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MnO$_x$ supported on metallic monoliths for the combustion of volatile organic compounds

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ABSTRACT

The most convenient way to prepare structured manganese oxide catalyst for the combustion of volatile organic compounds was studied. The preparation conditions (solid concentration in the slurry, the addition of a suspension stabilizer, and the immersion numbers) were studied. The catalytic properties of these catalysts were evaluated in ethanol, ethyl acetate and toluene combustion. The surface area and the catalytic activity of monoliths in VOCs combustion increased with the amount of catalyst retained. A higher catalyst loading and a more homogeneous and well adhered layer was obtained using a 30 wt% solid content suspension and performing two immersions. The addition of Nyacol® is not necessary to improve the stability of suspensions because these are stable by themselves. The washcoating of monoliths with a θ–δ-Al_2O_3 suspended in manganese acetate solution not only reduces the number of stages during the preparation procedure but also produces more active catalysts.

1. Introduction

The control of VOCs emissions is often carried out by thermal incineration (at temperatures higher than 1200 K) or adsorption, but catalytic oxidation is a promising abatement technology for VOCs, since it can be carried out at lower temperatures (below 800 K), allowing energy saving and promoting the removal of the pollutant by forming harmless products such as H_2O and CO_2 [1,2]. The most commonly used catalysts in the oxidation of VOC are based on supported noble metals, generally Pt and Pd. However, transition metal oxides, mainly of Co, Cu, Ni and Mn [3] have demonstrated a very good catalytic activity in oxidation reactions and have the additional advantage of having lower cost and greater resistance to deactivation by poisoning [4]. MnO$_x$ based materials are among the most interesting catalysts used in catalytic oxidation reactions. These catalysts have been identified as active phases in various processes, as in total oxidation of methane [5], oxidation of CO [6] and various hydrocarbons [7–9]. They are also considered environmental-friendly materials [10].

When large volumes of gas with low concentrations of VOCs must be treated, it is necessary to deposit the active phase on structured supports to ensure the passage of fluids with low pressure drops. The structured supports most widely used are monoliths formed by longitudinal parallel channels. The monoliths can be made of ceramic or metallic materials. The most habitual because of its widespread use in the automobile sector are ceramics, mainly cordierite [11], however they have certain limitations related to the minimum wall thickness for a proper extrusion and a low thermal conductivity [12]. Although metal monoliths have a higher cost than ceramics ones, they have a higher mechanical strength and thermal conductivity, and also have thinner walls allowing higher cell densities and lower pressure drops. The main disadvantage is the low adhesion of the coating that acts as support of the active phase. Nowadays, this is overcome by chemical modification in the preparation of the coating and the use of metals or alloys physicochemical and/or thermally treated. Those treatments allow the formation of an adherent and stable oxide layer that anchors the catalytic coating [13]. Ferritic alloys containing Al (such as FeCrAlloy®) are used in the fabrication of metallic monoliths because they support high temperatures. Besides, under oxidizing conditions at high temperatures aluminum segregates to the surface as an alumina layer in form of whiskers. Such a layer has an adequate roughness to hold the catalytic coating.

In a previous work [14] we have reported that supported manganese oxide catalysts showed a good catalytic performance in VOCs oxidation reactions. In particular, the catalyst prepared from manganese acetate as precursor and a θ–δ-Al_2O_3 as support, resulted the most active one in ethanol combustion.

The aim of this work is to study the most convenient way to prepare structured manganese oxide catalyst for the combustion of volatile organic compounds. The preparation conditions (solid concentration in the slurry, the addition of a suspension stabi-

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lizer, and the immersion numbers) to obtain a homogeneous and well-adhered washcoating were studied. Finally, the catalytic properties of these catalysts were evaluated in ethanol, ethyl acetate and toluene combustion.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Powdered catalyst

The synthesis procedure and characteristics of the support and catalyst were presented in a previous work [14]. Briefly, the catalyst was prepared by impregnation to incipient wetness of the θ–δ-Al_2O_3 support with an aqueous solution of 0.06 g/ml $Mn(CH_3COO)_2 \cdot 4H_2O$ (Fluka). The impregnation was carried out in multiple stages with drying in between at 100 °C for 1 h. The amount of added solution was the necessary to obtain a manganese loading equivalent to three theoretical monolayers of MnO_x. Finally, the sample was dried at 70 °C overnight and calcined at 500 °C for 3 h. The resulting catalyst presented 19 wt% of manganese content.

2.1.2. Structured catalysts

2.1.2.1. Preparation of monolithic supports. The monoliths were prepared from thin foils (0.05 mm of thickness) of FeCrAlloy® (Fe: 72.6%; Cr: 22%; Al: 4.8%; Si: 0.3%; and Y: 0.3%) by rolling around a spindle alternate flat and crimped foils. The resulting monoliths presented the following geometric characteristics: cylinder of 3 cm of long and 1.6 cm of diameter (330 cpi). Finally they were calcined at 900 °C for 22 h.

2.1.2.2. Active phase deposition. Washcoating with MnO_x/Al_2O_3 ready-made catalyst: MnO_x/Al_2O_3 catalyst was ball-milled at 400 rpm for 15 h. Then, aqueous suspensions with 30 and 40 wt% solids content with and without the addition of 6 wt% colloidal alumina (Nyacol® Al 20) as stabilizer were prepared. The pH 3 was adjusted employing diluted HNO_3 solution. The slurries were subjected to orbital agitation for 24 h before being used for washcoating. Monoliths were dipped into the MnO_x/Al_2O_3 catalyst slurries during 1 min and withdrawn to constant speed of 3 cm/min. The suspension excess was eliminated by centrifugation at 400 rpm for 10 min. Then, they were dried at 120 °C for 2 h. One and two immersions were performed with each slurry concentration. Finally, they were calcined at 500 °C for 2 h.

Washcoating with θ–δ-Al_2O_3 suspended in manganese acetate solution: θ–δ-Al_2O_3 was ball-milled for 5 h and suspended in manganese acetate solution. The concentration of the solution was the necessary to achieve a manganese loading equivalent to that of MnO_x/Al_2O_3 catalyst. Suspensions with 30 and 40 wt% solid adding 6 wt% colloidal alumina (Nyacol® Al 20) as stabilizer were prepared. The pH 3 was adjusted employing diluted HNO_3 solution. Two immersions were performed.

They were named *n*MzNy, where *n* = 1 or 2 depending on the number of immersions; M = F or FA indicating the washcoating with the ready-made catalyst or with the alumina suspended in manganese acetate respectively; *z* = 30 or 40 depending on the solid content of the suspension; and Ny when Nyacol is added to the suspension.

2.2. Characterization techniques

2.2.1. Particle size distribution

Particle size distribution of solids was determined with a laser particle size analyzer using a Mastersizer 2000 apparatus from Malvern Instrument. Typically, 3–5 ml of suspension prepared with 100 mg of solid and 10 ml of water were added to the sample chamber.

2.2.2. Isoelectric point (IEP)

The IEP measurements were carried out in a Zeta Meter System 3.0 apparatus, using 20 mg of sample dispersed in 250 ml of a 10^{-3} M KCl solution. The pH was adjusted with either 10^{-2} M KOH or HCl solutions.

2.2.3. X-ray diffraction (XRD)

XRD patterns were obtained by using a Rigaku diffractometer operated at 30 kV and 25 mA by employing Cu Kα radiation with Nickel filter (λ = 0.15418 nm).

2.2.4. Viscosity measurements

9 ml of suspension were used to determine the viscosity using a Haake Rotational Viscosimeter (range 2–103 mPa s at 25 °C) equipped with a NV sensor.

2.2.5. Adherence test

The adherence of the coatings was evaluated in terms of the weight loss after exposure of the monoliths to ultrasounds. The coated monoliths were immersed in 25 ml petroleum ether, inside a sealed beaker, and then treated in an ultrasound bath for 30 min. After that, the monoliths were dried at 80 °C for 2 h and calcined at 500 °C during 2 h. The coating weight loss (in wt%) was determined by measuring the weight of the samples both before and after the ultrasonic treatment.

2.2.6. Textural characteristics measurement

Adsorption–desorption isotherms of nitrogen at 77 K were performed in a Gemini V apparatus from Micromeritics after outgassing the monoliths at 120 °C. A home-made cell was used for the measurement of complete monoliths (cylinder of 3 cm of long and 1.6 cm of diameter).

2.3. Catalytic tests

The monolithic catalysts were evaluated in the combustion of ethanol, ethyl acetate and toluene. The reacting stream was 300 cm^3/min with a composition of 4000 mg C/m^3 diluted in synthetic air. The space velocity used in the catalytic test was 3750 h^{-1}, and the most active catalyst was also evaluated at a space velocity of 10,000 h^{-1}. The gaseous mixtures were analyzed before and after reaction by gas chromatography using a Buck Scientific Mod 910 equipped with a FID detector, a methanizer and a Carbowax 20M/Chromosorb W column.

The powdered catalyst was evaluated in ethyl acetate combustion using the same reaction conditions. Thus, 150 mg of catalyst was pelletized as particles of 0.5–0.8 mm diameter and diluted with glass particles of the same size in order to achieve the same volume of the monolith.

3. Results and discussion

3.1. Catalysts characteristics

The characterization results of MnO_x/Al_2O_3 powder catalyst are reported in an earlier paper [14]. This catalyst has demonstrated an excellent catalytic behavior in VOCs combustion. However, as the operating conditions of the catalysts in the volatile organic compounds combustion involve high space velocities of the gaseous stream, it was decided to deposit the active phase on FeCrAlloy monoliths. The main objective when preparing a metallic monolithic catalyst is to achieve a homogeneous and well-adhered catalyst layer on the monolith walls. Adhesion of the washcoat on

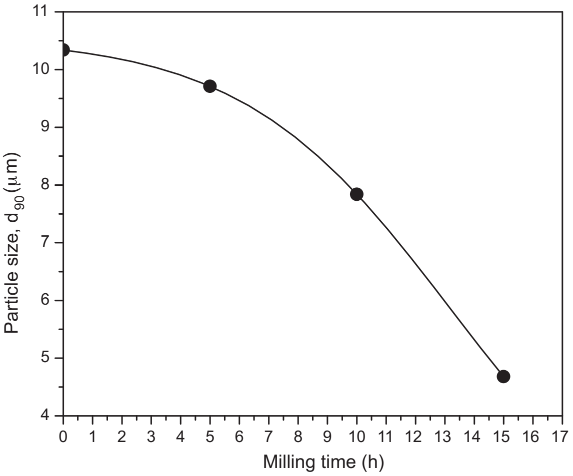

Fig. 1. Particle size (d_{90}) vs. milling time.

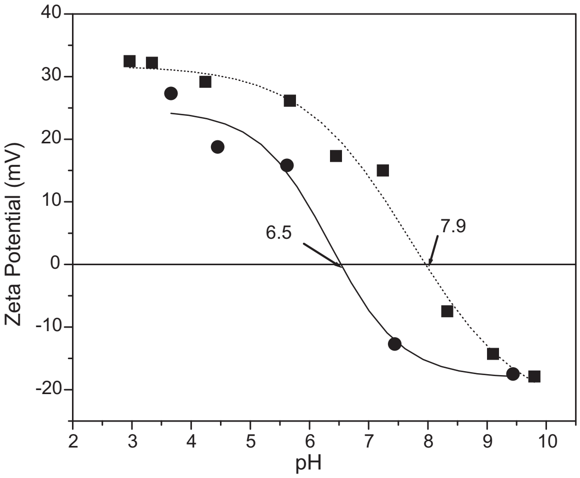

Fig. 2. Zeta potential vs. pH curves. θ–δ-Al_2O_3 (dotted line), MnO_x/Al_2O_3 (solid line).

the support takes place by mechanical mechanisms such as anchoring and interlocking of the coat particles among them as well as with the surface irregularities of the support [11]. Thus, FeCrAlloy was calcined at 900 °C during 22 h [15]. With this thermal treatment it is generated a surface roughness of aluminum oxide, α-Al_2O_3 in form of whiskers, which allows the anchoring of the coating. The preparation of stable suspensions and optimization of the rheological properties are essential to achieve homogeneous and stable coatings. It is well known that the adhesion with the support is affected by the size of the deposited particles. It has been demonstrated that the particles size has to be reduced to a value range around 5 μm [16]. The initial catalyst particle size indicated by d_{90} value (90% of the particles have a size smaller than this value) was 10.3 μm. Thus, it was necessary to mill the catalyst. Fig. 1 shows the catalyst particle size as a function of milling time. As noted, with 15 h of milling the particle size could be reduced to 4.7 μm. The suspensions were prepared in aqueous medium and adjusted to pH 3, a value far enough from the isoelectric point of the catalyst, PIE: 6.5 (Fig. 2), in order to enhance the repulsion between the particles and prevent them to agglomerate, then achieving stable suspensions. The suspensions resulted stable, nevertheless, the same suspensions were prepared with the addition of colloidal alumina (Nyacol) as stabilizer because its addition modifies the suspension viscosity and it could influence on the thickness of the coating [16]. The viscosities of 30 wt% and 40 wt% of catalyst suspensions without the addition of Nyacol resulted similar and around 4.2 cP. While the viscosities of 30 wt% and 40 wt% suspensions with Nyacol are 4.2 cP and 6.2 cP respectively. Several authors have investigated the effect of the solids content on both the slurry characteristics and the loading achieved on the monolith [17–19]. In general, they recommend slurry solids content between 30 and 50 wt%. In this work, the slurries were prepared with solids content of 30, and 40 wt%. As it can be observed in Table 1, the loading increases with the suspension concentration when a single immersion is made. In order to increase the retained catalyst loading, successive immersions can be made. In this work only one and two immersions were made because it has been demonstrated that higher number of immersions led to unstable active phase layers [17]. When two immersions of the monolith are made in the 30 wt% suspension, nearly the double amount of catalyst is retained (Table 1). However, a second immersion of the monolith in 40 wt% suspension is not enough to achieve the double of catalyst loading retained with a single immersion. This suggests that when a concentrated suspension is used, the surface roughness of the monolith, reached after the thermal treatment, decreases once the first layer of catalyst crystals is formed. Depending on the slurry viscosity the loading

Table 1
Retained catalyst amount, weight loss and S_{BET}.

Catalyst	Retained catalyst amount (mg)	Coating weight loss (%)	S_{BET} (m^2/monolith)
1F30	79.1	2.3	5.2
2F30	153.3	0.2	10.7
1F40	90.8	19.0	7.5
2F40	124.3	2.2	9.4
2F30Ny	55.5	0.7	4.9
2F40Ny	183.4	16.5	12.7
2FA30	80.2	2.0	7.2
2FA40	176.4	1.9	16.1

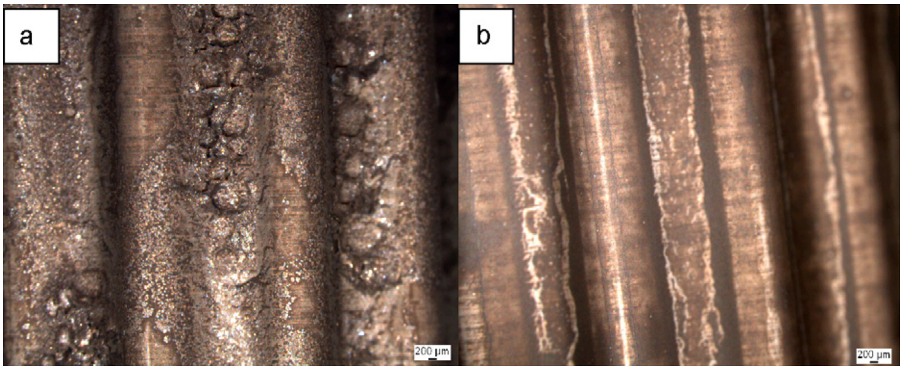

Fig. 3. View of monolith channels in: (a) 2F40Ny and (b) 2F30.

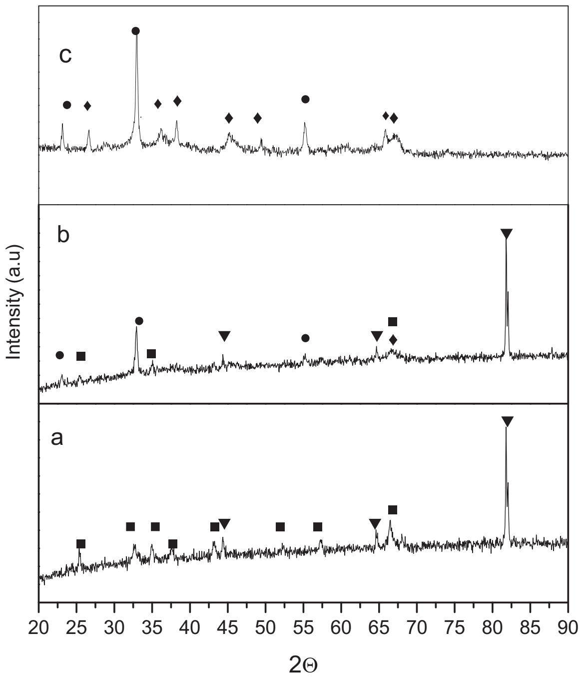

Fig. 4. Diffractograms of (a) FeCrAlloy monolith calcined at 900 °C for 22 h, (b) coated monolith, and (c) MnO_x/Al_2O_3 catalyst. (▼) FeCrAll, (■) α-Al_2O_3, (●) Mn_2O_3, (♦) θ–δ-Al_2O_3 phases.

achieved with the first immersion can be higher or lower than that achieved with successive immersions. This is determined by attractive forces occurring between the first washcoating layer and the subsequent one [17]. The addition of a stabilizer (Nyacol) to the 30 wt% suspension does not increase the amount of solid retained, but its addition to the 40 wt% suspension increases the amount of deposited catalyst. Considering the adhesion of the coating, the monoliths prepared with 40 wt% suspensions with and without Nyacol showed the highest weight loss. These results show that, in this case, the addition of Nyacol is not necessary to improve the stability of suspensions, because these are stable by themselves, and this stabilizer does not produce significant improvements in the amount of catalyst retained even when the suspension viscosity increases. Effectively, in Fig. 3 it is shown that the walls in 2F40Ny monolith are not homogeneously covered, showing a loading excess with low adherence. This figure also shows the 1F30 monolith walls. Even if this monolith retained a lower amount of catalyst, a homogeneous coverage which remains well adhered is observed. The good stability of the suspensions has lead to an excelent adhesion of the coating evidenced by the low values of weight loss, as it can be seen from Table 1, with the exception of 1F40 and 2F40Ny monoliths.

Coating a catalyst on metallic monoliths led to a surface area (S_{BET}) increase when compared to the metallic monolith itself. This could be explained by a more significant contribution of the powdered catalyst (87.5 m^2/g) to the overall surface area of the monolith. In fact, the catalysts which retained the higher manganese oxide loading presented the higher S_{BET} (Table 1). It is important to note that the catalyst (MnO_x/Al_2O_3) used for the monolith coating does not undergo any crystalline modification during the deposition procedure. Fig. 4 shows the diffractograms of MnO_x/Al_2O_3 powder catalyst, a bare Fecralloy monolith and a coated monolith. The diffractogram of MnO_x/Al_2O_3 catalyst shows the presence of Mn_2O_3 phase (PDF 24-508) and θ–δ Al_2O_3 phases (PDF 35-121 and 4-877). The coated monolith shows the most intense peaks attributed to the MnO_x/Al_2O_3 catalyst besides the peaks corresponding to the metallic substrate (ferritic FeCrAlloy).

With the aim of scaling-up the preparation of these monoliths, the possibility of reducing the number of stages that compose the preparation of the monolithic catalyst was studied. By this way, the costs of fabrication process would decrease. The washcoating of FeCrAlloy monoliths (calcined at 900 °C for 22 h) with θ–δ-Al_2O_3 suspended in a manganese acetate solution was explored. The suspension pH was adjusted to 3, far enough to 7.9, the isoelectric point of this alumina. The characteristic particle size d_{90} was 6.7 μm. The selected pH and characteristic particle size should produce stable suspensions. However, the suspensions were not enough stable to load a homogeneous solid layer. For this reason, the addition of stabilizer to the suspension was studied. Some tests dipping microscope slides into 30 and 40 wt% suspensions of alumina in manganese acetate without stabilizer (WS), with the addition of polyvinyl alcohol (PVA) and Nyacol addition (Ny) were carried out. In Fig. 5 it can be observed that a more homogeneous layer of the coating was obtained using Nyacol as stabilizer. The suspensions with the addition of Nyacol were stables with viscosities around 7.8 and 9.8 mPa s for 30 and 40 wt% suspensions, respectively. Two immersions were needed to achieve comparable catalyst loadings. These monoliths presented a very good adhesion of the coating indicated by the low values of weight loss, around 2%.

A higher amount of deposited solid was retained using the 40 wt% suspension obtaining by this way a catalyst with higher surface area (Table 1). In this case occurs the same observed on monoliths prepared from the ready-made catalyst, where the S_{BET} of monoliths depends on the retained solid amount. However in this case, the contribution of the high specific surface θ–δ-Al_2O_3 (98 m^2/g) to the monolith surface area is more important. Indeed, it favors a surface area increase of the *n*FAz compared to *n*Fz monoliths. Considering monoliths with similar retained solid amount, it can be seen that 2FA30 presented a higher S_{BET} compared to 1F30 monolith. The same tendency is observed considering monoliths with different retained solid amount. Similar surface area presented 1F40 and 2FA30 monoliths, even if 1F40 retained higher catalyst amount. This could be due to the double calcination that *n*Fz catalyst active phase suffers during the synthesis procedure.

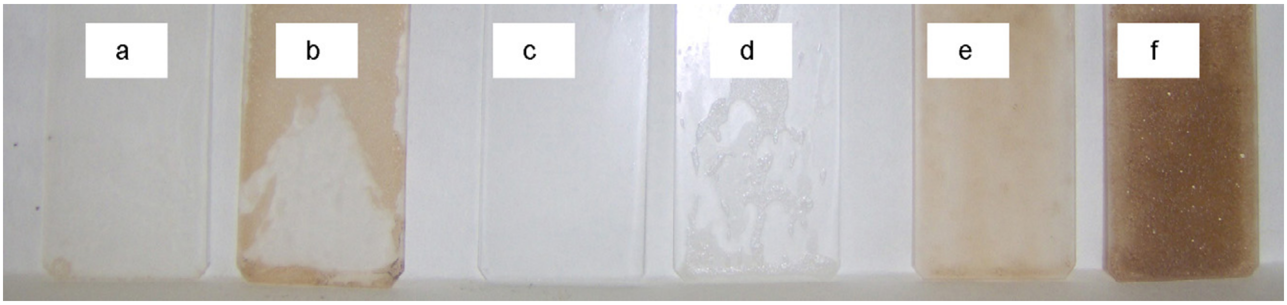

Fig. 5. Glass sheets covered with θ–δ-Al_2O_3 suspended in manganese acetate: (a) 30% WS, (b) 40% WS, (c) 30% PVA, (d) 40% PVA, (e) 30% Ny, and (f) 40% Ny.

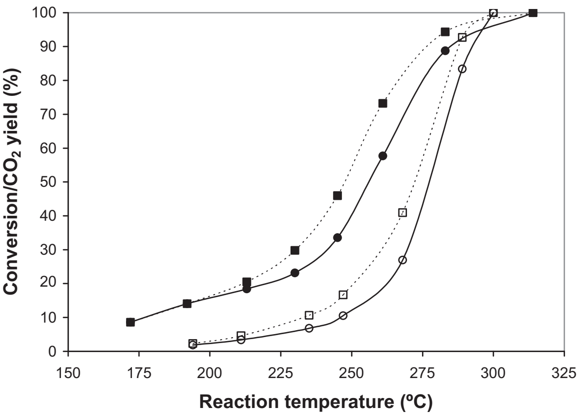

Fig. 6. Catalytic activity of powdered catalyst (open symbols) and 2F30 monolith (filled symbols). Ethyl acetate conversion (square) and CO$_2$ yield (circle).

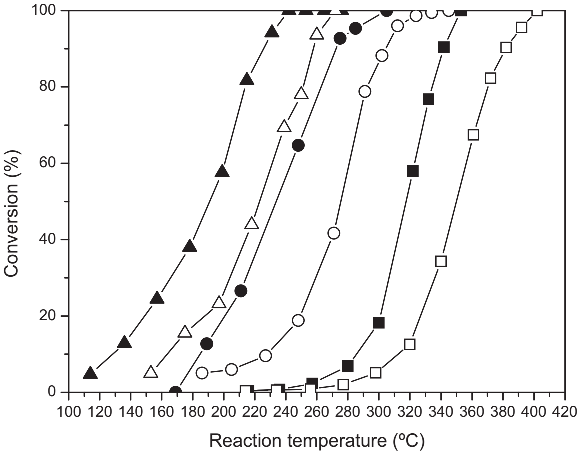

Fig. 7. Catalytic activity of 1F40 (open symbols) and 2FA30 (closed symbols) in ethanol (triangle), ethyl acetate (circle) and toluene (square) combustion.

3.2. Catalytic activity

These catalysts were evaluated in ethanol, ethyl acetate and toluene combustion. These VOCs are generally found in emissions of the printing industries. It is important to analyze the catalytic behavior of these monoliths in the combustion of each VOCs since they have different chemical character (alcohol, ester and aromatic hydrocarbon).

The most important measure of the success in the structured catalyst preparation is the preservation of the catalytic performance of the powder catalyst. In order to study the effect of monolith supporting on the catalytic activity, the catalytic results obtained for powdered and monolithic catalyst in the ethyl acetate combustion were compared. Fig. 6 presents ethyl acetate conversion and CO$_2$ yields as a function of the reaction temperature curves of 2F30 monolith and the powdered catalysts considering the same amount of active phase. The monolithic catalyst presented higher ethyl acetate conversion values in the whole range of reaction temperatures, showing differences of about 25 °C in T_{50} and T_{80} values (temperatures corresponding to 50 and 80% conversion). These differences were also observed considering CO$_2$ yields, since the intermediates ethanol and acetaldehyde are also formed during ethyl acetate oxidation. Even if the S_{BET} of the monolithic catalyst is lower than that of the powder catalyst for the same weight, the monolith presented higher ethyl acetate conversion and CO$_2$ yields values than powder catalyst. The better catalytic behavior that monolith presented could be due to the temperature adiabatic increase in the catalyst surface, which is produced as a consequence of the reaction heat. The reactor thermocouple is located upstream the monolith, though the measured temperature corresponds to an average value and it does not exactly correspond to the real temperature of the surface of the catalyst where the reaction proceeds. The high conductivity of the metallic monolith would allow developing a homogeneous temperature profile through the monolith obtaining by this way higher catalytic activity. Probably, the temperature profile in the packed bed reactor is not homogeneous, and higher surface temperatures due to the generated reaction heat are obtained only at high conversion levels [20]. This also could explain the small difference between powdered and monolith conversion curves at high conversion levels above 90% conversion. Even taking into account these considerations, very good results were obtained. This let us to think that the studied conditions are appropriate to support the catalyst.

The monoliths catalytic activity is presented in Table 2 where T_{10}, T_{50} and T_{80} values for the combustion of ethanol, ethyl acetate and toluene are presented. The effect of catalyst loading due to the increase of the number of immersions on the catalytic activity can be analyzed considering monoliths prepared from the 30 wt% suspension. Higher catalytic activities in the combustion of the three molecules studied were observed for 2F30. This was expected since it presented higher amount of retained catalyst and higher surface area (Tables 1 and 2). However, the amount of catalyst retained during the second immersion of monolith in the 40 wt% suspension does not increase the catalytic activity. The catalyst layer would not be homogeneous and this could be the responsible of its lower catalytic activity.

In order to analyse the effect of the suspension concentration, monoliths prepared from 30 and 40 wt% with a single immersion (1F30 and 1F40) are considered. Again the higher catalyst loading produces an increase of the catalytic activity. These results are in line with the increase of the surface area (Table 1). However, if catalysts with similar S_{BET} are compared (2F30 and 2F40) the former presented a higher catalytic activity. 2F30 catalyst resulted even more active than 2F40Ny despite having lower amount of catalyst

Table 2
Catalytic activity in ethanol, ethyl acetate and toluene combustion.

Catalyst	Ethanol			Ethyl acetate			Toluene		
	T_{10} (°C)	T_{50} (°C)	T_{80} (°C)	T_{10} (°C)	T_{50} (°C)	T_{80} (°C)	T_{10} (°C)	T_{50} (°C)	T_{80} (°C)
1F30	233	290	328	226	319	355	367	490	–
2F30	128	213	240	177	247	270	302	339	363
1F40	162	223	252	228	275	291	313	349	370
2F40	167	232	261	224	264	313	320	395	453
2F30Ny	188	245	265	232	286	302	330	377	398
z2F40Ny	138	218	239	213	260	275	393	330	349
2FA30	129	191	214	185	233	262	286	318	335
2FA40	110	176	201	197	230	240	271	301	330
2FA40[a]	–	–	–	–	–	–	274	310	340

[a] 2FA40 catalyst evaluated in toluene combustion with the same VOC feed composition, 4000 mg C/m^3 but different space velocity, 10,000 h^{-1}.

retained and lower surface area. As it was stated above the excess of loading presented by 2F40Ny was not homogeneous (Fig. 3) and presented low adherence (Table 1). These results indicate that the catalytic activity not only depends on the amount of active phase retained. The homogeneity and the good adherence of the coating are of great importance.

The influence of the synthesis procedure on the catalytic behavior of the monolithic catalysts can be observed in Table 2. In general, catalysts prepared from a suspension of the support (θ–δ-Al_2O_3) in a manganese acetate solution resulted more active than those prepared from the suspension of the ready-made catalyst. Fig. 7 shows the catalytic performance of 1F40 and 2FA30 catalysts which presented similar S_{BET} (7.5 and 7.2 m^2/monolith), Table 1. 2FA30 catalyst resulted more active in the combustion of the three molecules studied despite having lower amount of retained catalyst. If the same amount of catalyst is considered, as in the case of 2FA30 and 1F30 monoliths, again the former presented higher catalytic activity. Evidently the catalytic activity is influenced by the synthesis procedure. In fact, 2FA40 catalyst was the most active one. Its very good catalytic performance was also observed when it was evaluated at a higher space velocity, 10,000 h^{-1} in toluene combustion (Table 2). Only differences of about 10 °C in T_{50} and T_{80} values were observed compared to that observed with the test at 3750 h^{-1}.

Then, it could be concluded that following a procedure where the monoliths are immersed in a suspension of θ–δ-Al_2O_3 in manganese acetate solution, it is possible to reduce the number of stages during the synthesis of monoliths and increase considerably the catalytic activity.

4. Conclusions

A MnO_x/Al_2O_3 powdered catalyst was successfully deposited by a washcoating method on FeCrAlloy monoliths. This powdered catalyst has demonstrated an excellent catalytic performance in VOCs combustion; however, supporting it on a metallic monolith has considerably increased its catalytic activity. The surface area and the catalytic activity of monoliths in VOCs combustion increased with the amount of catalyst retained. A higher catalyst loading and a more homogeneous and well adhered layer was obtained using a 30 wt% solid content suspension and performing two immersions. The addition of Nyacol is not necessary to improve the stability of suspensions because these are stable by themselves.

Following the synthesis procedure of monoliths from a suspension of θ–δ-Al_2O_3 in manganese acetate solution it was possible to reduce the number of stages during the synthesis of monolithic catalysts decreasing the fabrication costs, and considerably increase the catalytic activity. Due to the simplicity of this synthesis method and the possibility of a future optimization, these monoliths are very interesting from the technological point of view.

Acknowledgements

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