ELSEVIER

Chemical Engineering Journal 139 (2008) 430–435

Chemical Engineering Journal

www.elsevier.com/locate/cej

Washcoating of metallic monoliths with a MnCu catalyst for catalytic combustion of volatile organic compounds

Bibiana P. Barbero [a], Luciano Costa-Almeida [b], Oihane Sanz [b],
María Roxana Morales [a], Luis E. Cadus [a], Mario Montes [b,*]

[a] *Instituto de Investigaciones en Tecnología Química (INTEQUI), Universidad Nacional de San Luis (UNSL), Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICET), Chacabuco y Pedernera, 5700 San Luis, Argentina*
[b] *Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Química de San Sebastián, Universidad del País Vasco, P. Manuel de Lardizabal 3, 20018 San Sebastián, Spain*

Received 9 July 2007; received in revised form 23 December 2007; accepted 28 December 2007

Abstract

A ready-made MnCu catalyst showing a good performance in the combustion of volatile organic compounds has been deposited on FeCrAlloy® metallic monoliths by means of washcoating. With the aim of depositing a homogeneous and well-adhered layer of catalyst on the monoliths, the effects of a pre-coating with colloidal alumina as a primer, the solid concentration in the slurry, the addition of a stabilizer to the slurry, and the immersions number of the monolith in the slurry were studied. The addition of a stabilizer to the slurry was necessary to prevent sedimentation and to achieve reproducible washcoatings. The pre-coating of the monolith with the primer improved the washcoating adherence obtained with one impregnation but a better adherence did not compensate a lower solid load due to a lower surface roughness. A higher amount of deposited material was obtained with the slurry at 35 wt% making two impregnations. The obtained monoliths showed excellent catalytic activity in the combustion of ethyl acetate and toluene. The activity as well as the surface area and pore volume of each monolith increased with the amount of retained solid.

Keywords: Metallic monoliths; Washcoating; VOC combustion; Toluene; Ethyl acetate

1. Introduction

The catalytic oxidation is the most attractive way to eliminate volatile organic compounds (VOCs) at low concentration in industrial gaseous effluent. For practical applications, the catalyst should be supported on a structured support to treat large gas flows with low pressure drop.

The most widely used structured supports are the monoliths with longitudinal parallel channels made of ceramic or metallic materials. Monoliths for polluted emissions control are being used since the sixties [1,2]. They are the substrate or matrix where a material of high surface area which acts as catalytic support is deposited. Then, the active phase is dispersed on the catalytic support.

The most popular supports with monolithic structure are the ceramic ones, due to their wide use in the automobile sector. They are made mainly of cordierite and obtained by extrusion. Despite their wide use, these monoliths have limitations related to the minimum wall thickness for a correct extrusion (100 μm) and a low thermal conductivity that, associated to the flow model in the longitudinal channels, origins a non-homogeneous radial thermal profile [3,4].

Although metallic monoliths are more expensive than ceramic ones, they present a smaller wall thickness (25–50 μm) and higher thermal conductivity [5]. However, the low adherence of the washcoating acting as support of the active phase is their main disadvantage. This problem can be solved by a combination of chemical modifications in the preparation of the washcoating and by the use of alumina bearing ferritic alloys (FeCrAlloy, Khantal, etc.) [6]. These ferritic alloys are used in the monolith manufacture for two reasons [7]. They support very well high temperatures and by means of adequate physical chemical treatments, they are covered with a well-adhered alumina layer that can act as substrate to deposit thicker layers of support. The alloy with 3–5% aluminum has the peculiarity that at high temperatures the aluminum migrates to the surface

---

[*] Corresponding author. Tel.: +34 943 018183; fax: +34 943 015270.
E-mail address: mario.montes@ehu.es (M. Montes).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.12.033

generating an alumina layer in form of whiskers that allows the anchoring of the washcoating [7–10].

The rheological properties of the suspension containing the catalyst are very important to obtain a satisfactory washcoating. The suspension should be stable and have an adequate viscosity to achieve a homogeneous coverage of the metallic monolith. Many factors influence on the suspension characteristics, mainly, the particle size of the solid [11–13], the nature of the dispersing medium [1], the solid concentration and the pH [14,15]. Agrafiotis and Tsetsekou [13] studied the effect of the pH on the slurry stability and viscosity. Also, Agrafiotis et al. [11,12] studied the effect of particle size on the adhesion properties of oxides washcoating on cordierite honeycombs, ball-milling the oxides for several periods of time. They found that there is a certain threshold value (around 5 μm) below which the particle size has to be reduced in order to get a satisfactory adhesion of the washcoating layer to the support.

In this work, the preparation of a manganese–copper mixed oxide catalyst washcoated on metallic monoliths is reported. This manganese–copper oxide catalyst has shown a very good catalytic behavior for the VOCs combustion [16]. The main goal was to find out the most convenient preparation conditions to obtain a homogeneous and well-adhered washcoating. For this purpose, the effects of a pre-coating with colloidal alumina as a primer, the solid concentration in the slurry, the addition of a suspension stabilizer, and the immersion numbers were studied. Finally, the catalytic performance was evaluated in the ethyl acetate and toluene combustion.

2. Experimental

2.1. Preparation of monolithic catalysts

Manufacture of the monoliths. The monoliths were prepared from thin foils (0.05 mm of thickness) of FeCrAlloy® (Fe: 72.8%; Cr: 22%; Al: 5%; Y: 0.1%; and Zr: 0.1%) by rolling around a spindle alternate flat and crimped foils. The monoliths (3 cm long and 1.6 cm of diameter; 330 cpi) were then calcined at 900 °C for 22 h.

Washcoating with the primer: colloidal alumina. The metallic monoliths were washcoated with pure Nyacol® Al 20 (20 wt% colloidal alumina) and aqueous dilutions Nyacol:water = 1:1; 1:2 and 1:4. The monoliths were dipped into the slurry for 10 s, withdrawn to constant speed of 3 cm min^{-1} and then, the suspension excess was eliminated by centrifugation at 400 rpm for 10 min. Finally, they were dried at 120 °C for 1 h and calcined at 500 °C for 2 h.

Washcoating with the active phase: MnCu catalyst. MnCu catalyst was obtained as a powder by the coprecipitation method from $Mn(NO_3)_2 \cdot 4H_2O$ and $Cu(NO_3)_2 \cdot 4H_2O$ with a molar ratio Mn:Cu = 1:1. The details of the synthesis procedure and characterization results were presented in a previous paper [16]. In order to be used for washcoating, the ready-made MnCu catalyst was ball-milled at 400 rpm for 5 h. Then, aqueous suspensions with 30, 35, and 40 wt% solids content adding colloidal alumina (Nyacol® Al 20) as stabilizer and a suspension with 40 wt% solid content without colloidal alumina were prepared. The pH 4 was adjusted employing diluted HNO_3. The slurries were subjected to orbital agitation for 17 h before being used for washcoating. The monoliths without and with a primer (denoted as MF and MF + Ny, respectively) were washcoated with the slurries of MnCu catalyst following the steps described for the washcoating with colloidal alumina. One and two immersions (indicated in the sample denomination by means of arabic number 1 or 2, respectively) were performed with each slurry concentration. Finally, they were calcined at 500 °C for 2 h.

2.2. Characterization techniques

Particle size distribution. Particle size distribution of the crushed MnCu catalyst 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 catalyst and 10 ml of water were added to the sample chamber.

Isoelectric point determination. A Zetasizer Nano series from Malvern Instruments was employed. The catalyst was dispersed in electrolytic solution of 0.003 M NaCl adjusting the pH with either NaOH or HNO_3 solutions.

Viscosity measurements. After the washcoating, 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.

Washcoating adherence test. The adherence of the washcoatings was evaluated in terms of the weight loss after exposure of the monoliths to ultrasounds. The coated monoliths were immersed in 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 was gravimetrically determined measuring the weight of the samples both before and after the ultrasonic treatment.

Textural characteristics measurement. Adsorption–desorption isotherms of liquid nitrogen at 77 K were performed in an ASAP 2000 apparatus from Micromeritics after outgassing the monoliths at 120 °C. A home-made cell was used for the measurement of complete monoliths.

Scanning electron microscopy (SEM). The morphology of samples was examined with a scanning electron microscope LEO 1450VP. The samples were covered with a thin gold layer to improve the images.

2.3. Catalytic tests

The monoliths were pretreated in air flow at 450 °C for 1 h. After cooling them at 100 °C, they were evaluated in the combustion of ethyl acetate and toluene. The reacting stream was 1000 cm^3/min (GHSV 10,000 h^{-1}) with a composition of 1000 mg C/m^3 diluted in purified air. The reaction was performed at atmospheric pressure. The temperature was increased at 2.5 °C/min between 100 and 400 °C. The gaseous mixtures were analyzed before and after reaction by gas chromatography, in the case of ethyl acetate combustion, and by mass spectrometry for toluene combustion. Also, CO_2 was measured with an on-line IR detector.

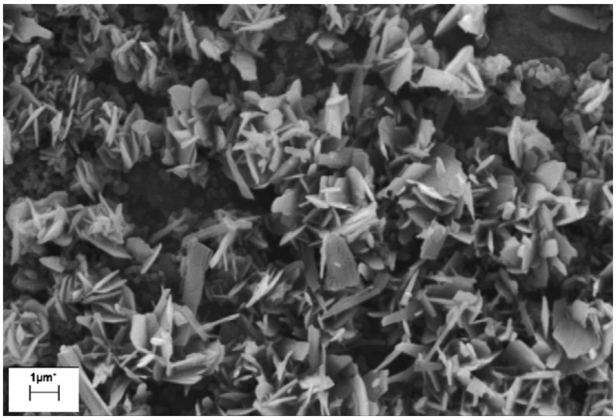

Fig. 1. SEM photograph of FeCrAlloy® calcined at 900 °C for 22 h.

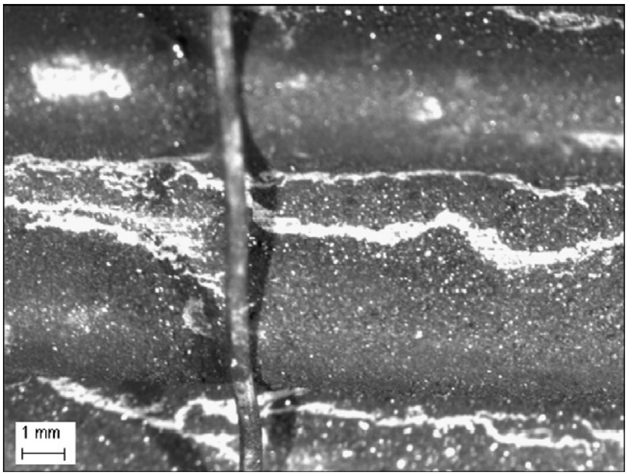

Fig. 3. View of the monolith channels with washcoating from the slurry at 40 wt% without colloidal alumina as stabilizer.

3. Results and discussion

3.1. Preliminary studies

When depositing an active phase on a metallic monolith by washcoating, the major challenge is to achieve a homogeneous and well-adhered catalyst layer on the monolith walls. The washcoating adherence is very important since the operating conditions of the catalysts in the volatile organic compounds combustion involve high space velocities of the gaseous stream. In order to favor the anchorage of the washcoating to the metallic substrate, the FeCrAlloy® monoliths were thermally treatment (900 °C for 22 h). In Fig. 1, the SEM micrograph of a treated FeCrAlloy® foil shows the alumina layer formed. Due to surface roughness, catalyst fine particles from a slurry are retained and the mechanical adherence to the metallic substrate is induced.

Considering the results reported by Agrafiotis et al. [11,13], the MnCu catalyst powder employed in this work was ball-milled in order to reduce the particle size. The characteristic particle size d_{90} (90% of the particles of the batch are smaller than that) was 4.5 μm after ball-milling it for 5 h.

To select the suspension pH, zeta potential measurements for the MnCu catalyst were made. Fig. 2 shows that the isoelectrical point of the catalyst is 7.7. The highest zeta potential was 27 mV at pH 4 and lower. Then, the suspensions were prepared in an aqueous medium and the pH was adjusted to a value of 4 with diluted HNO_3 for all the preparations.

The selected pH and a characteristic particle size, $d_{90} < 5$ μm [11] should produce stable suspensions but, only 10 min after stopping the agitation, the solid particles settled. However, washcoatings with the suspension of 40 wt% were assayed by dipping the monolith immediately after stopping the agitation. The amount of catalyst retained was very different in two monoliths prepared in the same way. Furthermore, the coating was non-uniform. The monolith showed channels with highly charged zones and some others, almost bare (Fig. 3). Performing a second immersion, the amount of solid retained was excessive and the monolith channels were plugged (Fig. 4).

In order to solve these problems and to improve the suspension stability, 6% colloidal alumina (Nyacol®) was added as stabilizer. Thus, the suspensions were stable (not settling in 24 h) with viscosities around 5.5 mPa s. The washcoatings obtained were homogeneous (Figs. 5 and 6) presenting good reproducibility (loading differences less than 10%).

As it is expected that the catalytic activity of the monoliths will be related to the amount of active phase retained, it

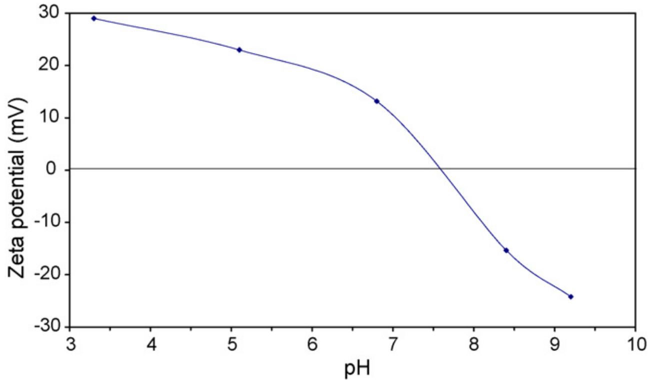

Fig. 2. Zeta potential vs. pH curve for the ready-made MnCu catalyst.

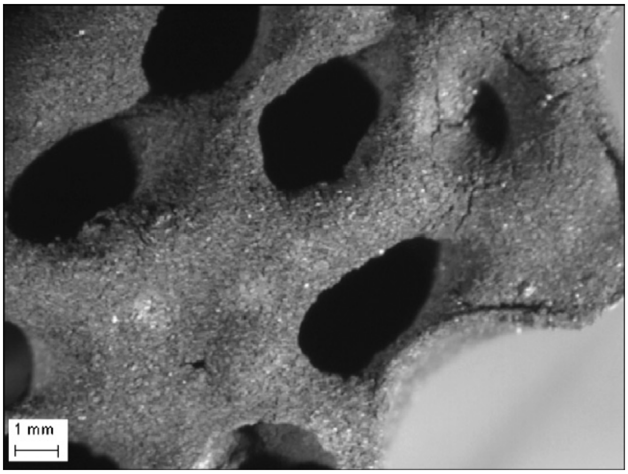

Fig. 4. Top view of a monolith with blocked channels.

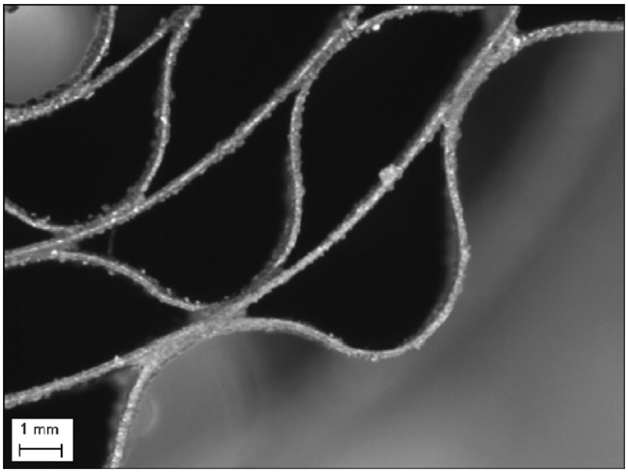

Fig. 5. Top view of a monolith with homogeneous washcoating.

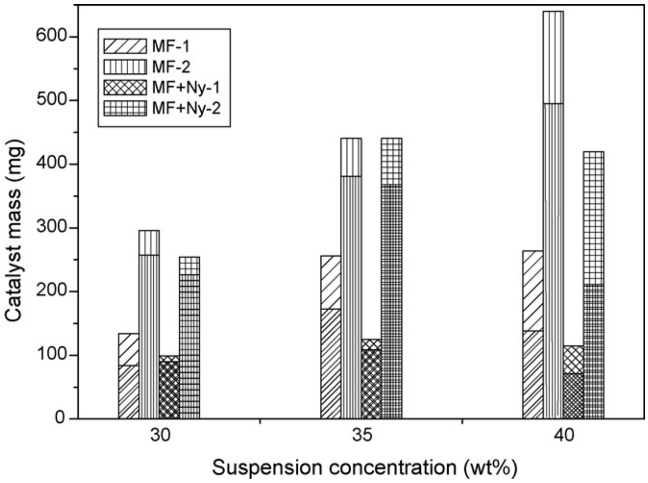

Fig. 7. Amount of catalysts retained after the washcoating (maximum value indicated by the bars) and after the adherence test (internal bar with denser traces) for the prepared monoliths.

is desirable that the highest possible amount of catalyst should be deposited homogenously on the surface. It is also important to obtain a good adherence of the deposited material since the catalyst loss would produce an activity loss. In this work, the effect of preparation variables on the amount of catalyst deposited and its adherence was evaluated. The results are summarized in Fig. 7 in which, for each solid content, the amount of catalyst retained during the washcoating (maximum value indicated by the bars) and the catalyst mass remnant after the adherence test (internal bar with denser traces) are shown. These results are discussed in detail below.

3.2. *Effect of the pre-coating with primer*

In some cases, the adherence of the active phase can be improved making a pre-coating of the metallic substrate with a primer [17,18]. With the objective of studying this possibility, washcoatings with aqueous dilutions of colloidal alumina (Nyacol® Al 20) in different concentrations were made. As it is expected, at a higher concentration of colloidal alumina, a higher amount of alumina is retained. However, this causes a loss of surface roughness which makes difficult the subsequent active phase washcoating. Therefore, the primer was added from a diluted suspension (Nyacol®:water = 1:4) which shows a loading around 0.17 wt% without losing completely the roughness. In Fig. 8, a SEM photography of the foil pre-coated with Nyacol®:water = 1:4 is shown.

Comparing the loading of the monoliths with and without a primer (Fig. 7), it is observed that the monoliths with primer (MF + Ny-1 and MF + Ny-2) retain lower amount of MnCu catalyst than those without primer. The washcoating with diluted colloidal alumina decreases the surface roughness of calcined FeCrAlloy® explaining the unfavorable effect with regard to the capacity to retain solids.

The adherence of the active phase can be evaluated by difference between the amount of catalyst before and after the adherence test (portion of the bar with sparser traces in Fig. 7). In this regard, a great difference of weight loss is observed between the monoliths with and without primer when a single immersion is made (MF-1 and MF + Ny-1). Evidently, the pre-coating with the primer improves the adherence of the active phase.

Fig. 6. Lateral view of a monolith with homogeneous washcoating.

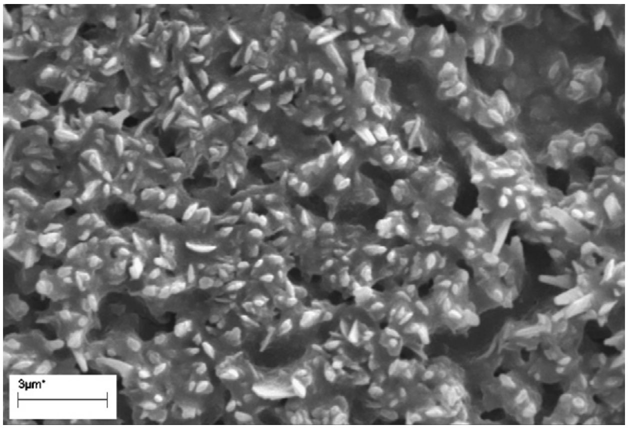

Fig. 8. SEM photograph of FeCrAlloy® pre-coated with diluted colloidal alumina (Nyacol®:water = 1:4).

However, considering the amount of solid remaining after the adherence test (Fig. 7, the portion of the bar with denser trace), it can be deduced that the increasing adherence is not enough to compensate the lower amount of solid retained.

The weight loss of the monoliths with two immersions (MF-2 and MF + Ny-2) is very similar, except for the suspension of 40 wt%. When the second immersion was carried out, the monolith surface was constituted mainly by a MnCu catalyst layer instead of an alumina layer. This could explain the disappearance of the primer effect on the catalyst adherence when two immersions are made.

Consequently, it can be concluded that in our case, the precoating with colloidal alumina as primer do not offer advantage on the final loading of catalyst.

3.3. *Effect of the number of immersions*

In order to increase the amount of catalyst washcoated on a monolith, successive immersions can be made. Depending on the slurry viscosity the loading achieved with the first immersion can be higher or lower than that achieved with the successive immersions. This is determined by attractive forces occurring between the first washcoating layer and the subsequent one [13].

As can be seen in Fig. 7, when two immersions of the monolith are made, more than the double amount of catalyst is retained. With regard to the adherence of the deposited solid making two immersions, the results on monoliths with and without primer are different. The lost amount of catalyst in the monoliths with primer and two immersions is about four times higher than in the monoliths with a single immersion. Although this difference is not so marked in terms of percentage, a higher weight loss is observed for the monoliths with two immersions. For the monoliths without primer, the weight loss with one or two immersions is similar (in the range of ±3.5%) irrespective of the suspension concentration. However, expressing the weight loss in percentage (Fig. 9), the monoliths with two immersions show a notably better adherence (lower weight loss).

In Fig. 7, it is clearly observed that the monoliths with two immersions retain more than the double amount of solid in comparison to the monoliths with a single immersion even after the adherence test (the portion of the bar with denser trace). In consequence, it is concluded that two immersions are an effective way to increase the deposited solid amount, which could increase the catalytic activity of the monolith.

3.4. *Effect of the solid content of the slurry*

Several authors have investigated the effect of solids content on both the slurry characteristics and the loading achieved on the monolith [13,15,19]. In general, they recommend slurry solids content between 35 and 50 wt%. In this work, the slurries were prepared with solids content of 30, 35, and 40 wt%. As can be observed in Fig. 7, the loading increases with the suspension concentration, although the difference between 35 and 40 wt% is very small with the exception of the monoliths without primer and with two immersions. The results of the adherence test (Fig. 9) show that the weight loss with the slurries of 30 wt% and 35 wt% are similar and, except in the case of the monoliths without primer and with one immersion, the weight loss percentages are very low. With the 40 wt% slurry, the highest weight loss is observed. From these results, it is clear that more concentrated slurry (40 wt%) do not give comparative advantages. Considering the remaining solid amount after the adherence test (Fig. 7), it can be concluded that the best results are obtained with the suspension at 35 wt%.

3.5. *Catalytic activity*

On the basis of the results presented until now, it was decided to evaluate the catalytic behavior of the monoliths washcoated with the slurry at 35 wt% in the combustion of two different VOC molecules, ethyl acetate and toluene. The results are presented in Figs. 10 and 11.

The results of the catalytic activity are very promissory. The monoliths showed very good activity in the ethyl acetate combustion as well as the toluene combustion and only the total oxidation products, CO_2 and H_2O, were detected under the experimental conditions employed in this study. The conversion of ethyl acetate starts at 150–170 °C and it is completed below

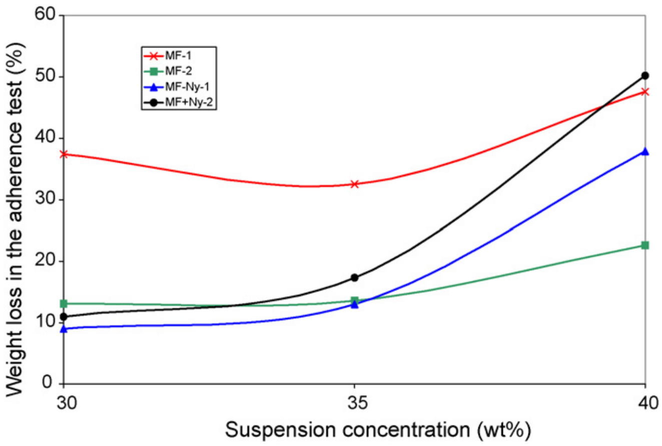

Fig. 9. Weight loss percentage during the adherence test.

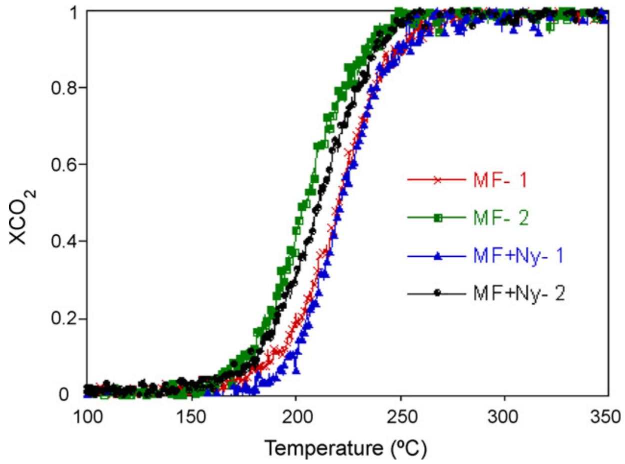

Fig. 10. Catalytic activity in the ethyl acetate combustion.

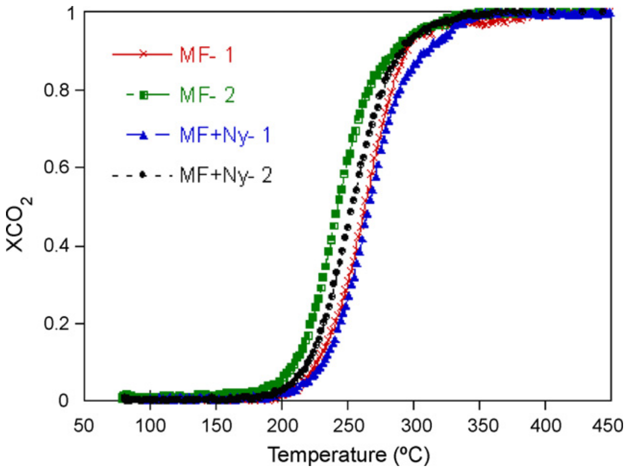

Fig. 11. Catalytic activity in the toluene combustion.

Table 1
Textural characteristics for the monoliths prepared with the suspension at 35 wt%

Monolith	Surface area (m^2/monolith)	Pore volume (cm^3/monolith)	Coating amount (g/monolith)
MF-1	3.7	0.020	0.173
MF-2	7.9	0.050	0.381
MF + Ny-1	3.5	0.016	0.109
MF + Ny-2	8.8	0.050	0.365

250–280 °C (Fig. 10), while the toluene conversion starts at about 170–200 °C and it is completed below 350 °C (Fig. 11). As it is expected, in both reactions, the catalytic activity increased with the increase in the amount of solid deposited.

Likewise, the monoliths with two immersions have surface areas (m^2/monolith) and pore volume (cm^3/monolith) higher than those with a single immersion (Table 1). Obviously, this is due to a higher amount of catalyst deposited.

4. Conclusions

The most relevant conclusion of this study is that a ready-made MnCu oxide catalyst with an excellent catalytic activity in the combustion of ethyl acetate and toluene was successfully washcoated on metallic monoliths. The activity, the surface area and the pore volume increased with the increasing amount of solid retained. A higher catalyst loading was obtained using the slurry with a solid content of 35 wt% and performing two immersions.

Colloidal alumina was used as stabilizer of the suspension and as a primer. The former option was necessary to obtain a stable suspension and reproducible washcoatings. The latter one did not produce significant improvement over the direct washcoating of the calcined FeCrAlloy monoliths.

Acknowledgements

The authors thank the financial support from MEC of Spain (Project MAT2003-0654), CYTED (Project PI0269), the Universidad Nacional de San Luis and CONICET of Argentina.

References

[1] J. Votruba, J. Sinkule, V. Hlavácej, J. Skrivánek, Chem. Eng. Sci. 30 (1975) 117.
[2] L.L. Hegedus, AIChE J. 21 (5) (1975) 849.
[3] D.A. Hickman, L.D. Schmidt, J. Catal. 136 (1992) 300.
[4] D.A. Hickman, L.D. Schmidt, J. Catal. 138 (1992) 267.
[5] C.J. Bennett, T.E. Hayes, S.T. Kolaczkowski, W.J. Thomas, Proc. R. Soc. Lond. A 439 (1992) 465.
[6] M.V. Twing, D.E. Webster, in: A. Cybulski, J.A. Moulijn (Eds.), Structured Catalysts and Reactors, Marcel Dekker Inc., New York, 1998, p. 59.
[7] P. Ávila, M. Montes, E. Miró, Chem. Eng. J. 109 (2005) 1.
[8] M.F.M. Zwinkels, S.G. Järas, P.G. Menon, Prep. Catalyst VI (1995) 85.
[9] A. Cybulski, J.A. Moulijn, Catal. Rev. Sci. Eng. 36 (2) (1994) 179.
[10] J.G. Irwin, Odor Renoval by Catalytic Oxidation, Warren Spring Lab., Report No. LR285 (AP).
[11] C. Agrafiotis, A. Tsersekou, J. Eur. Ceram. Soc. 20 (2000) 815.
[12] C. Agrafiotis, A. Tsetsekou, A. Ekonomakou, J. Mater. Sci. Lett. 18 (1999) 1421.
[13] C. Agrafiotis, A. Tsetsekou, J. Mater. Sci. 35 (2000) 951.
[14] J. Ren, W. Wang, S. Lu, J. Shen, F. Tang, Powder Technol. 137 (2003) 91.
[15] V. Blachoud, D. Goula, C. Philippopoulos, Ind. Eng. Chem. Res. 31 (1992) 364.
[16] M.R. Morales, B.P. Barbero, L.E. Cadús, Appl. Catal. B 74 (2007) 1.
[17] S. Yasaki, Y. Yoshino, K. Ihara, K. Ohkubo, US Patent No. 5,208,206 (1993).
[18] I.M. Axelsson, L. Lowendahl, J.E. Otterstedt, Appl. Catal. 44 (1988) 251.
[19] T. Shimrock, R.D. Taylor, J. Collins, Eur. Patent 0157651 (1985).