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A comparative study of V_2O_5/AC and V_2O_5/Al_2O_3 catalysts for the selective catalytic reduction of NO by NH_3

A. Boyano[a], M.J. Lázaro[a,*], C. Cristiani[b], F.J. Maldonado-Hodar[c], P. Forzatti[b], R. Moliner[a]

[a] Instituto de Carboquímica, CSIC, Miguel de Luesma Castán 4, 50018 Zaragoza, Spain
[b] Dipartimento de Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20322 Milano, Italy
[c] Departamento de Química Inorgánica, Facultad de Ciencias, Avda. Fuentenueva, s.n, 18071 Granada, Spain

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ABSTRACT

The influence of two different washcoats deposited on ceramic honeycombs (alumina and carbon) on the catalytic and mechanical properties of catalysts are examined in this work. A series of carbon and alumina washcoated samples was prepared through a dip-coating method and subsequently cured and treated to reach a suitable chemistry surface. Carbon-coated monoliths present a high washcoat homogeneity, high integrity and a suitable chemistry surface that favour NO reduction at low temperatures. The carbon washcoat was bonded perfectly to the ceramic monoliths. The high adherence between both materials, checked by vibrational tests, provides higher resistance indexes against axial compression and prevents crack propagation. Both facts are a consequence of the high mechanical strength of the catalyst.

On the other hand, alumina coatings present better temperature resistance, although their adherence to ceramic monoliths is not as good as in carbon-coated samples. The properties of alumina coatings are strongly dependent on the slurry viscosities, which influence the integrity of the washcoat, mechanical properties and even NO conversion. Both series of catalysts have shown a good NO conversion under on-board conditions, although the key parameters of each washcoat are completely different.

1. Introduction

The abatement of nitrogen oxides generated by diesel engines is a matter of both scientific and technological interest. Since Iwamoto et al. [1] and Hamada et al. [2] showed independently that hydrocarbons could be used as reducing agents to reduce NO_x in an oxidising atmosphere, many possible catalyst formulations have been extensively studied to find suitable catalysts and reductants, which are effective for the selective catalytic reduction (SCR) of NO_x in the exhaust *gases from* numerous applications, working under oxygen excess and *at lower temperatures*.

NO_x reduction efficiency by means of SCR technology depends on both catalysts and reductant agents. Typical reductants are hydrocarbons, ammonia or urea. Among them, ammonia is known to be very selective towards N_2 and provides high efficiencies [3]. However, it does not present the most desirable properties for its use in some applications, such as on-board applications, because of storage and handling difficulties. It should be generated in situ by hydrolysis and the decomposition of urea, which can reduce the efficiency [4].

A large number of materials have been tested as SCR catalysts. Catalysts are usually structured, as they present a lower pressure drop and handling feasibility [5]. Generally speaking, structured catalysts consist of three kinds of materials: the substrate, which gives the shape and most of the mechanical resistance properties; washcoats, which provides high surface area without interacting with the active element; and the active phase, which is the catalytic element.

In some application fields, a cordierite monolith is usually the substrate material due to its excellent properties [5]. Low-pressure drop in the exhaust system, good thermal shock resistance and refractoriness are some of its most important properties. However, cordierite presents a low surface area, which does not allow its direct use for catalytic approaches, and thus it should be coated with a porous phase. Good washcoat adherence and compatibility to washcoat and catalyst active phases are also required. In recent years, a great number of washcoats have been tested for the SCR of NO as well as different techniques for coating monoliths. A recent review [6] provides details about most of the coating methods (colloidal coating, sol–gel coating, slurry coating and polymer coating) using different materials (Al_2O_3, TiO_2, SiO_2 and ZnO_2 or activated carbon). All of them improve the porosity of the monolith to permit the high metal dispersion of the active phase.

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* Corresponding author. Tel.: +34 976733977; fax: +34 97673318.
E-mail address: mlazaro@icb.csic.es (M.J. Lázaro).

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The most widely used active phases for NO reduction are vanadium and copper. Supported vanadium oxides have been widely investigated in the last two decades [7]. The surface structures of vanadia supported either on metals oxides, such as Al_2O_3, SiO_2, ZrO_2 and TiO_2, or carbon materials are quite different from the bulk vanadia, as well the interaction between the active phase and supports. Consequently, the SCR efficiency of catalysts is highly dependent on the nature of the washcoat, the dispersion of the active phase and the presence of promoters/additives parameters that, in turn, are controlled by the method of preparation and pretreatments of both the washcoat and active phase.

For some uses, catalysts must be stable and active in a relatively low temperature region in the presence of excess oxygen, water vapour and sulphur dioxide, and they must resist some temperature peaks. These reasons make both alumina and activated carbon very promising candidates.

As a washcoat, Al_2O_3 has been widely reported [8–10] for its potential of supporting vanadium oxides as a SCR catalyst. Recently, researchers have focused on V_2O_5–alumina catalysts prepared by wet or dry impregnation methods for SCR-NH_3 of NO under lean-burn conditions [11]. Most of them have reported acceptable NO conversions at temperatures slightly higher than those required in on-board applications. However, today, several commercial catalysts based on γ-alumina pellets or monoliths are being used for the treatment of exhaust gases from nitric acid production plants at lower temperatures. In this application, copper–nickel oxides [12] and vanadium oxides [13] have shown the best results, and this opens up possibilities of use on-board as well.

As reported in the literatures [14,15], one of the most important parameters for catalyst preparation is the deposition of alumina on the monolith. Typical properties of an alumina coating slurry used to impregnate a 400 cpsi cordierite monolithic substrate are given by Shimrock et al. as summarizes Meille in [6]. They suggest that the solid loading of the slurry should range between 35 and 52 wt% and that the viscosity should range between 15 and 300 cP. Under these conditions, a predetermined amount of alumina coating could be achieved by means of the slurry rheological characteristics.

Alumina slurry preparation methods are very diverse, but ball-milling is the most widely used, especially in industrial applications. An examination of the slurry preparation and substrate coating procedures referenced in the literature does not reveal the parameters influencing the wet-milling process. However, it has been indicated that the H_2O/Al_2O_3 and H^+/Al_2O_3 ratios or the presence of active elements could be among them. The lack of studies on the influence of active elements on the rheological and deposition properties is very surprising. To the best of our knowledge, only Collic et al. [16,17] carried out explorative works to study the influence of active phase metals on the viscosity of slurries. They observed that the presence of alkaline in the slurry powder causes an increase in the viscosity, probably due to the higher amount of excluded ions.

Returning to the catalyst requirements, when SO_2 and particulate matter are also present in the exhaust gases, sulphur resistance and mechanical strength are necessary. Activated carbon-based catalysts are well known for resisting sulphur oxide poisoning [18]. In the last decades, there has been increasing interest in carbon-supported catalysts [19–22], although its use is not so widespread. On the basis of previous studies [19–22], it is known that activated carbon-based catalysts have been successfully tested for the SCR-NH_3 of NO for stationary applications. However, to the best of our knowledge, there are no previous studies where carbon-based catalysts have been applied to the emissions of other exhaust.

The well-established commercial vanadium catalysts based on metallic oxides present two main drawbacks. The narrow temperature window (350–450 °C) of the reactivity is the main obstacle for real applications, since it does not cover the main temperature range of some applications that work especially at low temperature (100–500 °C). Secondly, the deactivation caused by sulphur dioxide and dust contained in the exhaust gases is a problem [23]. Conversely, carbon-based catalysts have been demonstrated to be active at much lower temperature, i.e., 100–250 °C [19–22], and sulphur has a beneficial effect due to the formation of acidic compounds that improve the adsorption of NH_3 favouring its reaction [23,24]. In this way, carbon-based catalysts could be exposed directly without preheating and without the necessity of burning sulphur-free diesel fuels.

Although many works have been published on both alumina and activated carbon washcoat systems, they have rarely been compared under laboratory conditions close to real ones. We begin with a comparative study of the activity and deactivation causes for alumina and carbon-based catalysts. In this sense, this study deals with the washcoat quality and adherence as well as mechanical properties of various V_2O_5/Al_2O_3 and V_2O_5/AC catalysts prepared by dry and wet impregnation, respectively.

2. Experimental

2.1. Catalyst preparation

2.1.1. Catalysts based on carbon supports

Cordierite monoliths (400 cpsi, 1 cm diameter and 5 cm length) supplied by Cordering were coated with a polymer blend by the dip-coating method described elsewhere [19]. Briefly, this method consists of dipping the cordierite monolith into a liquid polymer that is subsequently cross-linked and carbonised. The polymers used were Furan resin (Huttens-Albertus) and polyethylenglycol (6000 mw, Sigma–Aldrich) as two carbon precursors. The first is in liquid state and the latter is solid, ground in a mill and sieved through a diameter less than 100 μm. The dip-coating was carried out with mixtures of Furan resin, PEG, acetone and HNO_3, as polymeration catalysts after withdrawing the monoliths from the blend; they were flushed with pressurised air to remove excess liquid in the channels. The carbon coating was cured first for 24 h at room temperature and later at 108 °C for 24 h to become a thermosetting polymer. The monoliths coated with the polymer were carbonised at 700 °C and later activated with CO_2 at 900 °C during 4 h to develop further surface area and porosity.

The as-prepared carbon-coated monoliths were treated with different oxidising agents to develop surface oxygen complexes. For this purpose, four different oxidation treatments with concentrated HNO_3, HNO_3(2N), H_2SO_4(2N) and H_2O_2 were applied. The liquid oxidation treatments of the activated coated monoliths were carried out for 24 h at room temperature. Subsequently, the monoliths were thoroughly rinsed with distilled water.

The oxidised carbon-coated monoliths were loaded with vanadium. The impregnation was carried out by the ion-exchange method with an excess of ammonium metavanadate solution (NH_4VO_3, Panreac, analysis grade) until equilibrium. To facilitate the dilution of ammonium metavanadate ca. 5 mg of oxalic acid was added. Under these conditions, the pH of solution remained neutral, and the solution had a yellow colour, indicative of the presence of VO^{2+} ions. These monoliths were placed in a holder containing 100 ml of the impregnating solution. The vessel was provided with a stirrer at the bottom to create a continuous flux of vanadium solution through the monolithic channels. This design allows vanadium to be deposited uniformly inside the channels. This process was extended for 24 h, which was enough time to reach equilibrium, where the solution became colourless. Subsequently, the monoliths were rinsed with distilled water in the same set up. After drying the monoliths, the catalysts were thermally treated in N_2

Table 1
Micro- and mesoporosity calculated by means of *t*-plot and BJH methods.

	Washcoat loading (wt%)	S_{BET} (m^2/g)	$V_{microp\,total}$ (cm^3/g)	V_{BJH} (cm^3/g)	$V_{microp<0.7\,nm}$ (cm^3/g)	$V_{microp\,medio}$ (cm^3/g)	Average diameter (A)
Plane cordierite	0	0.35	0.000	0.000	0.000	0.000	400
Al_2O_3 powder	–	145	0.003	0.457	0.000	0.003	149
Al_2O_3–3% V powder	–	136	0.006	0.473	0.000	0.006	142
Al_2O_3–5% V powder	–	138	0.006	0.391	0.000	0.006	139
V(3%)/Al_2O_3—(3.4)	7.2	102	0.001	0.040	0.000	0.001	121
V(3%)/Al_2O_3—(4)	3.9	–	–	–	–	–	–
V(5%)/Al_2O_3—(3.4)	7.9	137	0.000	0.022	0.000	0.000	92
V(5%)/Al_2O_3—(4)	4.9	48	0.001	0.003	0.000	0.001	–
AC coated monolith	6.0	807	0.017	0.033	0.012	0.005	–
V(3%)/AC + HNO_3(c)	6.5	273	0.009	0.028	0.006	0.003	63
V(3%)/AC + HNO_3(2N)	6.7	407	0.020	0.028	0.015	0.005	68
V(3%)/AC + H_2SO_4(2N)	6.2	608	0.017	0.028	0.013	0.004	65
V(3%)/AC + H_2O_2	6.1	458	0.014	0.022	0.010	0.004	67

at 350 °C. The nomenclature of the activated carbon-coated monoliths is as follows: V(*x*%)/AC + HNO_3(c) where V(*x*%) indicates the loading *weight* of V related to the carbon coating, AC indicates activated carbon washcoat and HNO_3(c) the oxidising agent used. The samples prepared are summarised in Table 1.

2.1.2. Catalysts based on alumina supports

The raw material used to synthesise V_2O_5/Al_2O_3 catalysts was commercial alumina supplied by Sasol and denoted Puralox SCFa140/L3. The alumina powder is characterised by a superficial area of around 150 m^2/g, a volume pore of 0.5 cm^3/g, a particle diameter lower than 100 nm and a 3% (w/w) of La_2O_3 that acts as an alumina stabiliser agent. Catalysts were prepared by doping the alumina powder with vanadium by means of a dry impregnation method and finally depositing the slurry prepared with the doped alumina powder on the monoliths by a dip-coating method.

First, Al_2O_3 powder was impregnated with an appropriate amount of V_2O_5 by means of a dry impregnation method. Stoichiometric amounts of NH_4VO_3 (Merck, 99% pure) were added to twice the amount of oxalic acid in a volume of distilled water equal to that of the γ-alumina porous volume. The solution was kept under continuous stirring and moderate heating to obtain the blue complex $(NH_4)_2[VO(C_2O_4)_2]$. Then the solutions were deposited on the γ-alumina by dry impregnation at room temperature, and the catalyst samples were dried for 12 h at 110 °C. Eventually, the catalysts were calcinated at 400 °C for 10 h with an increase and decrease temperature ramp of 2 °C/min to promote the removal of nitrates from the alumina powders.

In the chosen slurry route, the suitable ratios of HNO_3/Al_2O_3 and H_2O/Al_2O_3 play an important role. The most suitable ratios for achieving a proper alumina slurry deposition by means of the ball-milling process on a 400 cpsi monolith were previously studied [25]. In this work, the formulation of the slurry was only changed by varying the water/alumina ratio (from 3.4 to 4) and keeping the acid content constant to modify the wetting properties.

Washcoat deposition was carried out by means of a dip-coating method. Monoliths were introduced into a vessel with the as-prepared slurry until their inner channels were completely covered. Subsequently, monoliths were raised at a constant velocity (7 cm/s), and the excess of slurry dispersion blocking the pores was removed with an air jet with an empty tube velocity of 0.2 m/s that left a thin film around the inner wall channels. After that, monoliths were subjected to a flash heating, 5 min at 280 °C. The alumina samples follow this nomenclature: V(*x*%)/Al_2O_3(*y*), where *x* indicates the amount of V with respect to alumina powder and *y* represents the water/alumina ratio used in slurry preparation. The samples prepared are summarised in Table 1.

2.2. Catalyst characterisation

The monolithic catalysts were characterised regarding texture properties by N_2 physisorption, scanning electronic microscopic (SEM) and surface chemistry by temperature programmed desorption (TPD). Moreover, the coating was characterised by measuring its loading, thickness and adherence. The mechanical properties were studied from the corresponding strain–stress curves obtained from compression experiments.

Nitrogen adsorption was performed on a Micromeritics ASAP 2020 at −196 °C. Before N_2 adsorption measurements, the sample was dried at atmospheric pressure and 108 °C for several hours. The evacuation temperature was low to prevent the decomposition of oxygen surface complexes. From the physisorption measurements with N_2, the specific surface was calculated with the BET equation. The *t*-plot method was applied to calculate the micropore, whereas the BJH method was used to calculate the parameters related to mesoporosity.

SEM pictures were taken in an SEM EDX Hitachi S-3400 N with variable pressure up to 270 Pa and an EDX Röntec XFlash of Si(Li). This technique provides the external composition by means of the EDX runs as well as pictures of the surface.

Mechanical characterisation was carried out using a Shimazdu AGS-J 10 kN modular apparatus. The compression experiments between the parallel faces of the cylindrical pieces were carried out with a deformation velocity of 1 mm min^{-1}. In this way, the compressive stress is parallel to the wall channels. The Youngĭs modulus and compressive strengths of both uncoated and coated ceramic foams were determined from the corresponding compressive stress–strain curves.

Temperature programme desorption measurements were carried out in a Micromeritics apparatus. Before TPD runs, the sample was treated at 150 °C with 30 ml/min stream of He in order to release all physically adsorbed complexes. In the TPD, a temperature increase rate of 10 °C/min from 150 to 1050 °C was used. The CO_2 and CO evolved during the runs were detected by a gas chromatograph equipped with a thermal conductivity detector. In recent years, TPD methods have become rather popular. Surface oxygen groups on carbon materials decompose upon heating to release CO and CO_2 at different temperatures. There is some confusion in the literature with respect to the assignment of the TPD peaks to specific surface groups, as the peak temperatures may be affected by the texture of the material, the heating rate and the geometry of the experimental system used [26–28]. However, some trends can be established, as summarised in [28]. Thus, a CO_2 peak is the result of carboxylic acids that evolved at low temperatures, or lactones that evolved at higher temperatures. Carboxylic anhydrides originate both a CO and a CO_2 peak. In general, TPD spectra obtained with carbon materials show composite CO and CO_2 peaks, which must be deconvoluted before the surface composition can be estimated. Deconvolution was carried out by the commercial computer program ORIGIN.

The coating loading was calculated as the difference between the monolith weight before and after deposition and drying. The *coating thickness* was measured by cutting the sample in one section and measuring the coating thickness at different points by microscopy. The rheological behaviour of the prepared sol–gel dispersions was characterised in a rotational stress controlled rheometer Stresstech 500 from Reologica instruments. The instrument used flat plates of 40 mm diameter, and all the measurements were done at room temperature.

Finally, *coating adhesion* was quantified by measuring the *weight* loss after treatment in an ultrasonic bath for 30 min. This method was recently applied [29] for alumina layers on ceramic and metallic supports. In this work, the coated monoliths were subjected to ultrasound by immersing them in acetone or water in the case of carbon-coated monoliths, and inside a glass vessel with petroleum ether in the case of alumina-coated monoliths, and then in an ultrasonic bath for 30 min at room temperature. After that, the samples were dried for 2 h at 120 °C. The weight of the sample both before and after the ultrasonic treatment was measured. This method was employed to measure the washcoat adherence of different samples for comparison purposes. The selection of water, acetone or petroleum ether depends on the washcoat nature. The chosen agent should avoid solution interactions with the washcoat. In this sense, it is not suitable to use water for alumina washcoats as the *weight* loss would be due to both adherence and solution effects. The effect of differing thermal expansions on the stability of coatings was also tested by cycling a carbon-coated monolith between 500 °C and room temperature. The monolith was introduced in an oven at 500 °C and kept for 60 s at this temperature. Then it was quenched at room temperature. The procedure was repeated 10 times, after which the ultrasonic test was performed, and the sample was dried and weighed.

2.3. Catalyst test

The catalytic activity was measured by using a quartz fix-bed flow reactor heated with a furnace, and 2.2 g catalytic sample monoliths with a diameter of 1 cm and a length of 5 cm were used. The feed gas mixture contained 1000 ppm NO, 1000 ppm NH_3, 10% O_2 and argon as balance gas, unless otherwise specified. The gas flow rate was fixed at 100 cm^3/min. The effluent gases from the reactor were analysed on-line by a quadrupole mass spectrometer previously calibrated with cylinders of known concentrations. The NO conversion was calculated by means of the following reaction:

$$\%\ \text{NO reduction} = \frac{(C^i_{\text{NO}} - C_{\text{NO}})}{C^i_{\text{NO}}} \times 100 \tag{1}$$

where C^i_{NO} is the initial concentration of NO and C_{NO} corresponds to its concentration once steady state is reached.

MS equipment is one of the most commonly used detection systems to determine the concentration of various components in a gas stream. However, due to the presence of different components and steam, a calibration is often needed. Calibration was carried out before starting each run by means of cylinders of certified concentrations as follows: 7000 ppm of NO and 3,5% of O_2, 2000 ppm of NO, 3000 ppm of NH_3, 1000 ppm of N_2, 1000 ppm of N_2O and 7% O_2; all of them were in Ar as a balance gas.

3. Results and discussion

3.1. Comparison of the washcoat porous structure

A well-developed washcoat porous structure is a key factor for achieving a highly active catalyst. It is widely reported in the literature [20] that microporosity and mesoporosity allow a high dispersion of active metal on the washcoat surface and a close contact between the metal phase and the reactant gases. Both conditions are favoured when a coating is present.

The BET surface areas and the main structural parameters of the catalysts, obtained by means of BJH and *t*-plot methods, are summarised in Table 1. The results show that the surface areas of all activated carbon-coated catalysts are, regardless of the oxidation process, higher than those of the alumina-coated catalysts. This fact could be due to the higher microporosity volume developed on the activated carbon-coated monoliths instead of the poor values for alumina coatings. However, both activated carbon- and alumina-based catalysts show a high mesoporosity, exhibited by a broad hysteresis loop as well as the high BJH volume.

In the case of the carbon-coated catalysts, porous structure is mainly dependent on the oxidation process carried out on the sample. As widely reported in previous studies [30], oxidation causes destruction of the porous structure developed during the activation step with CO_2; the destruction carried out by the inorganic acid is higher than that caused by other milder oxidising agents such as H_2O_2. Moreover, the chemistry surface developed during the oxidation process influences equally the active metal adsorption and therefore the porous structure. A carbon coating subjected to a strong oxidation process favours vanadium adsorption and dispersion, which is without any doubt reflected in an important decrease in its porous structure. On the other hand, the oxidation process carried out with H_2O_2 triggers a slight decrease in the porous structure and likely a lower adsorption of vanadium, which results in higher BET surface areas.

Regarding alumina coatings, the main factor for determining its porous structure seems to be the alumina precursors. Viscosity depends greatly on the H^+/Al_2O_3 and H_2O/Al_2O_3 ratios and only slightly on the amount of active phase introduced during the preparation process. In this sense, although all samples present similar values of microporosity and mesoporosity, a slight decrease in mesoporosity after impregnation with the higher amount of vanadium loading could be observed. This suggests that vanadium induces a small pore plugging on alumina coating as well.

3.2. Comparison of the washcoat adherence

Under real conditions, the washcoat monolith catalysts are subjected to high gaseous flow rates and temperature fluctuations. As a result, adhesion loss is a likely cause for concern [32]. Although adhesion should be tested for stationary catalysts, it is a more critical factor for on-board catalysts, since the loss of the catalytic washcoat via attrition or erosion is also a serious source of irreversible deactivation.

In the case of carbon-coated monoliths, it has been observed in previous works [30,33] that carbon-based monoliths under flow rates and temperatures similar to those employed in environmental applications did not have any catalyst loss. Thus, a more severe stability test, which consists of an accelerated ultrasonic test, was employed. The treatment caused different degrees of erosion in the monolith washcoats. The degree of erosion was measured by weighing the sample before and after the ultrasonic treatment and

Table 2
Adherence carbon coating tests (vibrational and thermal tests).

Ultrasound bath diluting	ΔW_1, vibrational tests	ΔW_2, thermal tests
Water	4.96%	4.06%
Acetone	2.93%	1.98%

also by visualising the surface through SEM observations. The characterisation of sample weight loss after ultrasonic vibration and thermal shock was defined as follows:

$$\text{The weight loss of sample after ultrasonic vibration}:$$

$$\Delta W_1 = \left[\frac{(W_1 - W_2)}{W_1}\right] \times 100\%$$

$$\text{The weight loss of sample after thermal shock}:$$

$$\Delta W_2 = \left[\frac{(W_3 - W_4)}{W_3}\right] \times 100\%$$

W_1 is the washcoat weight before ultrasonic vibration, W_2 is the washcoat weight after ultrasonic vibration, W_3 is the washcoat weight before thermal shock, and W_4 is the washcoat weight after thermal shock.

The cohesions between the coatings and the ceramic monoliths as assessed by both ultrasonic and thermal shock are summarised in Tables 2 and 3, respectively. A comparison with other kinds of catalysts prepared for the same application and reported in the literature is shown in Table 4. Carbon coatings present a weight loss after ultrasonic vibration tests with water immersion of around 5 wt%. This value is slightly higher than obtained with acetone immersion (3%). The difference could have been related to the acid surface character evaluated by TPD runs and reported more extensively in previous work [30]. The data from the TPD runs are collected in Table 5. When carbon-based catalysts are subjected to an oxidising treatment, a high number of oxygen surface groups are created on the carbon coating. The amount and kind of these groups are highly depended on the oxidising agent used. As shown in [30], HNO_3 oxidation is able to create a large number of oxygen surface groups that evolve as CO_2 at lower temperatures and that could be attributed to carboxyl and lactone groups, according to [27,28]. On the contrary, H_2O_2 oxidation provides a high number of oxygen surface groups that are evolved at higher temperatures and that could be attributed to lactone and phenol groups. In this case, washcoat adherence tests have been performed to HNO_3 oxidised carbon-coated monoliths because they present the highest activity. Oxygen surface groups that were created after this oxidation process and evolved at lower temperatures as CO_2 have a strong hydrophilic character that favours their interaction with a polar dissolvent, such as water, and consequently these samples present a higher weight loss than if acetone is used as dissolvent.

Moreover, samples subjected to thermal shock and immersed in water also have a higher weight loss (4%) than those in acetone (2%). Nevertheless, it is worth noting that the thermal shock weight loss remains at the same order of magnitude as the vibrational test weight loss, which indicates that carbon and cordierite have similar thermal expansion coefficients.

Table 4
Comparison of washcoat adherence to other catalysts reported in the literature.

Washcoat	ΔW_1	ΔW_2	Reference
γ-Al2O3 (10 mPa s viscosity)	1.9%	21.3%	[14]
γ-Al2O3 (30 mPa s viscosity)	12.4%	20.1%	[14]
γ-Al2O3 (40 mPa s viscosity)	48.6%	30.4%	[14]
Zeolite (water bath)	2.9%	–	[35]
Zeolite (methyl alcohol bath)	29.1%	–	[35]
Zeolite (ethil alcohol bath)	21.7%	–	[35]
Zeolite (isoporpyl bath)	43.2%	–	[35]
KFerrierite	26%	–	[36]
Kferrierite with sílice as binder	11%	–	[36]
HNO_3/Al_2O_3	11.3%	–	[34]
HNO_3/Al_2O_3calcinated at 400 °C	1.6%	–	[34]
HNO_3/Al_2O_3calcinated at 700 °C	0.8%	–	[34]
HNO_3/Al_2O_3calcinated at 900 °C	0.08%	–	[34]
ZSM5	4.6%		[41]
ZSM5 with SiO_2 as binder	1.8%		[41]
Morderite	13%		[41]
Morderite with binder	2.3%		[41]
Ferrierite	26.1%		[41]
Ferrierite with binder	11%		[41]
Carbono (water bath)	4.96%	4.06%	This work
Carbono (acetone bath)	2.93%	1.98%	This work

Table 5
TPD results of carbon-coated monoliths before and after different oxidation treatments for 24 h at room temperature.

Oxidation treatment	CO (cm^3/g)	CO_2 (cm^3/g)	CO + CO_2 (cm^3/g)	CO/CO_2
None-activated coating	3.47	0.47	3.87	7.36
HNO_3(c)	2.26	1.11	3.37	2.04
HNO_3(2N)	2.01	0.91	2.92	2.22
H_2SO_4	1.77	0.71	2.48	2.49
H_2O_2	2.78	0.65	3.42	4.29

In the case of alumina-coated monoliths, only vibrational tests were carried out, as the excellent thermal resistance properties are widely known. Results are shown in Table 3. The coating adherence is highly dependent on the alumina slurry viscosity, which is in turn dependent on the H^+/Al_2O_3 and H_2O/Al_2O_3 ratios. Moreover, the alumina coating thickness and integrity also depend on viscosity, and both have an influence on the coating adherence. Both thickness and adherence parameters seem to be connected by a linear regression that can be due to the ability of low viscose alumina slurries to be introduced into the ceramic macropores, whereas this is impossible for high viscose slurries. Thus, it seems that suction forces favour, and on the contrary, viscosity forces discourage, washcoat adherence onto the ceramic support.

Comparing the results herein to those published recently in the literature (Table 4) [14,34–36], the as-prepared washcoats have great stability. In fact, in most of the cases, the weight loss is very low (between 1 and 5%), which could be considered to be less than experimental error.

Both ultrasonic treatments caused different degrees of erosion. The degrees of erosion were visualised by means of thorough SEM observations (not shown here). It was observed that the carbon washcoat stability of the samples treated by ultrasonic vibration is

Table 3
Adherence of alumina coatings (vibrational tests).

Ratio H + /Al_2O_3	Ratio H_2O/Al_2O_3	Vanadium loading	ΔW_1, vibrational test	Viscosity at shear rate, 10 MPa
1.4	4	5%	4.88%	0.05
1.4	3.4	5%	7.88%	0.11
1.4	4	3%	1.72%	0.02
1.4	3.4	3%	5.88%	0.08
1.4	3.0	3%	12.81%	0.11
1.4	2.6	3%	14.47%	0.13

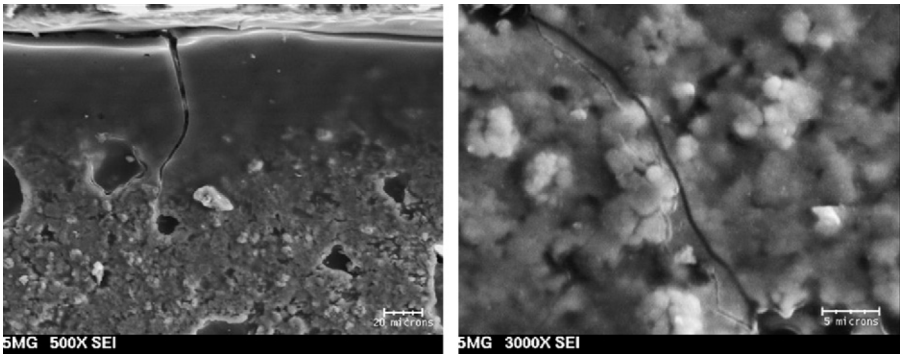


Fig. 1. Cracks of carbon coating after thermal vibrational resistance tests.

high enough to show a continuous surface with no sight of cracking on the whole surface. However, samples subjected to 10 thermal cycles show a deleterious effect. Fig. 1 shows some of these cracks. Despite these photographs, it should be pointed out that the number and depth of cracks are not high enough to become a limitation for catalytic activity.

According to these results, it can be stated that carbon washcoats can easily fulfil the requirements of stability for on-board applications, while alumina washcoats only fulfil these requirements depending on the viscosity of the slurries.

3.3. *Comparison of the washcoat thickness and integrity*

A detailed study of the coating layer was carried out by SEM observation. As an example, Figs. 2–5 present SEM images of coatings. Figs. 2 and 4 (parallel cuts) and Figs. 3 and 5 (perpendicular cuts) show coating layer characteristics on the walls of the cordierite honeycomb channels. SEM observations (not showed here) conducted at several distances from the top of the monolith did not show significant differences between the coating layer in the centre of the monolith and in the channel open ends, indicating that the synthesis solution is accessing the whole channel of the monolith during synthesis.

In Fig. 2, a carbon coating is shown, and uncovered regions in the monolith are not observed. Another relevant issue observed in Fig. 3 is the fact that carbon layers can also be introduced inside the cordierite macropores or remain on the channel surface of the ceramic monolith. This image shows that the solution is homogeneously distributed and can even penetrate into the cordierite macroporous structure during synthesis. Pore filling could explain the strong carbon anchorage to the support previously studied. After cleaning and curing the sample, the remaining carbon forms a compact structure in which the internal layer is connected to the ceramic, creating a unique and strong network.

In Figs. 4 and 5, an alumina coating is observed. It is important to note that only in the case of V(3%)/Al_2O_3(4) are small uncovered area observed, probably due to the low viscosity of the alumina slurry used. This finding is also in agreement with the lower BET surface area exhibited by this sample. Moreover, and according to the SEM images, alumina does not seem to be introduced into the macropores of cordierite remaining mainly on the surface. This fact can be the cause of the weaker interaction between the support and washcoat. Regarding the literature [31], two types of coating defects can be appreciated: pinholes and crackings. Pinholes are due to uncovered zones of cordierite materials, while crackings are mainly due to thermal and mechanical tensions suffered during the drying process. The first defect is observed in samples covered with the lowest viscosity slurry, whereas crackings are observed for the highest viscose slurries.

Perpendicularly cut SEM images are useful for measuring the thickness of both carbon and alumina layers at different points and in different samples. All carbon layers showed a thickness between 800 and 900 nm, without irregularities even in the inner channel corners. Conversely, alumina layers showed a thickness between 5 and 20 μm. It is important to highlight the fact that the alumina layer thickness is highly dependent on the viscosity. Alumina layers present considerably different thicknesses and areas if the slurries have a high viscosity. This fact is probably due to the irregular surface of the original cordierite support itself and/or alumina accumulation in some areas, because the connection force between particles is stronger and consequently the ability to remove the excess with air pressure blowing is more difficult.

3.4. *Comparison of mechanical properties*

The mechanical properties were evaluated with compressive strength tests. The compressive strength tests were performed along the axial axis, as described in Section 2. Table 6 and Fig. 6

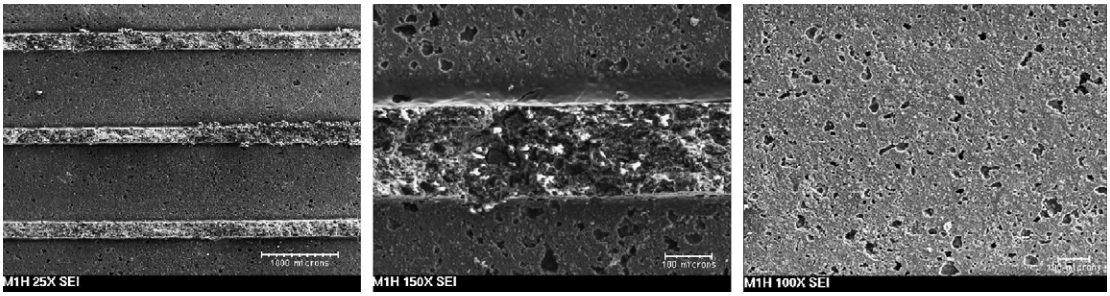


Fig. 2. Parallel cut of carbon-coated monoliths.

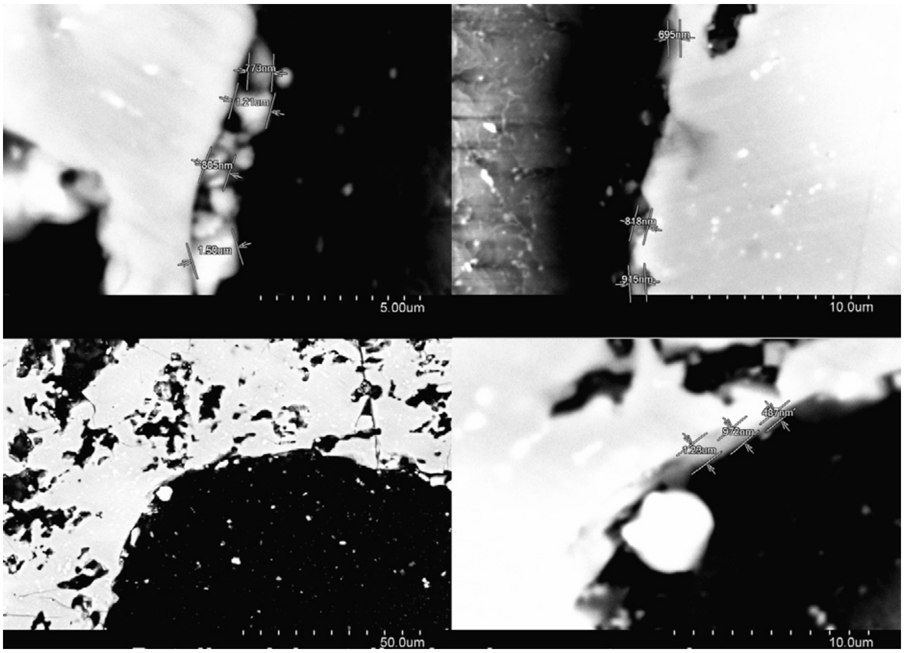
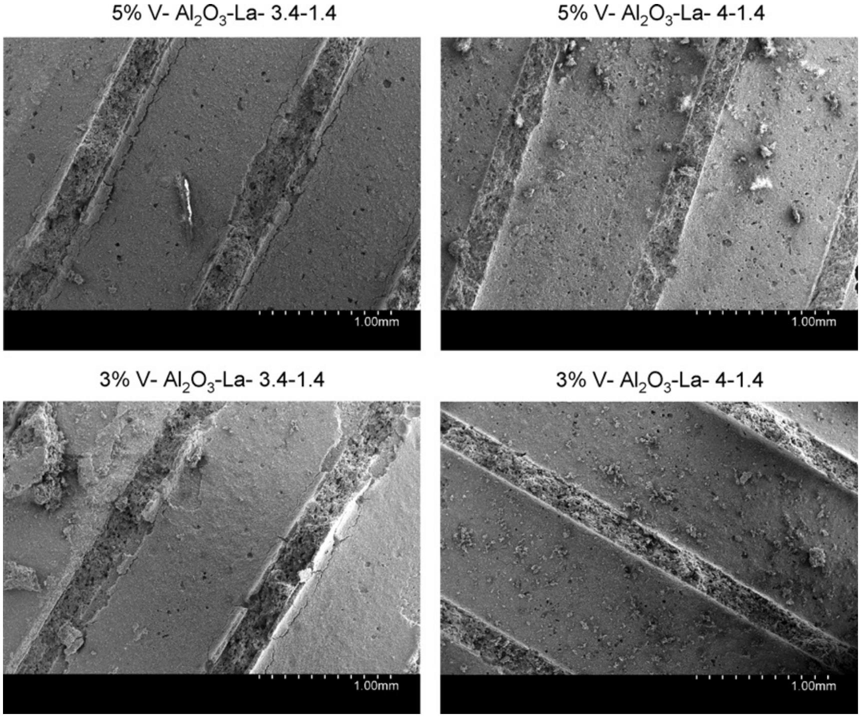


Fig. 3. Perpendicular cut of carbon-coated monoliths.

summarise the main mechanical parameters of the three supports (before and after washcoat application). The washcoated monoliths were V(3%)/Al_2O_3(3.4) and V(3%)/AC + HNO_3(2N). First, the values reached for both coated samples are very similar to those reported in the literatures [5,37], especially if monoliths have the same amount of cpsi.

As observed in Fig. 6, both carbon and alumina coatings lead to the reinforcement of the raw honeycomb monolith. At the beginning of the experiments, the relationship between the strain applied and the stress produced is linear, and the slope of these lines corresponds to the Young's modulus (E), which clearly increases in the following order: uncoated < alumina-coated < carbon-coated monolith. In the case of the uncoated cordierite monolith, the presence of small peaks indicates the formation of small cracks even before reaching the elastic limit. This behaviour is not observed for the coated monoliths. This is because E indicates of the rigidity of the material, showing how the elastic deformation (ε_e) progressively decreases as long as E increases (Table 6). Regarding the maximum strain (σ_{max}), a significant improvement in the case of carbon-coated monolith only is found. In this case, the deforma-


5% V- Al_2O_3-La- 3.4-1.4

5% V- Al_2O_3-La- 4-1.4

3% V- Al_2O_3-La- 3.4-1.4

3% V- Al_2O_3-La- 4-1.4

Fig. 4. Parallel cut of alumina-coated monoliths.

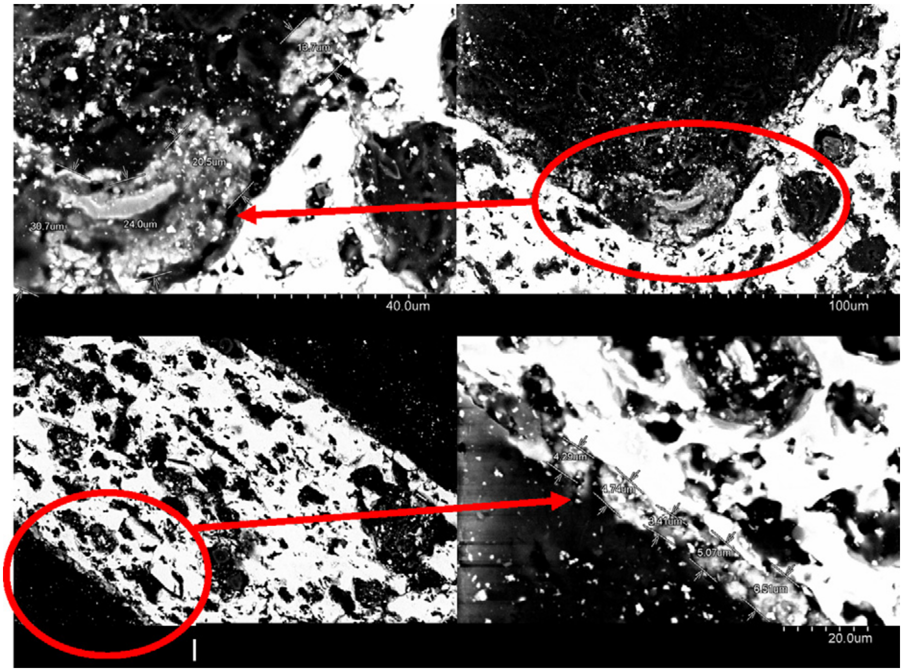


Fig. 5. Perpendicular cut of alumina-coated monoliths.

Table 6
Mechanical parameters obtained from strength vs. deformation plots.

	Cordierite monolith	Alumina washcoated monolith	Carbon washcoated monolith
Young module (MPa)	123	339	680
Elastic limit (MPa)	7.7	7.9	8.5
Elastic deformation (%)	8.3	4.0	1.9
Maxima resistance (MPa)	8.5	8.6	12.3

tion progressively increases up to 40% without a noticeable loss of mechanical resistance. This leads to a greater tenacity in opposition to the great rigidity of the cordierite monolith. The presence of small peaks points out once more the development of cracks.

The differences between the curves indicate that the breaking pathway is different. In the case of carbon-coated monoliths, the rigid character favours the development of crack advance parallel to the strain (along the wall channel). Thus, although some cracks produce the total fracture of the wall, the rest of wall remains in the same position, i.e. parallel to the effort, and continues to work collectively. Thus, even though the original piece is fractured progressively into smaller pieces, the total resistance they offer is quite similar to that of the non-cracked piece. The strong deformation recorded is due to the crushing produced in the extremes of the pieces. The uncoated monolith presents a greater elastic deformation, as previously commented, and also a significant plastic deformation (crushing) before a progressive loss of resistance occurs. This is due to the greater facility of cracks to progress in any direction because of the unfilled macropores. The alumina-coated monolith presents an intermediate behaviour: it is more rigid and resistant than the uncoated monolith, but it is not able to avoid crack propagation in the radial direction. The better performance of the carbon-coated monolith is related to the ability of the carbon precursor to fill the support porosity, resulting in an anchored and stable coating, as previously mentioned. It is well known that the strength of ceramic particles depends on porosity [38]. Exponential laws are usually used to determine the relation between the porosity and the strength [39]. Because of the nature of the ceramic material, macropores are the most important kind of pores. It is expected that the presence of these large pores may have a strong effect on the monolith strength, as they tend to act as stress concentrators [40]. The monolith reinforcement is increased, a consequence of filling the cordierite pores with the coating.

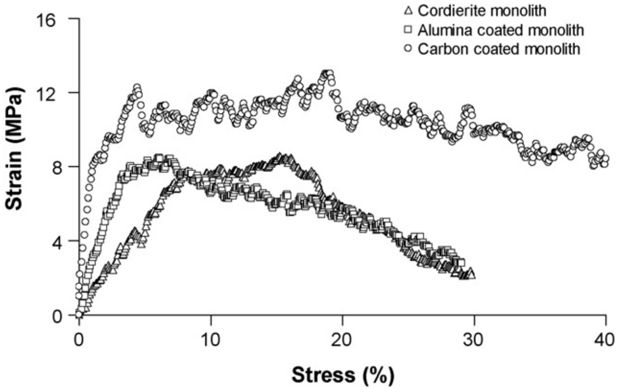


Fig. 6. Mechanical resistance. Axial compression tests.

3.5. Comparison of NO reduction activity

The catalytic activity in terms of NO conversion has been studied for some catalysts as a function of temperature. Steady-state isothermal experiments at three different temperatures (150, 250 and 350 °C) (Figs. 7 and 8) were carried out. Experimental conditions were chosen to be as close as possible to real conditions. Therefore, a GSHV of 34,000 h^{-1} was maintained for all runs. These conditions may cause external diffusion effects and consequently provide a lower NO conversion ratio. However, as NO conversion was calculated supposing a zero order reaction for O_2 and a first order reaction for NO, possible diffusion effects would be included into the kinetic constant. Despite this observation and as described below, further investigations are being carried out.

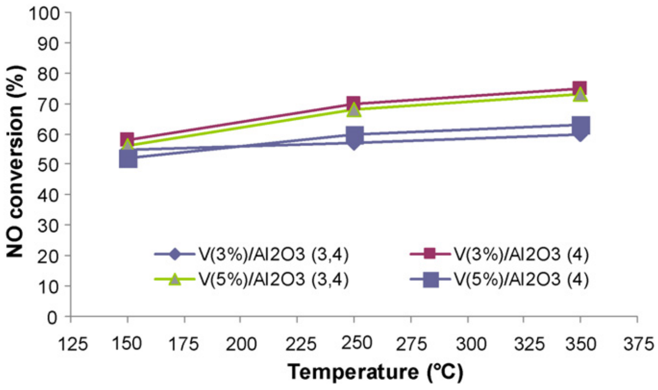


Fig. 7. Stationary conditions. NO conversion with alumina doped catalysts.

The catalytic activity of both kinds of catalysts is quite similar under stationary conditions. NO conversion varies from 50% to above 80%, showing a dependence on temperature. As expected for a catalytic process, a higher temperature causes higher NO conversions to a certain extend. At the highest temperature, carbon-coated catalysts show a slight decrease in activity that can be attributed a slight NH_3 oxidation.

Although catalytic conversion values for both kinds of catalyst are quite close, some differences can be observed. On one hand, the NO conversion of alumina-coated catalysts follows a trend according to slurry viscosity, since the highest NO conversion values are achieved when medium slurry viscosities are used in the preparation process. Lower or higher viscosity slurries provide catalysts with lower activity, indicating that structural features and homogeneity of the slurries play an important role in catalyst activity.

On the other hand, carbon-coated catalysts show the highest activity after a strong oxidation process. The highest activity is shown when carbon-coated monoliths have been subjected to an oxidation process with concentrated nitric acid. According to Table 5 and previous works reported in [30], the nitric acid oxidation process causes an acidification of the surface mainly by means of the creation of carboxyl groups. This kind of group favours the adsorption of vanadium. Moreover, the oxidation process produces a depletion of structural features of carbon-coated monoliths, but this fact is not as important as the acidification of the surface.

Both facts point out that the preparation process will determine the catalytic activity, but that the key parameters of each catalyst are completely different.

In order to compare the kinetic activity of both catalysts, the apparent activation energy was calculated, assuming a zero order reaction for O_2 and a first order reaction for NO. According to the data provided, carbon-based catalysts present an average apparent activation energy of around 7 kJ/mol, while alumina-based catalysts present an average apparent activation energy of 15 kJ/mol. Both apparent activation energy values are lower than those typically reported for commercial catalysts, which are around 60 kJ/mol. This fact can point out either that these catalysts much more readily react at lower temperature or that they are subjected to a strong internal and external mass transfer. Further investigations should be performed.

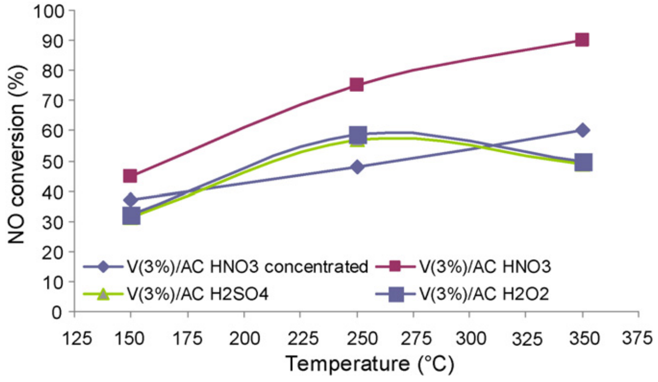


Fig. 8. Stationary conditions. NO conversion with carbon doped catalysts.

4. Conclusions

This study has demonstrated that the activity of catalysts in catalytic NO reduction with NH_3 can be affected by the nature of the washcoat. A rough comparison was carried out, taking into account two kinds of washcoats: carbon and alumina. Both kinds of catalysts were prepared through a dip-coating method and then cured and treated under different conditions to achieve the most suitable conditions for the SCR reaction at low temperatures.

The comparison of both washcoated catalysts, alumina- and carbon-coated catalysts, provides the following results: (i) the carbon washcoat is much thinner, better adhered to ceramic supports and provides a higher S_{BET} than the alumina washcoat; (ii) the carbon washcoat presents a higher thermal shock resistance and a higher vibration resistance than the alumina washcoat does; (iii) the alumina washcoat adherence and quality strongly depend on the slurry viscosity. Moreover, the slurry viscosity depends on the preparation process, making the determination of a key factor difficult. Al_2O_3 adherence could be governed by suction forces that allow the introduction of slurry into the ceramic macropores and viscose forces that avoid the incorporation to supports. Finally, (iv) the NO reduction activity reached by both kinds of catalysts is really close under steady-state conditions.

Acknowledgements

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References

[1] M. Iwamoto, H. Hamada, Removal of nitrogen monoxide from exhaust gases through novel catalytic processes, Catal. Today 10 (1991) 57–71.
[2] H. Hamada, Y. Kintaichi, T. Yoshinari, M. Tabata, M. Sasaki, T. Ito, Performance of solid acid type catalysts for the selective reduction of nitrogen oxides by hydrocarbons and alcohols, Catal. Today 17 (1993) 111–119.
[3] H. Bosch, F. Janssen, Catalytic reduction of nitrogen oxides—a review on the fundamentals and technology, Catal. Today 2 (1988) 369–529.
[4] M. Koebel, M. Elsener, M. Kleemann, Urea-SCR: a promising technique to reduce NO_x emissions from automotive diesel engines, Catal. Today 59 (2000) 335–345.
[5] A. Cybulski, J.A. Moulijn, Structured Catalysts and Reactors. Ed. Taylor, 2006.
[6] V. Meille, Review on methods to deposit catalysts on structured surfaces, Appl. Catal. A: Gen. 315 (2006) 1–17.
[7] B.M. Weckhuysen, D.E. Keller, Chemistry, spectroscopy and the role of supported vanadium oxides in heterogeneous catalysis, Catal. Today 78 (2003) 25–46.
[8] M.M. Khader, Surface acidity of V_2O_5/Al_2O_3 catalysts: IR and TPD studies, J. Mol. Catal. A: Chem. 104 (1995) 87–94.
[9] W.S. Kijlstra, J.C.M.L. Daamen, J.M. Van Der Graaf, B. Van Der Linden, E.K. Poels, A. Bliek, Inhibiting and deactivating effects of water on the selective catalytic reduction of nitric oxide with ammonia over MnO_x/Al_2O_3, Appl. Catal. B: Environ. 7 (1996) 337–357.
[10] E.P. Reddy, R.S. Varma, Preparation, characterization and activity of Al_2O_3-supported V_2O_5 catalysts, J. Catal. 221 (2004) 93–101.
[11] P. Avila, M. Montes, E.E. Miró, Monolithic reactors for environmental applications: a review on preparation technologies, Chem. Eng. J. 109 (2005) 11–36.
[12] Z. Zhu, Z. Liu, S. Liu, H. Niu, T. Hu, T. Liu, Y. Xie, NO reduction with NH_3 over an activated carbon-supported copper oxide catalyst at low temperatures, Appl. Catal. B: Environ. 26 (2000) 25–35.

[13] P. Avila, C. Barthelemy, A. Bahamonde, J. Blanco, Catalyst for NO_x removal in nitric-acid plant gaseous effluents, Atmos. Environ. Part A: Gen. Topics 27 (1993) 443–447.

[14] P. Jiang, G. Lu, Y. Guo, S. Zhang, X. Wang, Preparation and properties of y-Al_2O_3 washcoat deposited on a ceramic honeycomb, Surf. Coat. Technol. 19 (2005) 314–320.

[15] L. Jia, M. Shen, J. Wang, Preparation and characterization of dip-coated γ-alumina based ceramic materials on FeCrAl foils, Surf. Coat. Technol. 201 (2007) 7159–7165.

[16] M. Collic, D. Morse, Effects of amplitude of the radiofrequency electromagnetic radiation on aqueous suspensions and solutions, J. Colloid Interface Sci. 200 (1998) 265–272.

[17] M. Collic, M.L. Fisher, Effect of the size and affinity for water of excluded ions on interparticle forces, Chem. Phys. Lett. 291 (1998) 24–30.

[18] J.E. García-Bordejé, A. Monzón, M.J. Lázaro, R. Moliner, Promotion by a second metal or SO_2 over vanadium supported on mesoporous carbon-coated monoliths for the SCR of NO at low temperature, Catal. Today 102 (2005) 177–182.

[19] E. Garcia-Bordeje, F. Kapteijn, J.A. Moulijn, Preparation and characterization of carbon-coated monoliths for catalyst support, Carbon 40 (2002) 1079–1088.

[20] E. García-Bordejé, L. Calvillo, M.J. Lázaro, R. Moliner, Vanadium supported on carbon-coated monoliths for the SCR of NO at low temperature: effect of pore structure, Appl. Catal. B: Environ. 50 (2004) 235–242.

[21] G. Marbán, A.B. Fuertes, Low temperature SCR of NO_x with NH_3 over NomexTM rejects-based activated carbon fibre composite-supported manganese oxides. Part II. Effect of 242 procedures for impregnation and active phase formation, Appl. Catal. B. Environ. 34 (2001) 55–71.

[22] Z. Zhu, Z. Liu, S. Liu, H. Niu, A novel carbon-supported vanadium oxide catalyst for NO reduction with NH_3 at low temperatures, Appl. Catal. B: Environ. 23 (1999) L229–L233.

[23] Å. Kling, C. Andersson, Å. Myringer, D. Eskilsson, S.G. Järås, Alkali deactivation of high-dust SCR catalysts used for NO_x reduction exposed to flue gas from 100 MW-scale biofuel and peat fired boilers: influence of flue gas composition, Appl. Catal. B: Environ. 69 (2007) 240–251.

[24] Z. Zhu, Z. Liu, S. Liu, H. Niu, S. Liu, T. Hu, T. Liu, Y. Xie, Mechanism of SO_2 promotion for NO reduction with NH_3 over activated carbon-supported vanadium oxide catalyst, J. Catal. 197 (2001) 6–16.

[25] C. Cristiani, A. Grossale, Forzatti, Study of the physico-chemical characteristics Q6 and rheological behaviuor of boehmite dispersions for dip-coating applications, submitted for publication.

[26] H.P. Boehm, Surface oxides on carbon and their analysis: a critical assessment, Carbon 40 (2002) 145–149.

[27] G.S. Szymański, Z. Karpiński, S. Biniak, A. Świątkowski, The effect of the gradual thermal decomposition of surface oxygen species on the chemical and catalytic properties of oxidized activated carbon, Carbon 40 (2002) 2627–2639.

[28] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Orfão, Modification of the surface chemistry of activated carbons, Carbon 37 (1999) 1379–1389.

[29] J. Jia, J. Zhou, J. Zhang, Z. Yuan, S. Wang, The influence of preparative parameters on the adhesion of alumina washcoats deposited on metallic supports, Appl. Surf. Sci. 253 (2007) 9099–9104.

[30] A. Boyano, I. Malpartida, M.A. Larrubia, J.L. Alemany, M.J. Lazaro, Vanadium-loaded carbon-based monoliths for on-board NO reduction: Influence of nature and concentration of the oxidation agent on activity, Catal. Today 137 (2008) 222–227.

[31] B. Wu, B. Xu, B. Zhang, S. Dong, The effects of parameters on the mechanical properties of Ni-based coatings prepared by automatic brush plating technology, Surf. Coat. Technol. 201 (2007) 5758–5765.

[32] R.M. Heck, R.J. Farrauto, Automobile exhaust catalysts, Appl. Catal. A: Gen. 221 (2001) 443–457.

[33] A. Boyano, N. Lombardo, M.E. Gálvez, M.J. Lázaro, R. Moliner, Vanadium-loaded carbon-based monoliths for the on-board NO reduction: Experimental study of operating conditions, Chem. Eng. J. 144 (2008) 343–351.

[34] M. Valentini, G. Groppi, C. Cristiani, M. Levi, E. Tronconi, P. Forzatti, The deposition of y-Al_2O_3 layers on ceramic and metallic supports for the preparation of structured catalysts, Catal. Today 69 (2001) 307–314.

[35] J.M. Zamaro, M.A. Ulla, E.E. Miro, Zeolite washcoating onto cordierite honeycomb reactors for environmental applications, Chem. Eng. J. 106 (2005) 25–33.

[36] A.V. Boix, J.M. Zamaro, E.A. Lombardo, E.E. Miro, The beneficial effect of silica on the activity and thermal stability of PtCoFerrierite-washcoated cordierite monoliths for the SCR of NO with CH_4, Appl. Catal. B: Environ. 49 (2003) 121–132.

[37] ASTM E 1269-05, Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry.

[38] M.M. Jordan, M.A. Montero, S. Meseguer, T. Sanfeliu, Influence of firing temperature and mineralogical composition on bending strength and porosity of ceramic tile bodies, Applied Clay Science 42 (2008) 266–271.

[39] P. Colombo, Engineering porosity in polymer-derived ceramics, Journal of the European Ceramic Society 28 (2008) 1389-1395.

[40] Q. Liu, Z. Liu, Z. Huang, G. Xie, A honeycomb catalyst for simultaneous NO and SO_2 removal from flue gas: preparation and evaluation, Catal. Today 93–95 (2004) 833–837.

[41] J.M. Zamaro, M.A. Ulla, E.E. Miró, The effect of different slurry compositions and solvents upon the properties of ZSM5-washcoated cordierite honeycombs for the SCR of NOx with methane, Catal. Today 107–108 (2005) 86–93.