EtOH}]_{\text{inlet}} \quad (4)$$

With Q the volumetric flowrate ($m^3.h^{-1}$).

$$n_{Ru} = 0.1\text{wt.}\,\% \times \frac{m_{foam}}{MW_{Ru}} \quad (5)$$

With MW_{Ru} the molecular weight of Ru (g.mol^{-1}) and m_{foam} the mass of the glass foam (g).

Table 1. Inlet concentration of the VOCs and programming of the GC for analysis

VOC	Molecular weight (g.mol^{-1})	Inlet concentration (g.m^{-3} / ppmv)	GC analysis	
			Oven temperature (°C)	Retention time (min)
Ethanol	46	0.2 – 1.0 g.m^{-3} / 106 – 532 ppmv	28	3.6
Acetone	58	2.0 g.m^{-3} / 843 ppmv	28	4.2
Toluene	92	1.0 g/m^{-3} / 266 ppmv	80	6.3
Heptane	100	1.0 g.m^{-3} / 245 ppmv	80	4.1

3. RESULTS AND DISCUSSION

3.1. Characterization the catalytic glass foam

The catalytic glass foam has a porous structure (**Figure 2**) and possesses an open porosity of 92%, with a mean pore diameter of 0.59 mm. These values of open porosity and mean pore diameter are in the upper range for glass foams.[28] According to BET analysis, the surface area is 0.4±0.1 m^2.g^{-1}. Compared with ceramic and metallic foams, the open porosity, mean pore size diameter and surface area of the glass foam are in the same range of values [17-22] but the synthesis of glass foam remains less expensive with cheaper raw materials (recycling of glass cullet), and milder synthesis conditions (around 800°C against 1,300°C for ceramic ones).

Figure 2 shows a real photo, SEM picture and TEM picture of the glass foam. The SEM picture confirms the mean pore diameter obtained with image treatment with ImageJ 1.52

software. On the TEM pictures, the ruthenium nanoparticles are clearly visible (black dots) and well dispersed on the support. Spherical nanoparticles were observed with a diameter ranging from 2 to 5 nm and it was estimated through treatment of the image (with ImageJ 1.52 software) that around 23% of the glass foam surface was covered with nanoparticles.

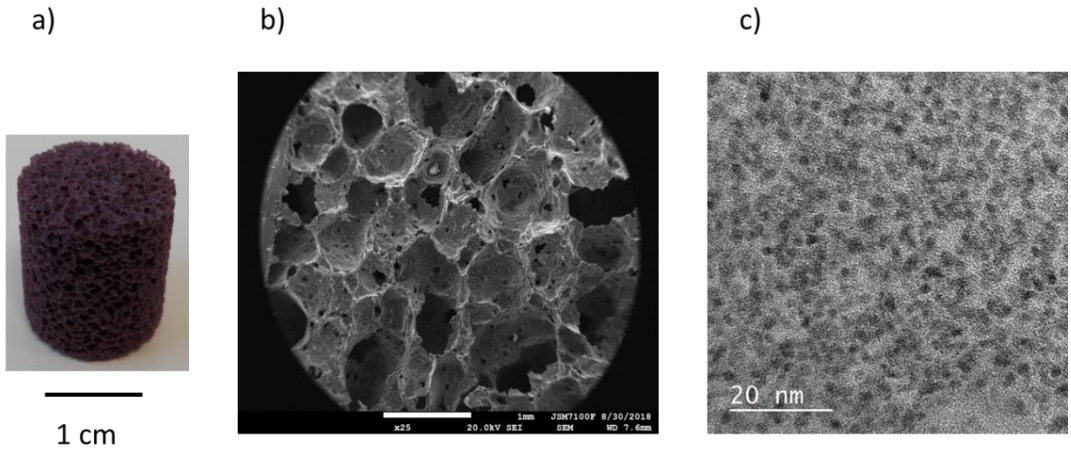

Figure 2. Real photo (a), SEM picture (b) and TEM picture (c) of the catalytic glass foam impregnated with ruthenium nanoparticles

The extremely low release of ruthenium nanoparticles under air flow at room temperature (0.4 $m.s^{-1}$ during 72h, representing 21 m^3 of air that passed through the catalyst) was already demonstrated and confirmed the quite strong interaction between the nanoparticles and the glass foam support.[28]

The thermal stability of the catalytic glass foam at high temperature was also validated before using it for thermocatalytic oxidation. **Figure 3** shows the curves obtained for the DTA-TGA measurement performed under air on the catalytic glass foam. The glass transition is observed at around 550°C (endothermic step). At lower temperatures (up to 400°C which is the maximal temperature tested for the removal of VOC in air), no significant change of the catalyst mass was observed highlighting the thermal resistance of both the glass foam support and the impregnated ruthenium nanoparticles. This result was strengthened by a measure of

the dilation of the glass foam at high temperatures with a parallel-plate viscometer. It showed that the glass foam does not sinter until 545°C.

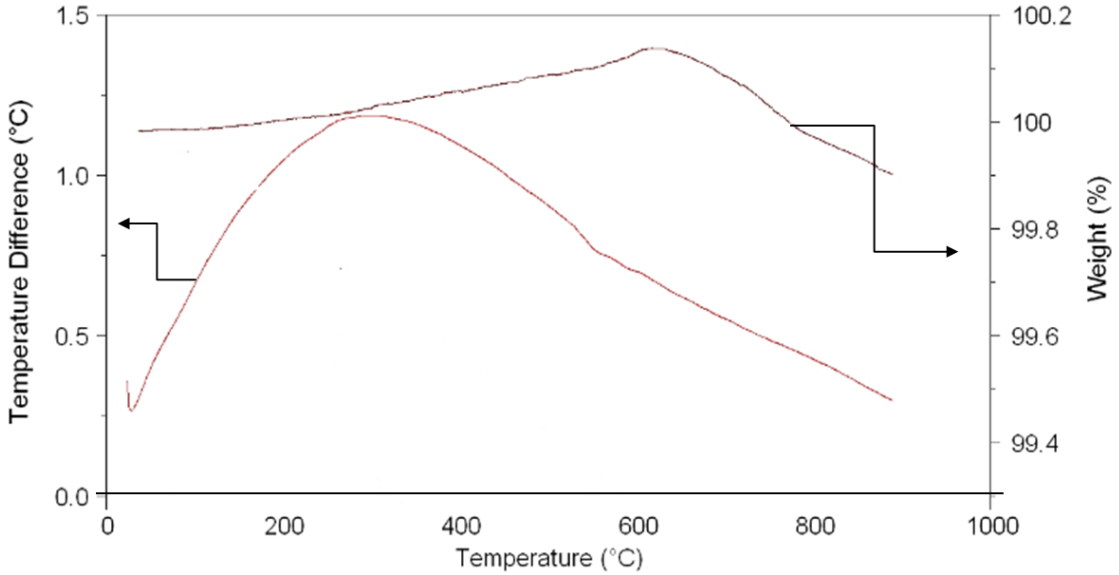

Figure 3. DTA-TGA curves obtained for the catalytic glass foam under air

3.2. Performances of the catalytic glass foam for the removal of various VOCs

The catalytic glass foam was evaluated for the removal of four VOCs presenting different functional groups (alcohol, ketone, aromatic and aliphatic), at a superficial gas velocity of 0.010 $m.s^{-1}$ and inlet concentration of 1.0 $g.m^{-3}$ or 2.0 $g.m^{-3}$ depending on the VOC (**Figure ~~2~~4**).

Abatements ranging from 8% to 100%, depending on the VOC and the temperature, were achieved, thus proving the potential of glass foams impregnated with ruthenium nanoparticles for thermocatalytic oxidation. From a general point of view, the higher the temperature is, the more efficient the removal is. This result is in agreement with literature data [6] and can be explained by the fact that the energy required to initiate the oxidation is easier to overpass at high temperatures.

Ethanol is the easiest VOC to be removed and almost 100% of abatement was reached from 200°C. The removal of acetone was also very efficient with a sharp increase after 100°C and reaching a complete abatement at 250°C. Toluene and even more heptane required higher temperatures of 300-350°C to be fully eliminated. Nevertheless, high abatements were already achieved at 250°C for toluene (94%) and 300°C for heptane (88%), highlighting that full removal can be achieved with a longer reactor (namely a longer residence time) with these milder operating conditions. When 100% of abatement is achieved, no by-product is observed by GC analysis, thus confirming the complete mineralization of the VOCs.

Anyway, these results clearly highlight the efficiency of the catalytic glass foams as new catalyst for VOC treatment and illustrate the high oxidative power of ruthenium species even at a low load of only 0.1 wt.%. In addition with their moderate pressure drops,[28] these catalysts can be efficient alternative to conventional industrial materials.

Table 2 compares the results for the removal of VOCs by thermocatalytic oxidation obtained with the catalytic glass foam and with other heterogeneous catalysts. The results are compared in terms of TOF (equation (3)) rather than abatements to consider the amount of catalytic active species involved in the process. The TOF were calculated at low conversion (around 20%) to ensure reliable values. Obviously, the TOF also depends on other parameters that may significantly change its value such as the gas velocity and inlet concentration, but the goal here is to draw an initial assessment of the performances of catalytic glass foams. Moreover, the comparison is not exhaustive at all and other already existing catalysts may have better performances.

The TOF developed with the glass foam impregnated with ruthenium nanoparticles ranged between ~~2.3~~0.4 h^{-1} (heptane and toluene) and ~~6.9~~2.3 h^{-1} (acetone). The differences could be attributed to the various inlet VOC concentrations (in $mol.m^{-3}$) and intrinsic VOC reactivity.

These TOF values remain significantly lower than orders of magnitude encountered for other catalytic applications, mainly because VOC treatment involved low VOC loading and competition with O_2 for the active sites. In comparison with other applications for oxidation of VOCs, these values are close to the study of Sanz *et al.*[24] with aluminium foam impregnated with Pt and Gallegos *et al.*[29] with manganese oxide active species. Zhao *et al.*[30] and Delimaris and Ioannides[31] found lower TOF (10 times lower) because the amount of active species was high (around 10 wt%). On the other hand, higher TOFs were also found with other catalysts (around 10 times higher than the ones found in this study),[26, 32] this result could be explained by a high feed flowrate and also to expensive Pt and gold particles involved in the process that achieved efficient catalytic oxidation (but they could be found in relatively high amount such as 1.0 wt% for the gold particles). Anyway, these results highlight that the ruthenium-doped catalytic glass foams are competitive with other catalysts recently developed. This good efficiency mainly comes from the high active surface area even at the low loading of metal active species (0.1 wt%). Associated to the previously explained eco-friendly synthesis and characteristics (recycling of glass waste, synthesis and impregnation under mild conditions and without washcoating, high porosity), the catalytic glass foams are competitive catalysts whose use could be considered in the chemical and environmental industries.

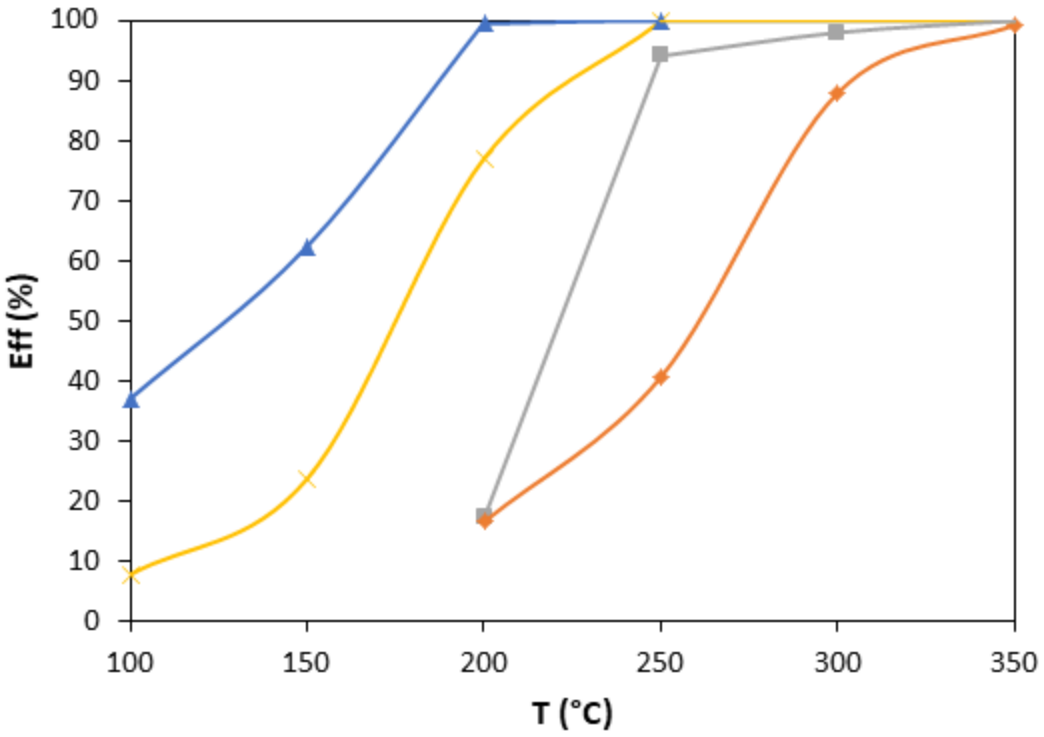

Figure 24. Removal efficiency of VOCs versus temperature (v = 10 mm.s^{-1} – residence time = 8.8 s) - ▲: ethanol (inlet concentration: 1.0 g.m^{-3}) - ×: acetone (inlet concentration: 2.0 g.m^{-3}) - ■: toluene (inlet concentration: 1.0 g.m^{-3}) - ◆: heptane (inlet concentration: 1.0 g.m^{-3})

Table 2. TOF values for oxidation of VOCs and comparison with literature data

VOC	Type of catalyst	Temperature (°C)	TOF (h^{-1})	Reference
Ethanol	Glass foam impregnated with	200	4.9	This study
Acetone	0.1 wt% Ru(0) NPs	250	6.9	
Toluene		300	3.6	
Heptane		350	2.3	
Toluene	Pt impregnated on aluminium foam	210	6.4	[24]
Toluene	Pt zeolite coated cordierite foam	230	53.4	[26]
Ethanol	Manganese oxide	200	4.3	[29]
Heptane		450	4.3	
Acetone	Cobalt oxide	190	0.2	[30]
Toluene		230	0.2	
Ethanol	CuO-CeO_2	220	0.2	[31]
Toluene		260	0.1	
Toluene	Au impregnated on different supports	264 - >400	56.1	[32]

VOC	Type of catalyst	Temperature (°C)	Eff (%)	TOF (h^{-1})	Reference
Ethanol	Glass foam	100	22	0.9	This study
Acetone	impregnated with 0.1	150	24	2.3	
Toluene	wt% Ru(0) NPs	200	17	0.4	
Heptane		200	17	0.4	
Toluene	Pt impregnated on aluminium foam	170	≈20	1.3	[24]
Toluene	Pt zeolite coated cordierite foam	200	≈20	10.7	[26]
Ethanol	Manganese oxide	150	≈30	1.3	[29]
Heptane		210	≈40	1.7	
Acetone	Cobalt oxide	150	≈20	0.03	[30]
Toluene		190	≈20	0.04	
Ethanol	$CuO\text{-}CeO_2$	200	≈20	0.05	[31]
Toluene		220	≈20	0.02	
Toluene	Au impregnated on different supports	247	20	22.4	[32]

3.3. Influence of other operating conditions on ethanol removal

In addition to the temperature, the influence of two other operating conditions on the abatement was investigated: (i) the inlet concentration and (ii) the superficial gas velocity. This evaluation was performed only with ethanol and similar behaviors are expected for the other VOCs. The effect of these two parameters was assessed at low temperatures (100°C, 125°C and 150°C) since the abatement can reach 100% at higher temperatures (**Figure ~~24~~**).

The results are summarized in **Table 3** in terms of abatement, TOF and rate of reaction. Acetaldehyde was the only by-product detected and quantified by GC during the experiment and so its outlet concentration was also recorded. Other researchers highlighted that acetaldehyde was the only by-product observed during the oxidation of ethanol.[33-35] It seemed that the other steps of the oxidation were very fast once acetaldehyde has been oxidized. Therefore, a two-step mechanism was assumed (equation (6) and equation (7)). Equation (7) obviously means that for each mole of acetaldehyde oxidized, two moles of CO_2 are produced.

Step 1, oxidation of ethanol: $C_2H_5OH + 1/2\ O_2 \rightarrow C_2H_4O + H_2O$ (6)

Step 2, oxidation of acetaldehyde: $C_2H_4O + 5/2\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O$ (7)

According to mass balance, the mineralization (quantity of ethanol oxidized into CO_2) is calculated with equation (8):

$$\text{Mineralization} = \frac{n_{\text{EtOH mineralized}}}{n_{\text{EtOH inlet}}} = \frac{[\text{EtOH}]_{\text{inlet}} - [\text{EtOH}]_{\text{outlet}} - [\text{Acetaldehyde}]_{\text{outlet}}}{[\text{EtOH}]_{\text{inlet}}} \quad (8)$$

With $n_{\text{EtOH mineralized}}$ the number of moles of ethanol mineralized into CO_2 (mol), $n_{\text{EtOH inlet}}$ the number of moles of ethanol which entered in the process (mol), $[\text{EtOH}]_{\text{inlet}}$ the ethanol inlet concentration ($mol.m^{-3}$), $[\text{EtOH}]_{\text{outlet}}$ the outlet ethanol concentration ($mol.m^{-3}$) and $[\text{Acetaldehyde}]_{\text{outlet}}$ the outlet acetaldehyde concentration ($mol.m^{-3}$) at the temperature and pressure of the process.

Whatever the temperature, the rate of ethanol removal increased with an increase in the superficial gas velocity (**Table 3**). It shows that the process is still limited by mass transfer in the range of gas velocities tested and it is in agreement with the previous results about ozone

removal in air at room temperature with similar catalytic glass foams.[28] At the same time, the ethanol abatement decreased (or remained almost constant) with an increase in the superficial gas velocity. Actually, two opposite effects are involved: on the one hand, the rate of reaction increases when the gas velocity rises (less mass transfer limitation) and on the other hand, the residence time decreases (from 8.8 s at 0.010 $m.s^{-1}$ to 2.7 s at 0.032 $m.s^{-1}$). Thus, for the same residence time, higher abatements would be expected at higher superficial gas velocity. Another way to decrease the mass transfer limitations would be to play on the structure of the glass foam support (smaller pores and lower open porosities). However, Incera-Garrido et *al.*[20] have already showed for ceramic foams that the effect of these parameters is small. In addition, the suggested modifications of the structure of the support significantly increases the pressure drops [28] and so the operating cost of the process.

The effect of the inlet concentration was also the same whatsoever the temperature and superficial gas velocity. The higher the inlet concentration is, the higher the reaction rate is. The removal efficiency of ethanol decreased with higher inlet concentrations due to a non-compensation of the increase of the VOC molar flow rate by a better oxidation kinetics. It declined to 22% only at 100°C and 1.0 $g.m^{-3}$ inlet concentration. However, these experiments were performed with high inlet concentrations and low catalyst load (0.1 wt.% of ruthenium). The TOF values (at 1.0 $g.m^{-3}$ inlet concentration and 0.010 $m.s^{-1}$) increase according to the temperature in the following order: 1.1 h^{-1} at 100°C, 1.8 h^{-1} at 125°C and 3.3 h^{-1} at 150°C.

We could presume that at lower inlet ethanol concentration, very high removal efficiency would be achieved. Actually, the removal efficiency of ethanol reached 93% at 150°C, 0.2 $g.m^{-3}$ inlet concentration and 0.010 $m.s^{-1}$ superficial gas velocity.

Concerning the outlet acetaldehyde concentration, we observed that the higher the ethanol abatement is, the greater the acetaldehyde concentration is. In fact, the outlet acetaldehyde

concentration increased with a raise in temperature and also in ethanol inlet concentration while it decreased when elevating the superficial gas velocity. Quite high values are achieved depending on the operating conditions, reaching 0.50 $g.m^{-3}$ at 150°C, 0.010 $m.s^{-1}$ and 1.0 $g.m^{-3}$ ethanol inlet concentration, which is half of the ethanol inlet concentration. It implied that the mineralization was quite low whatsoever the experiments (between 6% and 17%) because most of the oxidized ethanol remained acetaldehyde until the outlet of the process. A higher temperature or a higher residence time would be necessary to remove effectively acetaldehyde.

Finally, the experiment at 100°C, 0.010 $m.s^{-1}$ and 1.0 $g.m^{-3}$ inlet concentration was duplicated after around 40 hours of use of the catalyst. The same rate of reaction was found in both experiments highlighting that the catalyst was not deactivated after some tens of hours of use. Moreover, this promising result also showed the good thermal resistance of the overall structured catalyst.

Table 3. Performances of the glass foam impregnated with ruthenium nanoparticles for the removal of ethanol - influence of the temperature, inlet concentration and superficial gas velocity

T (°C)	$[EtOH]_{inlet}$ ($g.m^{-3}$)	v ($m.s^{-1}$)	τ (s)	Eff (%)	r ($g.m^{-3}.s^{-1}$)	TOF (h^{-1})	$[Acetaldehyde]_{outlet}$ ($g.m^{-3}$)	Mineralization (%)
100	1.0	0.010	8.8	22	0.026	1.1	0.11	7
100	1.0	0.016	5.5	19	0.037	1.6	0.04	15
100	1.0	0.023	3.7	17	0.049	2.1	0.03	15
100	1.0	0.032	2.7	18	0.070	3.0	0.02	16
100	0.2	0.010	8.8	38	0.009	0.4	0.06	8
100	0.5	0.010	8.8	29	0.015	0.7	0.09	10
100	0.8	0.010	8.8	22	0.020	0.9	0.09	11
100	0.2	0.032	2.7	27	0.018	0.9	0.02	15
125	1.0	0.010	8.8	39	0.042	1.8	0.30	10
125	1.0	0.016	5.5	26	0.046	2.0	0.17	8
125	1.0	0.023	3.7	24	0.061	2.6	0.08	16
125	1.0	0.032	2.7	24	0.083	3.6	0.07	17
125	0.2	0.010	8.8	74	0.017	0.7	0.12	10
125	0.5	0.010	8.8	57	0.031	1.3	0.21	11
125	0.8	0.010	8.8	42	0.034	1.5	0.24	8
150	1.0	0.010	8.8	62	0.077	3.3	0.50	14
150	1.0	0.016	5.5	45	0.083	3.5	0.38	6
150	1.0	0.023	3.7	45	0.134	5.7	0.37	10
150	1.0	0.032	2.7	38	0.157	6.7	0.29	11
150	0.2	0.010	8.8	93	0.023	1.0	0.17	12
150	0.5	0.010	8.8	85	0.052	2.2	0.37	14
150	0.8	0.010	8.8	74	0.072	3.1	0.47	17
150	0.2	0.032	2.7	73	0.051	2.2	0.10	16

3.4. Modeling and simulations of ethanol abatement

3.4.1. Equations and assumptions of the model

In order to get more insights into the removal of ethanol by thermocatalytic oxidation with the catalytic glass foam, and to start thinking about upscaling, modeling and predictive simulations were performed. Several assumptions were done for the modeling: (i) temperature

and pressure are constant, (ii) oxygen is in large excess for the oxidation reaction and so its concentration is assumed to be constant, (iii) only acetaldehyde is taken into account as by-product, (iv) the glass foam catalyst is assumed to be a plug-flow reactor, (v) a steady-state flow is assumed and (vi) CO_2 and H_2O produced do not influence the kinetic of reaction. The same assumptions were already done by Rodríguez and Cadús[36] who modelled the oxidation of ethanol in a monolithic reactor.

A power law kinetic was chosen to deal with the influence of the ethanol concentration, as already used to try to model the removal of toluene by catalytic ozonation [37] or for the removal of ethanol by thermocatalytic oxidation.[38] The Arrhenius law considered the influence of the temperature.[36] Finally, the mass transfer resistance was taken into account.[36] Owing to similar diffusion coefficients in air, the mass-transfer coefficients k_m for ethanol and acetaldehyde were considered identical.

On the basis of these assumptions and remarks, ethanol and acetaldehyde concentrations along the reactor in the gas phase and at the surface of the catalyst were modelled with equations (9) to (12). The ethanol reaction rate (equation (9) and equation (10)) is independent of the acetaldehyde behavior while the acetaldehyde concentration depends on the removal of ethanol (equation (11)).

$$v \times \frac{d[EtOH]}{dx} + k_m \times a_v \times ([EtOH] - [EtOH]_{surface}) = 0 \quad (9)$$

$$k_m \times a_v \times ([EtOH] - [EtOH]_{surface}) = A_{EtOH} \times \exp\left(\frac{-E_{a,EtOH}}{R \times T}\right) \times [EtOH]_{surface}{}^{n} \quad (10)$$

$$v \times \frac{d[Acetaldehyde]}{dx} + k_m \times a_v \times ([Acetaldehyde] - [Acetaldehyde]_{surface}) = v \times \frac{d[EtOH]}{dx} + k_m \times a_v \times ([EtOH] - [EtOH]_{surface}) \quad (11)$$

$$k_m \times a_v \times ([Acetaldehyde] - [Acetaldehyde]_{surface}) = A_{Acetaldehyde} \times \exp\left(\frac{-E_{a,Acetaldehyde}}{R \times T}\right) \times [Acetaldehyde]_{surface}{}^{m} \quad (12)$$

With v the empty tube superficial gas velocity ($m.s^{-1}$), [EtOH] the ethanol concentration in the gas phase ($mol.m^{-3}$), k_m the mass transfer coefficient ($m.s^{-1}$), a_v the superficial area (m^{-1}), $[EtOH]_{surface}$ the ethanol concentration at the surface of the catalyst ($mol.m^{-3}$), A_{EtOH} the pre-exponential factor for ethanol removal, $E_{a,EtOH}$ the activation energy for ethanol removal ($kJ.mol^{-1}$), R the ideal gas constant ($J.mol^{-1}.K^{-1}$), T the temperature (K), n the order of reaction for ethanol (-),[Acetaldehyde] the acetaldehyde concentration in the gas phase ($mol.m^{-3}$), $[Acetaldehyde]_{surface}$ the acetaldehyde concentration at the surface of the catalyst ($mol.m^{-3}$), $A_{Acetaldehyde}$ the pre-exponential factor for acetaldehyde removal, $E_{a,Acetaldehyde}$ the activation energy for acetaldehyde removal ($kJ.mol^{-1}$) and m the order of reaction for acetaldehyde (-).

In equations (9) to (12), the mass transfer was described with the term $k_m \times a_v$. There are several correlations in the literature to calculate the mass transfer coefficient k_m in ceramic and metallic foams.[18, 20, 39] They depend on Reynolds and Schmidt numbers, and on the geometric properties of the foam such as the open porosity, mean pore diameter or shape of the struts. However, these equations are accurate for gas velocities higher than 0.5 $m.s^{-1}$, which is clearly higher than the values in this study (between 0.010 and 0.032 $m.s^{-1}$). On this basis, a general power law correlation depending on the gas velocity v and 2 constants A and B, was used to deal with the mass transfer (equation (13)). It was also assumed that, in the range of temperatures tested (100-150°C), the mass transfer coefficient did not depend on the temperature. This assumption was strengthened by Richardson et *al.*[39] who demonstrated that the mass transfer coefficient had a small dependence with the temperature for ceramic foams.

$$k_m \times a_v = A \times v^B \quad (13)$$

It makes a total of 8 unknown parameters (two for the mass transfer, three for the kinetics of ethanol abatement and three for the kinetics of acetaldehyde abatement) to fit with 23 experiments (46 data according to ethanol and acetaldehyde outlet concentrations). The differential equations system was solved with Scilab 6.1 with a space interval of 0.05 mm. The inlet concentration was specified to carry out the calculation. Fitting of the parameters was performed with a Levenberg-Marquardt algorithm.

3.4.2. Preliminary analysis of the experimental data

In order to ease the fitting of the model parameters, a preliminary analysis was performed to roughly estimate some parameters before adjusting the whole model.

The energy of activation of ethanol oxidation was first evaluated. For a given gas velocity and inlet concentration, it was assumed that the order of the kinetic power law was 1 and so the apparent kinetic constant of ethanol abatement (k_{EtOH} in s^{-1}) can be calculated with the inlet and outlet concentrations. The slope of the plot of the logarithm of the apparent kinetic constant in function of the inverse of the temperature give the energy of activation according to the law of Arrhenius (equation (14)).

$$\ln(k_{EtOH}) = \ln(A_{EtOH}) - \frac{E_{a,EtOH}}{R \times T} \quad (14)$$

The calculation was performed for each set of experimental superficial gas velocity and inlet concentration (**Supplementary material S2**). The values ranged between 24 $kJ.mol^{-1}$ and 46 $kJ.mol^{-1}$ that are in the range of experimental data found with other catalysts.[6] The average value is of 37 $kJ.mol^{-1}$ and was used as initial energy of activation for model fitting.

The order of the power law cannot be *a priori* determined. The regression of the ethanol and acetaldehyde outlet concentration versus the ethanol inlet concentration was nevertheless

performed with a power law to estimate the values of n and m in equations (10) and (12), respectively. The average value of the order of the power law is 0.6 (for both ethanol and acetaldehyde) and was considered as initial model parameter.

Finally, the influence of superficial gas velocity on the rate of ethanol abatement was performed using a power law to estimate the value of B in Eq. (13). The value is 0.6 and was also used as initial model parameter.

3.4.3. Determination of the parameters of the model

According to the previously estimated initial model parameters, the model was adjusted to the experimental data. There is a good agreement between the experimental values of the outlet ethanol concentrations and those deduced from the model (12% of average relative error, **Supplementary Material S3**). The fitted parameters for ethanol were: $A_{EtOH} = 800$ $m^{1.5}.mol^{-0.5}.s^{-1}$; $E_{a,EtOH} = 38\,kJ.mol^{-1}$; n=0.5 ; A=15 $s^{0.7}.m^{-0.7}$ and B=0.7. The fitted activation energy, order of kinetic reaction and order of power law mass transfer limitations were close to the estimated values, highlighting that the proposed methodology of estimation (see above part 3.4.2) can be accurately used. The dependence of the gas velocity to the mass transfer (B=0.7) is slightly higher than the literature data. Richardson et *al.*[39] found an exponent of 0.565 to describe the dependence of the external mass transfer with the superficial velocity and Incera-Garrido et *al.*[20] an average value of 0.47 for ceramic foams with porosities ranging from 75% to 85%. Nevertheless the comparison of the data has to be considered carefully because the gas velocities are very different between this study (around 0.01 $m.s^{-1}$) and the literature cited (around 1 $m.s^{-1}$).

There was also a quite good agreement between the model and the experiments for acetaldehyde, especially at temperatures of 125°C and 150°C (less than 15% of average error for most of the experiments, **Supplementary Material S3**). The fitted parameters for

acetaldehyde were: $A_{Acetaldehyde} = 15\ m^{1.2}.mol^{-0.4}.s^{-1}$; $E_{a,Acetaldehyde} = 25\ kJ.mol^{-1}$ and m=0.6, and the mass transfer parameters A and B were the same as for ethanol.

In order to improve the accuracy of the model, other types of equations based on a Langmuir-Hinshelwood mechanisms and taking into account the adsorption of the VOCs on the catalyst surface could be used.[6, 36-37, 40-41] In any case, the model developed here can be used to predict the abatement of ethanol (into acetaldehyde and CO_2) with this catalytic glass foam in the range of operating conditions tested.

3.4.4. Predictive simulations

The model presented above was finally used to size an efficient catalytic reactor to get complete abatement of ethanol and full mineralization (no more acetaldehyde by-product) with an inlet concentration of 140 ppmv (0.23 $g.m^{-3}$).

A temperature of 150°C was first used and the superficial gas velocity was 0.010 $m.s^{-1}$. In these conditions, a reactor of 30 cm length allowed to completely remove ethanol until full mineralization (**Figure ~~3~~5-a**). The ethanol concentration decreased fast and was null near the middle of the reactor. At the same time, acetaldehyde concentration increased up to 0.11 $g.m^{-3}$ and slowly decreased until the outlet of the process where it was fully oxidized into CO_2. At 100°C (**Figure ~~3~~5-b**), a similar behavior was simulated but it needed a reactor of 75 cm length to get the same results as at 150°C. These results highlight that a compromise needs to be found between performances, energy consumption and compactness of the reactor.

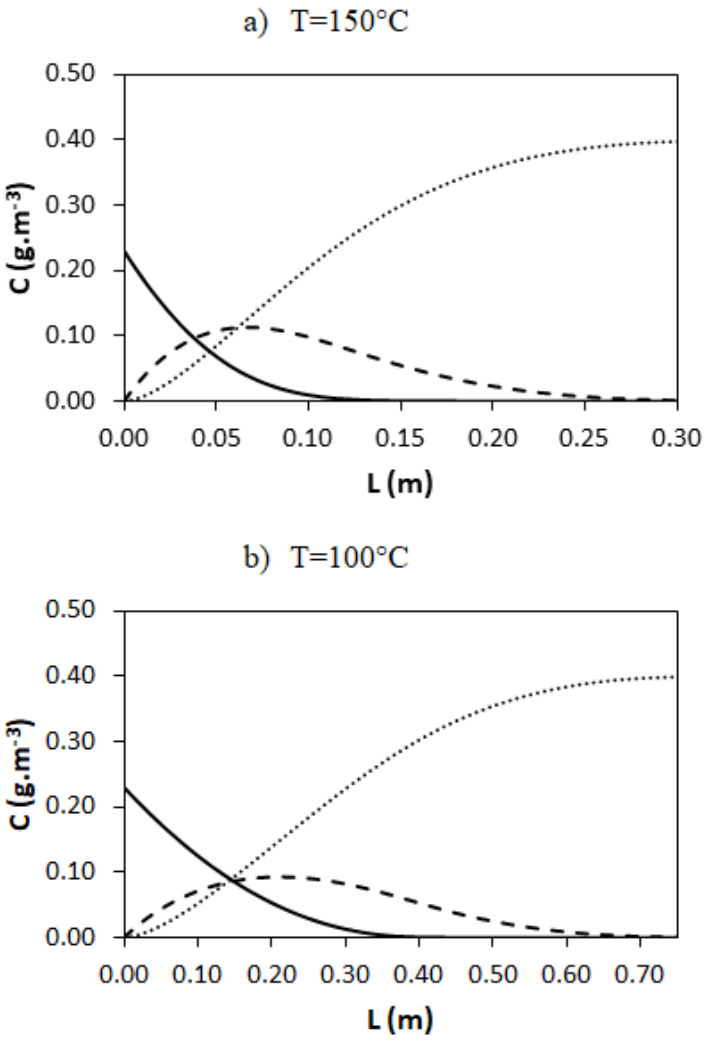

Figure 35. Concentrations of ethanol (full line), acetaldehyde (dashed line) and CO_2 (pointed line) along the reactor simulated for v=0.010 $m.s^{-1}$ and ethanol inlet concentration of 140 ppmv (0.23 $g.m^{-3}$) – a) T=150°C – b) T=100°C

Finally, the rates of ethanol and acetaldehyde oxidation ($A \times \exp\left(\frac{-E_a}{R \times T}\right) \times C^{n \text{ or } m}$) were calculated and compared at each temperature simulated for half the inlet simulated ethanol concentration which is about the maximum acetaldehyde concentration. The goal of this calculation was to determine the limiting oxidation step.

The rates of oxidation obviously increase with the temperature and are more than 10 times higher at 150°C than at 100°C (for ethanol: 1.9×10^{-4} $mol.m^{-3}.s^{-1}$ at 100°C and 6.4×10^{-3}

$mol.m^{-3}.s^{-1}$ at 150°C ; for acetaldehyde: 1.3×10^{-4} $mol.m^{-3}.s^{-1}$ at 100°C and 1.4×10^{-3} $mol.m^{-3}.s^{-1}$ at 150°C). Whatsoever the temperature, the rate of acetaldehyde oxidation was lower than the one for ethanol meaning that acetaldehyde removal was the limiting step, highlighting the difficulty to fully remove acetaldehyde. To improve its removal, higher temperature (200°C for instance) could be applied in the second half of the reactor.

4. CONCLUSION

A heterogeneous catalyst composed of a glass foam support doped with ruthenium nanoparticles was synthesized, characterized (porosity, mean pore diameter and pressure drops) and applied for the first time to remove VOCs from air through a thermocatalytic oxidation process. This nanocomposite material presents many advantages: (i) it offers a reduced environmental footprint, being synthesized from recycled glass and easily doped with catalytic species by a mild wet impregnation method in neat water, without washcoating, (ii) relevant process performances are reached, whatsoever in terms of pressure drops, mass transfer efficiency due to its high tortuosity, and for the removal of various VOCs that could be obtained even at very low ruthenium loading of 0.1 wt.%. Actually, abatements up to 100% were achieved for ethanol, acetone, toluene and heptane at 350°C in a residence time of 8.8 seconds. Even lower temperatures (around 250°C) can be used to fully eliminate ethanol and acetone, making this catalyst competitive compared to the available technologies.

Even if the catalyst lifetime still needs to be evaluated (around 40 hours of use here and no deactivation observed) and remains a decisive index for implementation, scale-up could be envisaged to prove the feasibility for industrial applications. To this aim, the behavior of ethanol was modelled considering mass transfer limitations, power law reaction kinetic and acetaldehyde as the only by-product. An accurate predictive model was fitted with an energy of activation of ethanol oxidation of 38 $kJ.mol^{-1}$, an apparent kinetic of 0.5 order and the

influence of the gas velocity followed a 0.7 order power law. Predictive simulations were finally carried out and showed that full abatement with full mineralization of ethanol into CO_2 can be achieved at low temperature (150°C) with a moderate reactor dimension (30 cm). A tradeoff might be found between performances, energy consumption (temperature and pumping) and compactness of the process (reactor length) with a cost analysis.

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SUPPLEMENTARY MATERIALS

Supplementary material S1: Detailed synthesis and characterization of the catalytic glass foam

Supplementary material S2: Estimated energy of activation of ethanol oxidation

Supplementary material S3: Comparison between the model and the experimental data

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