

Influence of the Support on MnOx Metallic Monoliths for the Combustion of Volatile Organic Compounds

Fabiola N. Aguero,^{*,†} Bibiana P. Barbero,[†] Oihane Sanz,[‡] Francisco J. Echave Lozano,[‡] Mario Montes,[‡] and Luis E. Cadús[†]

Instituto de Investigaciones en Tecnología Química (INTEQUI), Universidad Nacional de San Luis (UNSL)—Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICET), Casilla de correo 290, 5700 San Luis, Argentina, and Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Química de San Sebastián, Universidad del País Vasco, P. Manuel de Lordizabal, 3, 20009, San Sebastián, Spain

The influence of the alumina layer nature which acts as the support on the preparation of structured catalysts and on the catalytic performance in VOC combustion was studied. Anodized aluminum and a ferritic alloy covered with colloidal alumina (Nyacol) and θ - δ -Al₂O₃ were the materials used to prepare the monolith catalysts. The impregnation was performed in one and two stages using two different concentrations of manganese acetate solutions. The catalytic properties of these catalysts were evaluated in ethanol, ethyl acetate, and toluene combustion. The most active catalysts in the combustion of the three molecules were those prepared using a θ - δ -Al₂O₃ as a support. The low activity of aluminum monoliths anodized with H₂SO₄ is due to the presence of SO₄²⁻ ions which act as catalyst poison. The anodization with H₂C₂O₄ is a preferable method to prepare MnOx monolithic catalysts.

1. Introduction

Catalytic combustion is a widely used technology to control the emissions of volatile organic compounds (VOCs).¹ Moreover, the catalytic abatement of pollutants in industrial emissions requires catalysts with a high attrition resistance and a low pressure drop, due to the high flows of the emitted pollutants.² These problems can be overcome by the use of structured supports.³ The most popular structured supports are monoliths. Monolithic supports are unibody structures composed of longitudinal parallel channels. They can be made of ceramics or metallic alloys. In recent years metallic monoliths have become increasingly popular due to their high thermal conductivities, lower heat capacities, greater thermal and mechanical shock resistance, and smaller wall thickness allowing higher cell density and lower pressure drop than ceramic ones.⁴ However, one of the main problems presented by metallic monoliths is the low adherence between the metallic matrix and the catalyst.² Actually, this problem is solved by the use of metals or alloys that can produce an adherent stable oxide layer with excellent properties for anchoring the catalytic coating.⁵ 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 the form of whiskers. Such a layer has an adequate roughness to attach the catalytic coating. Due to the low specific surface area that these monoliths present, it is necessary to deposit a porous material (e.g., Al₂O₃) with high surface area over the metallic substrate to act as a real catalytic support. Among the methods used to obtain a catalytic coating on a metallic structure, dip coating or washcoating from the liquid phase using a sol or slurry is the most versatile and simple one to be used in practice. Boehmite sol is generally used to deposit alumina coatings on metallic supports.⁶ Valentini et al.⁷ have described the deposition of γ -Al₂O₃ on α -Al₂O₃, aluminum, and FeCrAlloy structures. Jia et al.⁸ prepared well-

adhered alumina washcoats on FeCrAl structures using boehmite sols and alumina slurries.

Another interesting material to prepare metallic monoliths when the working temperature is not too high is aluminum. It has excellent mechanical and thermal properties, and it can be anodized producing very adherent alumina layers with adequate textural properties to be used as a catalytic support.^{2,9,10} Many studies on catalytic combustion over supported noble metals, generally Pd and Pt, have been carried out.^{3,11,12} However, a more economical alternative is the use of transition metal oxides (mainly Co, Cu, Ni, and Mn¹³) which have demonstrated excellent catalytic behavior in oxidation reactions. In a previous work¹⁴ we have reported that supported manganese oxide catalysts in the form of powder showed a good catalytic performance in VOC oxidation reactions. In particular, the catalyst prepared from manganese acetate as precursor and a θ - δ -Al₂O₃ support resulted as the most active one in ethanol combustion.

This paper presents the results of studies on the influence of the alumina used to prepare structured catalysts on the coating process and on the catalytic performance in VOC combustion. The catalytic properties of these structured systems were evaluated in ethanol, ethyl acetate, and toluene combustion. These VOCs are generally found in emissions of the printing industries. Aluminum and a ferritic alloy were the metal substrates used to prepare the monolith catalysts.

2. Experimental Section

2.1. Preparation of the Structured Catalyst. 2.1.1. Preparation of Monolithic Substrates. The monoliths were prepared from pure aluminum foils (Alloy 1050) of 0.125 mm and thin foils (0.05 mm of thickness) of FeCrAlloy (Fe, 72.6%; Cr, 22%; Al, 4.8%; Si, 0.3%; Y, 0.3%) by rolling around a spindle alternate flat and crimped foils. The resulting monoliths presented the following geometric characteristics: cylinder 3 cm long and 1.6 cm in diameter (330 cpi). The aluminum sheets were anodized using H₂SO₄ or H₂C₂O₄ as electrolyte. Previous studies carried out in our laboratory using aluminum sheets and foams^{15,16} showed that anodized treatments could produce

* To whom correspondence should be addressed. E-mail: naguero@fices.unsl.edu.ar.

[†] UNSL.

[‡] Universidad del País Vasco.

surface cracks wider than the catalyst particle size increasing the adhesion of catalyst washcoating, due to mechanical anchoring caused by the presence of deep cracks that allocate the catalyst particles. In this sense, the alumina morphologies obtained at 30 °C, 50 min, 2 A dm⁻², and 2.6 M sulfuric acid¹⁶ and at 50 °C, 40 min, 2 A dm⁻², and 1.6 M oxalic acid² were used to obtain Al₂O₃/Al monoliths as a structured support in this work. FeCrAlloy monoliths were calcined at 900 °C for 22 h to obtain a well-adhered alumina layer. This layer can act as a substrate to deposit thicker layers of support. Some of these monoliths were covered with an alumina layer by the washcoating method. The monoliths were dipped into a slurry of colloidal alumina (Nyacol, 20 wt % Al₂O₃, 50 nm particle size, 10 cP viscosity) or a slurry of θ - δ -Al₂O₃ (20 wt % Al₂O₃, 6.7 μ m particle size, 11.5 cP viscosity) for 1 min and withdrawn at a constant speed of 3 cm/min. The suspension excess was eliminated by centrifugation at 400 rpm or by blowing dry air for 10 min. Then, they were dried at 120 °C for 2 h. This procedure was repeated three times, and finally they were calcined at 500 °C for 2 h.

2.1.2. Impregnation with the Active Phase. The anodized aluminum and the FeCrAlloy monoliths previously covered with Nyacol or θ - δ -Al₂O₃ were impregnated with (CH₃CO₂)₂Mn·4H₂O aqueous solutions with two different concentrations: 0.6 and 0.3 g/mL. Monoliths were immersed in the (CH₃CO₂)₂Mn·4H₂O solution and rotatory mixed for 1 h. Finally they were dried at 60 °C for 4 h and calcined at 500 °C for 3 h. One or two impregnations were made. Samples were referred to as *nMx*, where *n* is 1 or 2 depending on the number of impregnations; M is AIS, AIO, F, or FA if anodized aluminum with sulfuric acid or oxalic acid, FeCrAlloy with Nyacol, or FeCrAlloy with θ - δ -Al₂O₃ is used; and *x* is 0.3 or 0.6 depending on the concentration of the impregnating solution.

2.2. Characterization Techniques. 2.2.1. Particle Size Distribution. The particle size distribution of solids was determined with a laser particle size analyzer using a Mastersizer 2000 apparatus from Malvern Instruments. Typically, 3–5 mL of suspension prepared with 100 mg of solid and 10 mL of water was 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. Viscosity Measurements. Nine milliliters of suspension was used to determine the viscosity with a Haake Rotational Viscosimeter (range 2–103 mPa s at 25 °C) equipped with an NV sensor.

2.2.4. Adherence Test. The adherence of the coatings was evaluated in terms of the weight loss after submitting the monoliths to ultrasound. The coated monoliths were immersed in 25 mL of 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. The weight loss is presented as the percentage of the total coating.

2.2.5. 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 homemade cell was used for the measurement of complete monoliths.

2.2.6. Scanning Electron Microscopy (SEM). The morphology of samples was examined with a LEO 1450 VP scanning electron microscope provided with energy dispersive X-ray analysis (EDAX) equipment for the quantitative analysis. The

Table 1. Alumina Loading, Active Phase Loading, Weight Loss, and S_{BET}

catalyst	alumina loading (mg)	active phase loading (mg)	weight loss ^a (%)	S _{BET} (m ² /monolith)
Al–S	1160	–	0.2	34.6
Al–O	2270	–	0.1	15.2
FeCrAlloy + Ny	–	–	–	5.3
1AIS0.6	1160	29.2	1.2	19.7
2AIS0.6	1160	53.0	3.4	28.4
1AIS0.3	1160	13.9	3.4	28.7
2AIS0.3	1160	27.9	2.9	28.0
1AIO0.3 ^b	2270	85.0	3.5	45.0
2AIS0.3 ^b	1160	117.0	4.5	107.9
1F0.6	30.5	19.8	3.5	6.8
2F0.6	35.9	30.5	2.8	5.3
1F0.3	41.7	13.5	2.3	5.2
2F0.3	40.3	16.6	6.1	12.0
1FA0.6	353.6	77.6	1.3	33.8
2FA0.6	327.1	115.2	3.1	39.2
1FA0.3	353.4	41.9	0.5	36.0
2FA0.3	349.5	132.3	1.3	33.5

^a Weight loss (%) is calculated considering both active phase and alumina loading. ^b The loading excess was eliminated by blowing air.

samples were covered with a thin gold layer to improve image quality and with carbon for the EDAX measurements.

2.3. Catalytic Tests. The monoliths were evaluated in the combustion of ethanol, ethyl acetate, and toluene. The reacting stream was 300 cm³/min with a composition of 4000 mg of C/m³ diluted in synthetic air. The space velocity was 3000 h⁻¹. The gaseous mixtures were analyzed before and after reaction by gas chromatography using a Buck Scientific Model 910 equipped with a flame ionization detector, a methanizer, and a Carbowax 20M/Chromosorb W column.

3. Results and Discussion

Monolithic catalysts are composed by the structural material or substrate and the catalyst itself, which covers the monolith walls, and is normally composed by an active phase dispersed on a catalytic support. FeCrAlloy calcined at 900 °C for 22 h⁴ was one of the substrates used in this paper. These conditions are the necessary to generate a surface roughness which allows the anchoring of the coating. An alumina layer in the form of whiskers is formed after the thermal treatment.¹⁷ This texture is beneficial for the anchoring of alumina coatings on the metallic supports.¹⁸ Due to their low specific surface area, these monoliths were covered with a colloidal alumina (Nyacol) or θ - δ -Al₂O₃ layer since it has been found to be an excellent catalytic support in oxidation reactions.¹⁴

Anodized aluminum was also studied as a metallic substrate because it is an economical alternative presenting a porous alumina layer on the surface with adequate textural characteristics, 34.6 m²/monolith, for being used as catalyst support.²

Table 1 shows that higher manganese loadings are obtained using a concentrated manganese acetate solution (0.6 mg/L), and the loading increases with the number of impregnations considering the catalytic supports separately. These results have direct consequences in the catalytic performance, as can be seen in Table 2, where *T*₁₀, *T*₅₀, and *T*₈₀ values (temperatures corresponding to 10, 50, and 80% conversion) in ethanol, ethyl acetate, and toluene combustion are shown. For each support in particular, the catalytic activity increases with the manganese loading. The same tendency was observed on the combustion of the three molecules. In a previous paper¹⁹ it has been proposed that aromatic and oxygenated compounds combustion over MnOx/Al₂O₃ catalysts occur through different mechanisms. The first stage of the ethanol oxidation process is the adsorption

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)
1AlS0.6	175	255	284	255	345	360	346	397	422
2AlS0.6	180	228	269	229	297	320	315	371	399
1AlS0.3	198	274	305	224	348	371	377	437	465
2AlS0.3	166	225	265	254	295	324	335	413	454
1F0.6	152	205	222	178	245	275	273	329	357
2F0.6	154	196	218	192	250	270	284	319	339
1F0.3	153	203	231	219	262	289	292	341	367
2F0.3	105	193	223	196	242	270	281	319	350
1FA0.6	100	188	206	184	216	231	245	262	275
2FA0.6	105	173	201	183	208	225	211	243	255
1FA0.3	109	175	206	182	207	221	231	259	277
2FA0.3	112	180	203	161	200	216	215	254	266

of the molecule on the surface, and then it reacts with the lattice oxygen of the catalyst through a Mars–van Krevelen mechanism.²⁰ Further, it was proposed that toluene oxidation does not occur from chemisorbed species on the surface, but it would mainly react with chemisorbed oxygen species on the catalyst surface, following a Rideal–Eley mechanism. This was also suggested by Burgos et al.²¹ on Pt catalysts supported over anodized aluminum monoliths.

Comparing monoliths prepared from anodized aluminum and FeCrAlloy covered with Nyacol, it can be observed that higher manganese loading is retained on *nAlx* catalysts. The increase of manganese loading is more important considering the information obtained with a second impregnation. A second impregnation doubles the active phase loading on the Al₂O₃ layer of the anodized aluminum monoliths. However, on FeCrAlloy monoliths covered with Nyacol, the MnOx loading increases around 50% when a second impregnation is made with a concentrated solution and around 20% using the diluted solution. The higher manganese loading retained on anodized aluminum monoliths can be due to the higher specific surface area that this support presents. The metallic substrate effect and therefore the catalytic support effect on the catalyst behavior can be analyzed comparing catalysts with the same manganese loading, such as 1AlS0.6 with an active phase loading of 29.2 mg and 2F0.6 with 30.5 mg. The catalyst prepared from FeCrAlloy coated with Nyacol support was more active than the anodized aluminum one, showing differences of about 65, 90, and 85 °C in T_{80} values corresponding to the combustion of ethanol, ethyl acetate, and toluene, respectively. Nevertheless, the support effect can be better analyzed from the comparison of catalysts with low manganese loading, such as 1AlS0.3 and 1F0.3 (Figure 1). Again, the FeCrAlloy monolith was more active than the aluminum one in spite of its lower specific surface area, 5.2 m²/monolith compared to 28.7 m²/monolith of 1AlS0.3 monolith. Evidently, the manganese oxide generated on 1F0.3 is qualitatively different. It is well-known that the catalytic properties of MnOx may depend on several factors such as the oxidation number, the crystalline structure, and mainly the dispersion of the active phase on the support surface.¹⁴ In Table 1 it is shown that the manganese acetate impregnation process did not modify the specific surface area of FeCrAlloy coated with Nyacol monolith, while the specific surface area of the aluminum monolith decreased from 34.6 to 28.7 m²/monolith. Probably, manganese provokes a blocking effect of the support pores causing a reduction of the specific surface area.

The SEM micrographs acquired by means of the backscattered electron mode, Figure 2, show the morphology of these monoliths. It can be observed that the aluminum monolith has a rougher surface than FeCrAlloy. In order to analyze the dispersion of the active phase on the support surface, a Mn mapping using SEM–EDS (energy dispersive spectrometry) was made. As can be observed from Figure 3, the Mn distribution is more homogeneous and the coverage is higher on the

aluminum monolith. The higher manganese loading retained by the anodized aluminum monolith is also detected from EDS analysis, Figure 4, where it can be observed that the manganese loading is proportional to the signal intensity. The elements present in FeCrAlloy monolith are those corresponding to the metallic substrate (Fe, Cr, Al) and manganese oxide (Mn, O). In the aluminum monolith besides the lines corresponding to the support (Al) and active phase (Mn, O), a line corresponding to sulfur was also detected. The sulfur presence in this monolith can be due to the anodization process that was carried out using H₂SO₄ as electrolyte.

Many authors have observed that, during the anodization process, ions of the electrolyte used, in this case SO₄²⁻ ions, remain retained in the generated alumina.^{2,22} The presence of these ions can influence the support acidity and the catalyst activity (SO₄²⁻ as catalyst poison).⁴ Sulfur would be in the form of Al₂(SO₄)₃ on the monolith surface, which would form MnSO₄ when the monolith is impregnated with manganese acetate. This reaction is thermodynamically favored, as has been verified using HSC Chemistry 5.11 software. Thus, part of the manganese would form MnSO₄ instead of manganese oxide species, which are the catalytically active ones. This fact could be the reason for the low catalytic activity of the aluminum monoliths. In order to corroborate this, it was intended to eliminate the sulfur content on the surface by water wash since it is known that Al₂(SO₄)₃ is soluble in water. Thus, samples of 1 cm² of H₂SO₄-anodized aluminum sheets were placed in a U-tube and water was recycled at 30 cm³/min using a peristaltic pump for 30 and 90 min. One of the samples was calcined at 500 °C for 3 h after the wash treatment in order to analyze if sulfur content

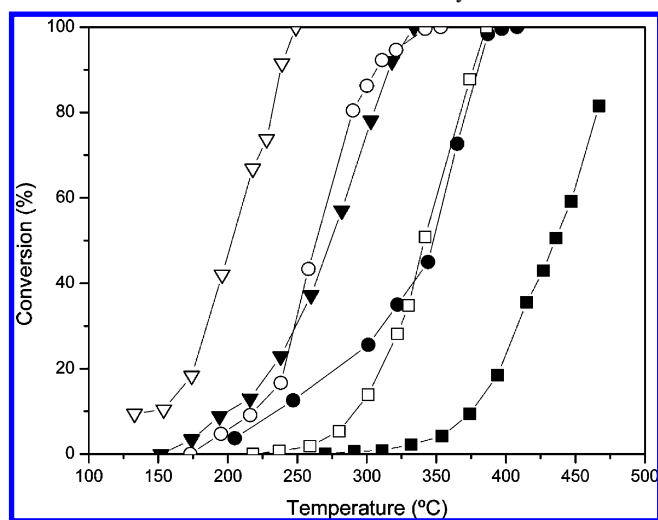


Figure 1. Catalytic activity of 1AlS0.3 (closed symbols) and 1F0.3 (open symbols) on ethanol (triangles), ethyl acetate (circles), and toluene (squares) combustion.

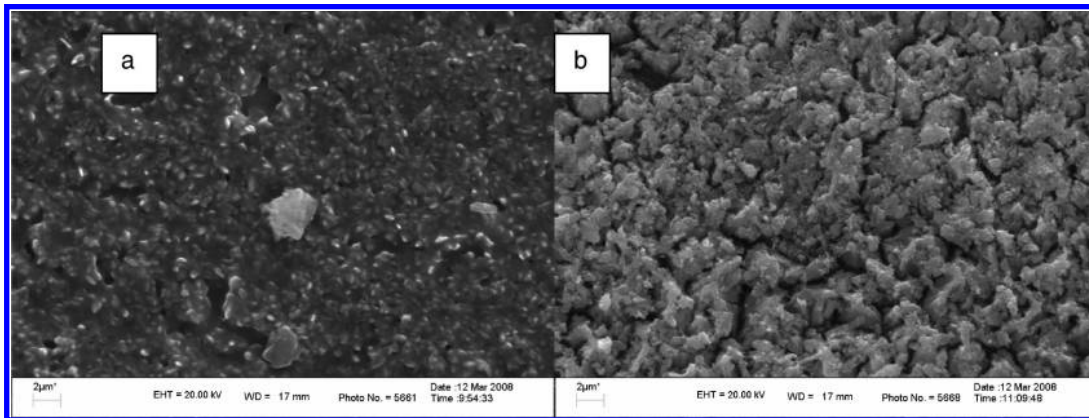


Figure 2. SEM micrographs of (a) 1F0.3 and (b) 1AIS0.3.

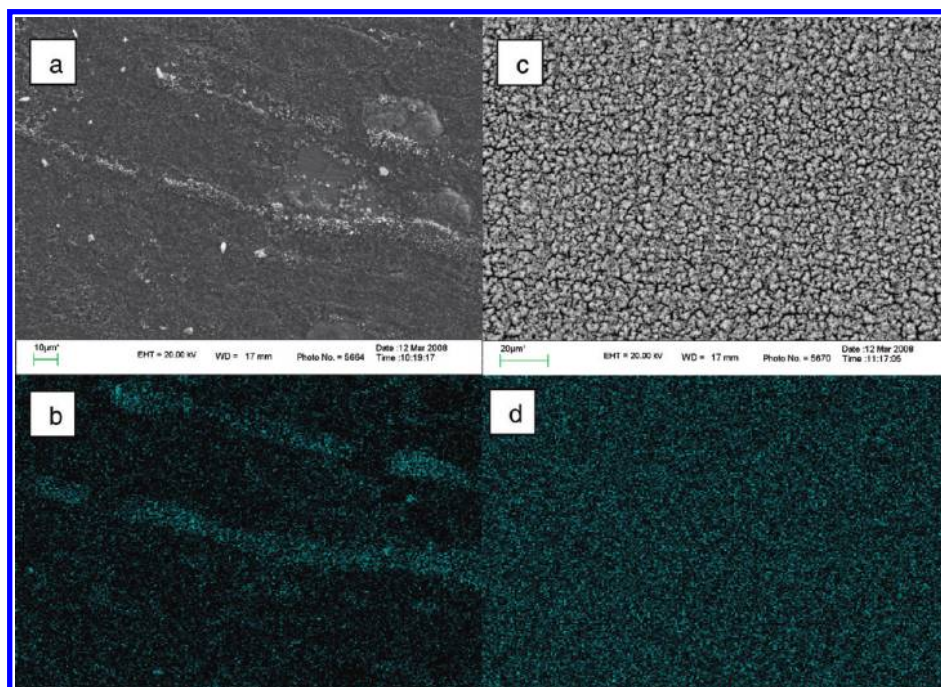


Figure 3. (a) SEM micrograph of 1F0.3, (b) Mn mapping on 1F0.3, (c) SEM micrograph of 1AIS0.3, and (d) Mn mapping on 1AIS0.3.

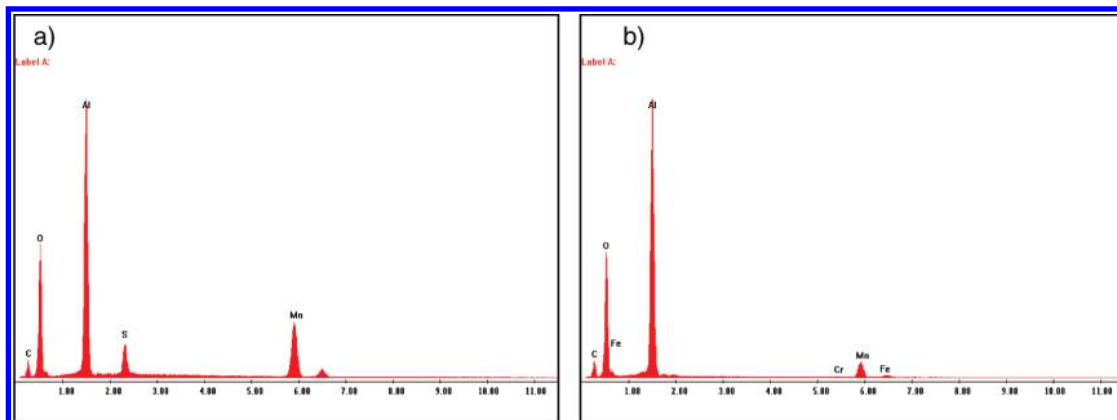


Figure 4. EDS spectra of (a) 1AIS0.3 and (b) 1F0.3.

varies on the surface, since monoliths are calcined at that temperature after the impregnation process. Sulfur content determined by EDS after the water treatment is shown in Table 3. It decreases with the increase of the washing time; however, an increase in sulfur content is observed when the sheet is calcined after the washing process. This could indicate that sulfur

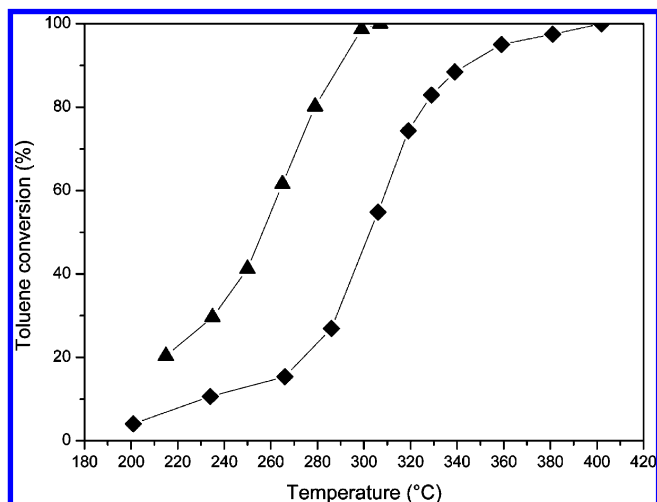
migrates to the surface when the sample is calcined. Therefore, it was concluded that this method is not appropriate to eliminate SO_4^{2-} ions. For this reason, it was decided to change the anodization process, avoiding the use of sulfuric acid. Thus, an aluminum monolith was anodized using oxalic acid ($H_2C_2O_4$) as electrolyte, because although $C_2O_4^{2-}$ ions could remain

Table 3. Wash Conditions of the Anodized Aluminum Sheets and Sulfur Content

sample	washing time (min)	calcination temperature (°C)	sulfur content (wt %)
A ₁	—	—	6.5
A ₂	30	—	6.1
A ₃	90	—	5.6
A ₄	90	500	6.8

retained, they are easily eliminated during the calcination of the sample.²³ The characteristics of this monolith (AIO) are shown in Table 1. The AIO specific surface area is approximately half of the AIS (H₂SO₄-anodized aluminum monolith) specific surface area. However, a higher active phase loading was obtained after the impregnation with 0.3 mg/L manganese acetate solution (1AIO0.3). This could be related to the elimination of the impregnating solution excess, which was removed by blowing air instead of by centrifugation. In addition to a higher manganese loading, an increase in the specific surface area of the monoliths is observed, indicating that during the impregnation the alumina area changes by dissolution–precipitation, causing microporosity. These characteristics are very important from the catalytic point of view. In order to verify that eliminating solution excess by blowing air results in a greater retention of active phase, an aluminum monolith anodized with H₂SO₄ was impregnated and the excess was eliminated using this procedure. Actually, 45 mg of active phase (this value is not shown in Table 1) was retained instead of 13.9 mg obtained by centrifugation. Later, to increase the active phase loading to a value comparable to that obtained with 1AIO0.3, a second impregnation of this monolith was carried out, resulting in 2AIS0.3 catalyst. As shown in Table 1, both the amount of active phase and the specific surface area significantly increased but this was not enough to achieve the higher catalytic activity presented by the 1AIO0.3 catalyst (Figure 5). Catalyst prepared from H₂C₂O₄-anodized aluminum monolith was much more active than catalyst from H₂SO₄-anodized aluminum, despite having lower manganese loading and lower specific surface area. As stated above, the presence of sulfate ions can influence the acidity of the medium during impregnation or can form inactive manganese sulfate and thus affect the catalytic activity.

It has been published that, when oxalic acid is used in the anodizing process, thicker layers of alumina are formed because this electrolyte has less ability to dissolve oxides than sulfuric

**Figure 5.** Catalytic activity in toluene combustion of 1AIO0.3 (▲) and 2AIS0.3 (◆) catalysts.

acid.^{24,25} The pore number obtained with H₂C₂O₄ is lower than that obtained with H₂SO₄.² The local temperature increase produced by the current passage through the pores is higher when the number of pores is lower (higher current density). The increase of temperature within the pores produces the dissolution of pore walls, producing pores of larger size. Thus, the specific surface area of the alumina layer formed using H₂C₂O₄ is lower due to the lower pore number and its larger size.²⁶ While the anodizing process using H₂SO₄ as electrolyte produces a more porous layer than the H₂C₂O₄ anodizing process,⁴ the latter method is preferable when using manganese oxide as active phase since the sulfate remaining on the surface even after washing causes the poisoning of the catalyst.

Due to the excellent results obtained using θ - δ -Al₂O₃ as a support for manganese oxide powder catalyst,¹⁴ it was decided to use this support for monolithic catalysts. FeCrAlloy monoliths were coated with a layer of θ - δ -Al₂O₃ and then impregnated with manganese acetate solutions. Many factors influence the suspension characteristics, mainly the particle size of the solid,^{27,28} the nature of the dispersing medium,²⁹ the solid concentration, and the pH.³⁰ Agrafiotis and Tsetsekou²⁸ studied the effect of the pH on the slurry stability and viscosity. The alumina coating was made from a 20 wt % suspension of particles 6.7 μ m in size. The isoelectric point of θ - δ -Al₂O₃ is around 7.9; thus, the pH of the suspension was adjusted to 3 in order to avoid the agglomeration of particles and to have a stable suspension. The excess loading for both alumina coating and manganese acetate solution during the impregnation was removed using the technique of blowing air. As demonstrated above, this technique is preferable because it achieves higher loading without blocking the channels. The characteristics of these catalysts (*n*FAX) are shown in Table 1. Indeed, alumina loading during the coating was higher in *n*FAX monoliths than that in monoliths coated with Nyacol. It is important to analyze the influence of the studied impregnating variables (number of stages and solution concentration) on the amount of active phase deposited. In all studied cases the second impregnation favors an increase of the active phase loading. However, the increase is different depending on the origin of the alumina used. The results obtained with *n*Fx and *n*Alx catalysts are different from those observed with *n*FAX, where the same conclusion as in the painting of a surface is observed, that multiple diluted layers are preferable to a single concentrated layer. Besides the amount of active phase deposited, it is important to determine whether this material is well adhered to the substrate. As shown in Table 1, the weight loss was similar and was about 2.5% in all catalysts prepared by this method, indicating a good adhesion of the alumina and manganese coating.

It is expected that a higher amount of MnOx loading causes an increase in catalytic activity. This is verified in general terms by considering the significantly higher catalytic activity of the *n*FAX monoliths in the combustion of the three studied molecules (Table 2). Differences of about 50 and 100 °C in *T*₈₀ values in ethyl acetate and toluene combustion respectively were observed when *n*Fx and *n*FAX catalysts are compared. The higher amount of alumina and its higher specific surface area could explain the higher amount of active phase retained and, therefore, its higher catalytic activity. Particularly 2FA0.6 and 2FA0.3 catalysts were significantly more active, showing *T*₈₀ values of 255 and 266 °C, respectively, in the combustion of toluene, the more difficult molecule to oxidize among the three compounds studied.

The impact of pore diffusion has been discarded using the flat plate expression of the Weisz modulus³¹ that is useful for interpreting experimental results since it only includes observable parameters. The value obtained in the most adverse conditions

(toluene total conversion with the monolith presenting the maximum amount of coating, 482 mg in 2FA0.3, which means an average coating thickness of less than 25 μm) was 0.05, far from the limit value of 0.15, below which there is no resistance to pore diffusion. This result is coherent with the thin catalytic coating deposited on monoliths that means a very short diffusion path.

It is interesting to analyze the catalytic performance of 1FA0.6 and 1FA0.3 monoliths. These catalysts presented a similar catalytic performance evidenced by similar T_{80} values in ethanol and toluene combustion despite having different manganese oxide loadings. This fact could indicate that not only the active phase loading influences the catalytic performance but also MnOx dispersion plays an important role. As also observed in a previous paper, a better catalytic performance was reached when highly dispersed manganese oxide species were generated on the surface.¹⁴ Thus, it could be assumed that the higher manganese loading retained in 1FA0.6 is compensated by higher manganese oxide dispersion on 1FA0.3 catalyst, and this could explain the similar catalytic behaviors that these catalysts presented.

4. Conclusions

Considering the catalytic supports separately, higher manganese loading is obtained using a concentrated manganese acetate solution (0.6 mg/L), and the loading increases with the number of impregnations. The type of alumina acting as a support of the active phase (manganese oxide) influences the catalytic activity in combustion reactions. Monolithic catalysts prepared on FeCrAlloy coated with colloidal alumina (Nyacol) were more active than those prepared on H_2SO_4 -anodized aluminum despite similar manganese loadings and lower surface areas. The low activity of aluminum monoliths is due to the presence of residual SO_4^{2-} ions from the anodization process that poisons the catalyst, forming MnSO_4 . This problem is solved when the anodization process is carried out with oxalic acid. A structured catalyst prepared on $\text{H}_2\text{C}_2\text{O}_4$ -anodized aluminum showed excellent catalytic behavior in the toluene combustion.

The method used to remove the loading excess has a direct consequence on the retained active phase loading. Higher active phase loadings were obtained blowing air instead of using centrifugation.

Catalysts prepared from FeCrAlloy covered with θ - δ - Al_2O_3 were the most active in this study, allowing the total combustion of toluene at about 260 °C.

Acknowledgment

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