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Vanadium-loaded carbon-based monoliths for the on-board NO reduction: Experimental study of operating conditions

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Abstract

Selective catalytic reduction (SCR) with NH_3 and most probably with urea is unanimously regarded as one of the most promising technologies for the abatement of NO_x on-board. For this application at low temperatures, carbon-based monolithic catalysts have been prepared using a blend of polymers on cordierite monoliths, doped with two different vanadium compounds and two different loadings (3 and 5%). The active phase precursors were either the ashes of a petroleum coke (PCA) or a commercial NH_4VO_3. An experimental design was carried out to study the reduction of NO emissions, the selectivity towards N_2 and the release of ammonia-slip in the outlet reactor gasses. Both primary measures (temperature, gas space velocity per hour (GSVH) and the molar ratio of NH_3/NO) as well as secondary SNR influences were evaluated using a 2^3 factorial design for the two types of catalysts. Polinomial modellings were deducted from statistical analysis of the experiments, and a good agreement between models and measured data was obtained. The evaluation showed that the temperature is the variable which has a greater influence on all the response variables studied. Spatial velocity shows approximately an equal importance on NO conversion and selectivity towards N_2 whereas the molar ratio of NH_3/NO is only an important factor in the interaction to other parameters. Catalysts prepared using PCA have similar catalytic behaviour than those prepared with NH_4VO_3. Although they show a slightly lower catalytic activity, similar selectivity towards N_2 and higher values of ammonia-slip.

The physical–chemical features of the catalysts, analysed by N_2 physisorption, ammonia adsorption and temperature programme desorption have a close relation with the catalysts behaviour. The physical–chemical features are of key importance for achieving a considerable catalytic activity. The values of apparent activation energy calculated for the catalysts presented in this paper were similar to other carbon-based catalysts and smaller than the ones corresponding to TiO_2-supported systems.

Keywords: SCR on-board; Carbon-based catalysts; Operational conditions

1. Introduction

Selective catalytic reduction (SCR) with NH_3/urea is unanimously regarded as one of the most promising technologies for the abatement of NO_x emissions from vehicles [1]: in fact its commercialization, particularly for heavy-duty diesel engines, is being currently implemented in Europe to meet the emission limits associated not only with the EURO IV but also with the forthcoming EURO V regulations [2–4]. Indeed, the design and development of the SCR systems is a complex process involving the optimization of several parameters, like the urea dosing strategy, the position size and cell density of the SCR monolith catalyst, as well as the interaction between engine and after treatment system. In the view of shortening development cycles and reducing development costs, it is important to assess the performance of different setups and to understand the influence of different design parameters in an early stage. In this respect, the study of the interaction between different operational conditions could be a key factor for the whole SCR performance.

This task is facilitated in principle by the fact that the SCR technology is not new. NH_3-SCR over vanadia-type catalysts, wherein one molecule of NO is reduced by one molecule of ammonia in the presence of oxygen to give harmless dinitrogen and water, has represented for the last two decades the most effective commercial deNO_xing process for stack gases from power plants and other stationary sources [5]. However, the use of carbon-based catalysts is not so widespread and in fact, for the best of our knowledge, there are no previous studies where carbon-based catalysts are applied for the reduction of nitric oxide from diesel exhaust gases.

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In this framework, the catalytic behaviour of commercial and new developed catalysts has been previously investigated. The well-established commercial catalysts based on vanadium on metallic oxides present two main drawbacks for its application on-board. The narrow temperature window (300–400 °C) of their reactivity is the main obstacle for real application, since it does not cover the entire temperature range of diesel exhaust gases (100–500 °C); and secondly, the problem of deactivation of these catalysts caused by sulphur dioxide and dust contained in the exhaust gases [6]. For these reasons, there is a rising interest in developing the low-temperature (100–300 °C) and sulphur resistant SCR catalysts.

Carbon-based catalysts have shown to be active at much lower temperature, i.e. 100–250 °C [7–9], and moreover they seem to have a beneficial effect by the sulphur content in exhaust gases in the catalytic activity due to the formation of some acidic compounds that improve the adsorption of NH_3 favouring its reaction [10,11]. In this way, the SCR unit could be used directly on-board without preheating diesel exhaust gases and without the necessity of burning free sulphur diesel fuels.

Due to their great effects on the SCR system performances, the operating parameters including catalyst composition, reaction temperature and ammonia concentration were experimentally studied. To be able to understand and optimize the NO emission with the NH_3 dosing, models which are capable of describing the distribution of NO through the catalysts as function of the operating conditions are required. Ideally, such a model should be able to describe the influence of the separate factors on the NO conversion and selectivity towards dinitrogen as well as their interaction effects. This kind of model can be estimated by using statistically designed experiments which are then utilized for a better understanding, as well as optimization of the process. To our knowledge, no such studies concerning NO conversion on carbon-based monoliths for SCR of NO with NH_3 from diesel exhaust gases have previously been reported, although statistical designs have been used to study other catalyst behaviours.

The aims of the present work were therefore to use statistical designs to elucidate the role of primary and secondary parameters on the reduction of NO in a small laboratory plant, and:

- to identify those factors affecting the total reduction;
- to evaluate the influence of interaction effects, and finally;
- to determine approximately how efficiently NO emissions can be minimized.

2. Experimental

2.1. Catalysts preparation

Cordierite monoliths were coated with a carbon layer by means of the dipcoating method as described in details elsewhere [12]. Briefly, it consists of dipping the cordierite monolith (400 cpsi, 1 cm diameter and 5 cm length) into a liquid polymer that is subsequently cross-linked and carbonised. To coat the monoliths two carbon precursors were used polyethylene–glycol 6000 mol wt (Sigma–Aldrich) (PEG) and Furan resin (Huttenes–Albertus). The first is in liquid state and the latter is solid grounded in a mill and sieved to diameter lower than 100 μm. The dipcoating was carried out with mixtures of Furan resin, PEG, acetone and HNO_3 as polymerization catalysts, after withdrawing the monoliths from the blend; they were flushed with pressurized air to remove the excess of liquid in the channels. The polymer-coated monoliths were cured at room temperature overnight and for 12 h at 108 °C. Carbonization of the coated monoliths was carried out in a stainless steel reactor for 4 h at 700 °C in a flow of Argon. Afterwards, they were activated with CO_2 at 900 °C for 4 h and treated for 24 h with HNO_3 1 N at room temperature to create oxygen surface groups. These conditions have been established in a previous work [13].

The as-prepared carbon-coated monoliths were loaded with vanadium 3 or 5% wt. The impregnation was carried out by ion-exchange with a solution of either NH_4VO_3 or the ashes of a petroleum coke (PCA). On one hand, commercial NH_4VO_3 (Panreac) was used as precursor of the active phase. The amount of NH_4VO_3 in the suspension in distilled water was calculated as the stoichiometric amount to get the desired vanadium loading on carbon as described in [13]. To facilitate the dilution of ammonium metavanadate ca. 10 mg of oxalic acid was added. In these conditions, the cation VO_2^+ exchanges with the protons of carbon functional groups.

On the other hand, coke from the Delayed Coke Unit in the REPSOL refinery in Puertollano, Spain, was used for the production of PCA, by combustion under air at a temperature up to 650 °C. Open flat ceramic vessels were used to contain the coke. The temperature was raised at a rate of 10 °C/min. The PCA contain 23% (w/w) of V, 3.5% (w/w) of Fe and 3% (w/w) of Ni, determined by atomic absorption spectroscopy. Other components such as Mg, Zn, Cu, Cr, Mn, Pb, Sb and Ca are also present in this material. A more complex description of PCA can be found in [14]. In this case, a suspension/slurry of PCA, that is not fully soluble in water, was prepared before immersing the carbon-based monolith.

The solution of either NH_4VO_3 or PCA was stirred for 18 h and after this process the monoliths were rinsed with distilled water in the same setup. After drying the monoliths first at room temperature overnight and later 2 h at 110 °C, the catalyst was calcined in Ar at 350 °C.

2.2. Experimental design

In the process of optimization (or evaluation) there has always been a strong belief that to determine how one factor influences a response, all other factors must be held constant while only varying that particular factor. As a result, many investigations are still carried out using the inefficient "changing one separate factor at a time" approach that offers an incomplete mapping of the behaviour of the system, often resulting in poor understanding, as well as incorrect conclusions.

In 1930, Fischer [15] showed that this method is only applicable when there are no interactions among the studied factors. Interaction effects are measures of how the "slope" of the response, *y*, changes, with respect to a factor, as another factor changes. To obtain information on the influence of one single factor on a response, at least two experiments have to be performed. Normally 2^k experiments are required for evaluating a process with *k* factors if non-linear relations are also to be estimated. The number of experiments depends not only on the number of factors involved but also on the degree of information desired (the complexity of the model to be estimated).

We carried out a factorial experiment design with 3 factors at 2 levels at a central point with three replications, i.e. 11 experiments in total for each catalysts prepared, since, according to the explanation above, we considered that a 2^3 factorial design would be enough to get a good understanding of the catalyst behaviour. The factors chosen for the design were the temperature, the spatial velocity and the molar ratio of NH_3/NO. According to the literature, the NO conversion, the selectivity towards N_2 and the ammonia slip depend on these factors [16] which have been previously studied in the literature in a separate way, thus the factors values were chosen taking into account these data as well as the preliminary experiments carried out in our labs. The temperature values were 150, 250 and 350 °C. The values of spatial velocity chosen were 22,000, 34,000 and 45,500 h^{-1} and finally the molar ratio of NH_3/NO varies between 0.7 and 1.3. Table 2 shows the experiments carried out for each catalyst prepared.

2.3. Catalytic activity

The activity tests were carried out in a quartz reactor with a gas containing 1000 ppmv NO, 1000 ppmv NH_3 and 10% O_2 (v/v) an Argon to balance at 250 °C as central point conditions. The gas flow rate used in the experiments reported here varied according to the factorial design but its central point was 120 ml/min that gives rise to a space velocity of around 34,000 h^{-1}. For the determination of the influence of the spatial velocity, inlet NH_3 concentration and evaluation of ammonia slip, activity tests changing inlet gas compositions and residence time of the gas in the catalytic bed was changed by modifying the gas low entering the reactor.

The gases were dosed by means of mass flow meters and fed to the cylindrical quartz reactor heated by an electric oven. The concentrations of NO, NH_3, O_2, N_2 and N_2O in the outlet gases were continuously measured in a mass spectrometer (Balzers 422) connected on-line. The mass spectrometer was calibrated using cylinders of known concentration. The quantification of the several species measured was carefully performed and checked regularly in order to guarantee an accurate measurement of their concentrations. Calibration was performed using certified calibrated mixtures of 1800 ppm of NO in Ar, 3000 ppm of NH_3, 7% of O_2 in Ar, 1000 ppm of N_2 in Ar and 1000 ppm of N_2O in Ar. The component matrix measurement was created assigning the following *m*/*z* values: 30 for NO, 17 for NH_3, 32 for O_2, 44 for N_2O, 28 for N_2 and 40 for Ar (defined as internal standard). Moreover, other actions as backing (heating up) to clean up the chamber from adsorbed substances and peak position calibration have been carried out very often.

The percentage of NO reduction and the selectivity towards N_3 were calculated as follows:

$$\%\text{NO conversion} = 100 \times \frac{(C_{NO}^{i} - C_{NO})}{C_{NO}^{i}} \quad (1)$$

$$\%\text{Selectivity toward } N_2 \quad (2)$$

$$= 100 \times \frac{(C_{N_2} - C_{N_2}^{i})}{[(C_{N_2} - C_{N_2}^{i}) + (C_{N_2O} - C_{N_2O}^{i})]} \quad (2)$$

where C_{NO}^{i}, $C_{N_2}^{i}$ and $C_{N_2O}^{i}$ are the measured initial concentrations of NO, N_2 and N_2O respectively, and C_{NO}, C_{N_2}, C_{N_2O} the concentrations of those gases once the steady state is reached.

2.4. Catalyst characterization

Both NH_4VO_3 and PCA doped catalysts as well as supports were physically and chemically characterized by means of different techniques and methods:

(1) *Nitrogen adsorption isotherms at 77 K* were obtained in a Micromeritics ASAP 2020 unit. Prior to tests, the samples were outgassed at 200 °C up to a steady vacuum of 1×10^{-6} Torr was achieved. The specific surface area (SSA) was calculated applying the Brunauer–Emmett–Teller (BET) equation to these isotherms. Empirical *t*-plot method was used for the calculation of micropore volume. Mesopore volume was calculated by means of BJH method.

(2) *Ammonia chemisorption* was carried out in a Micromeritics Pulse Chemisorb 2700 apparatus. The samples of 200–300 mg were dried before carrying out the chemisorption at the same temperature around 20 min. Chemisorption was performed injecting pulses of 108 μl of pure ammonia, and measuring the amount of ammonia consumed by means of a thermal conductivity detector. Ammonia is a basic molecule that is desorbed either on Brönsted acid sites through the formation of NH_4^+ ion or in Lewis acid sites through coordinative complexation.

(3) *Temperature-programmed desorption* was performed using 0.6 g of sample place inside a quartz U-tube, under a stream of He flowing through a 30 ml/min. The sample was heated up by an electric oven to a temperature of 1050 °C, at a heating rate of 10 °C/min. The gases evolved with each increase of 100 °C were stored in special bags and further analysed by gas chromatography (Porapack Q and molecular sieve 13× columns) to determine the amounts of CO and CO_2 desorbed. This method has become rather popular among the different techniques used to characterize the functional groups on carbon surface [17,18]. The surface chemistry of a carbon material is basically determined by the acidic and basic character of its funcionalities such as carboxyls, lactones and phenols while pyrones, chromenes, ethers and carbonyls are responsible for basic properties on carbon surfaces [19,20]. Although there is not total agreement in literature with respect to the TPD peaks assignment to specific surface groups, some general trends can be established:

CO_2 peaks result from carboxylic acids at low temperatures or lactones at higher temperatures, carboxylic anhydrides originate both CO and CO_2, and phenols, ethers, carbonlys and quinones evolve mainly as CO.

3. Results and discussion

3.1. *Influence of single operating parameters*

Initial experiments to determine practical range of the different variable factor were performed at the same time when a literature research was carried out. The results obtained in this kind of experiments are presented and discussed in this section.

3.1.1. *Reaction temperature*

The variations of NO conversion at central point gas composition and GHSV but different temperatures (50–400 °C) were shown in Fig. 1 for the catalysts doped with 5% wt of vanadium from NH_4VO_3. In Fig. 1, runs were carried out at different temperatures but GSHV always remains constant (34,000 h^{-1}). The results indicated that temperature had a significant effect on the SCR activity. Catalytic behaviour related to temperature agrees with previous studies carried out by this group [21,22]. Briefly, the activity initially decreases with temperature and then rises again once a temperature of 125 °C is reached. This change in the slope of the curve is indicative of a change in the reaction mechanism, or at least in the rate controlling step with the reaction temperature. Higher conversions measured at the lowest temperatures can be due to favoured adsorption of any of the reactants under these conditions, most probably of NH_3. As proposed in [43], NH_3 adsorption is a decisive step in the SCR reaction and consequently at lower temperatures, the higher NH_3 adsorption promotes NO conversion. From 125 °C on, NO conversion increases proportionally to temperature showing the reaction controls in this range of temperatures. For the sake of comparison to other catalysts (Table 1), apparent activation energy as well as apparent kinetic constants have been fitted to a first order kinetic reaction only in this range of temperatures. From 300 °C on, NO conversion remains approximately constant, likely due to a poor NH_3 adsorption that does not promote the SCR reaction.

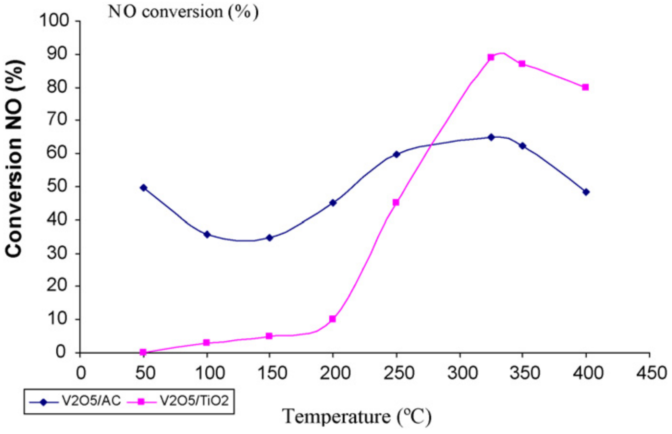

Fig. 1. NO reduction efficiency at different reaction temperatures.

Table 1
Apparent activation energy for several SCR catalysts

Catalysts	E_{app} (kJ/mol)	Reference
5% V_2O_5/AC-A	30.1	[29]
5% V_2O_5/AC–5%ZrO_2/AC	28	[27]
15% Mn/ACF	27.5	[33]
1.4% V_2O_5–9%WO_3/TiO_2	59.4	[32]
Ciadielle		[23]
SCA750PCA (Powder)	31.7	[21]
SCA750NH_4VO_3 (Powder)	25.1	[21]
2%V/C monoliths	15	[39]
3% V/C monolith	15.6	This work
5% V/C monolith	13.5	This work

Fig. 1 also shows the activity curve corresponding to a TiO_2-based catalysts, V_2O_5 (>2%V)-WO_3/TiO_2, presented in the work of Ciardelli et al. [23], measured using 0.16 g, GSHV of 36,000 h^{-1} and a gas composition of 1000 ppmv of NH_3, 1000 ppmv NO and 10% (v/v) of O_2 and He to balance. It can be clearly observed that the activity of the TiO_2-based catalysts is lower than the one measured for the carbon-based catalyst, when working at temperatures lower than 275 °C.

Similar studies were carried out by other authors to study the influence of temperature on carbon-based catalysts [24–30] finding that, generally speaking, the higher temperature is, the higher NO conversion. However, there are some studies where a conversion peak was found out in the temperature range of 110–300 °C for catalysts doped with Cu.

Apparent activation energy was a significant parameter to evaluate the performance of catalyst. Table 1 shows the apparent energy of activation calculated for the catalysts presented in this work, some other similar carbon-based catalysts commented above and also for the commercial TiO_2-based catalyst whose activity curve also appears in Fig. 1. For the calculation, we should obtain the rate constant at different temperatures and then first order kinetics with respect to NO was assumed. The value of energy of activation was calculated from the slope of the respective Arrhenius plot. The values of energy of activation calculated for the catalysts presented in this work are quite similar to those presented in literature for the other carbon-based SCR catalysts and significantly lower than the ones measured for the TiO_2-based catalysts. It indicates that less energy is needed for activation in the reaction. Therefore the catalytic activity is significantly improved and NO conversion should be increased.

A well-known limitation of the use of carbon-based catalysts is the possible gasification of the carbon support in the presence of reactant gases containing O_2. Preliminary experiments confirmed the absence of gasification of the carbon support up to a temperature of 400 °C. The stability of the catalysts was proved by means of gas chromatography tests confirming lack of either CO or CO_2 in the outlet gas.

3.1.2. *Infuence of gas residence time*

The effect of the gas residence time was also tested as an only effect, since it represents an important factor that could greatly

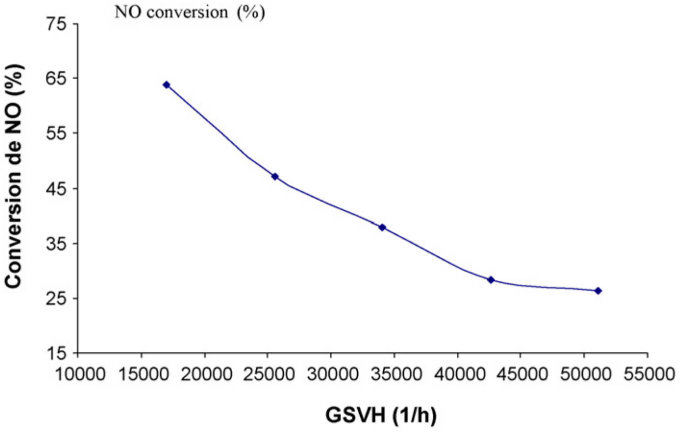

Fig. 2. NO reduction efficiency at different GSVH values.

influence the NO conversion of on-board systems. Fig. 2 shows the NO reduction profiles obtained for the 5% wt vanadium (NH_4VO_3) at several GSHV while remaining constant gas composition and the temperature at the central point (250 °C). It can be clearly observed that the activity decreases if spatial velocity increases. When a GSHV of 17,000 h^{-1} is employed a conversion of NO up to 65% is reached. However, a spatial velocity of 52,000 h^{-1} leads to conversions as low as approximately 30%. These results are in a complete agreement with other authors [7,21,24,31] who studied previously the influence of the residence time on carbon-based catalysts. Moreover, these results are also in agreement with those obtained by this researcher's group with carbon-based catalysts in powder shape [43]. Powder catalysts show that an increase in the spatial velocity causes a decrease in the NO conversion and just in the other way round a decrease in the spatial velocity causes an increase in the NO conversion.

A checking of diffusion limitation effects has been carried out following the Uberoi and Pereira's method [42]. According to this method if the calculated mass transfer coefficient presents a much higher value than the kinetic coefficient, there is no doubt about the non-existence of diffusion limitations in the system.

Fig. 3 shows the influence of the mass transfer coefficients in the total reaction control for a range of temperatures between 150 and 300 °C and GSHV between 22,000 and 45,500 h^{-1}. As observed, diffusion limitation reaches a value of 18% under

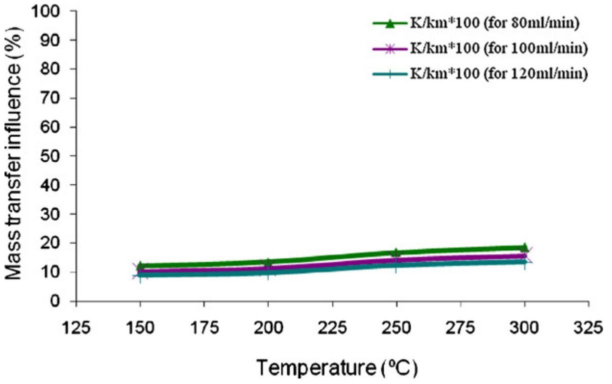

Fig. 3. Influence of diffusion limitation on the total reaction control.

Table 2
Results of the experiment design for all the catalysts prepared

Exp	Factors			% NO conversion				% Selectivity towards N_2				Ammonia-slip (ppmv)			
	NH_3/NO	T (°C)	GSHV (h^{-1})	3% NH_4VO_3	5% NH_4VO_3	3% PCA	5% PCA	3% NH_4VO_3	5% NH_4VO_3	3% PCA	5% PCA	3% NH_4VO_3	5% NH_4VO_3	3% PCA	5% PCA
4	0.7	150	22000	55	61	56	51	99.27	99.42	99.62	98.63	0	0	0	0
2	0.7	150	45500	37	53	34	36	97.81	96.28	98.29	99.70	0	0	0	32
8	0.7	350	22000	69	75	67	64	66.75	61.43	64.20	58.90	0	0	0	0
5	0.7	350	45500	70	66	62	67	20.99	99.85	52.63	76.80	75	0	30	12
9	1	250	34000	80	63	48	67	98.71	97.65	97.27	97.99	74	29.6	3	21
1	1	250	34000	83	66	44	71	97.80	99.78	97.82	98.29	13.4	0	11	51
3	1	250	34000	78	60	45	67	84.07	97.69	97.92	98.43	95	15	6	44
10	1.3	150	22000	59	49	47	61	100	99.68	99.17	99.53	88	0	0	37
6	1.3	150	45500	46	58	33	25	86.40	100	97.41	97.09	0	29	0	34
11	1.3	350	22000	89	75	80	85	99.83	25	73.00	70.16	67	0	0	17
7	1.3	350	45500	72	70	75	80	71.40	81	64.49	57.06	0	0	19	49

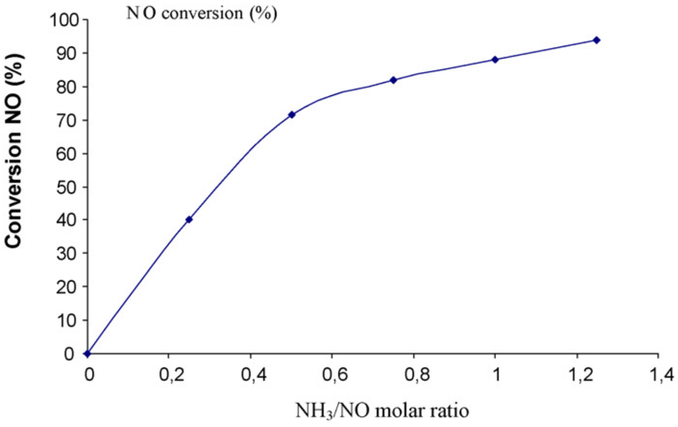

Fig. 4. Influence of NH_3/NO inlet molar ratio in the catalytic activity.

the worst conditions. Regarding this value, experiments can be considered free of diffusion limitations.

3.1.3. *Influence of the molar ratio NH_3/NO*

The effect of NH_3 concentration on the reaction is shown in Fig. 4. When the ratio [NH_3]/[NO] was low, NO conversion increased quickly as long as the NH_3 concentration increases. Subsequently, the increase of NO becomes slower. When NH_3 concentration was in excess, NO conversion trended to a constant value.

These results are once again completely in agreement with what other authors state for similar carbon-based [21,33,34] as well as TiO_2-based catalysts [35–38]. These studies mentioned that NH_3 and NO had little reactivity in the gas phase. In the reaction, ammonia was adsorbed on the surface of the catalyst and then reacted with NO. In this way, when the concentration of NH_3 is low an increase of NH_3 concentration triggers than more NH_3 could be adsorbed on the catalyst and react with NO. However, when the concentration is in excess (>0.65), the adsorbed sites were limited, and no further NH_3 could be adsorbed to catalyst. Therefore, NO conversion becomes independent with NH_3 concentration.

3.2. *Influence of interaction of operating conditions*

Table 2 compiles the results of all experiments carried out according to the experiment design. The first column of result shows the NO conversion, the second column the selectivity towards N_2 and the third one the ammonia-slip detected by the mass spectrometer for each catalyst tested. The impact of the studied variables on the three responses, along with the fitting coefficient was calculated with MINITAB, following the fundamentals of the experimental design analysis, for a significance level of $\alpha = 0.05$.

The variables which had a significant effect on the response had been taken into account for the mathematical modelling shown in Table 3. The evaluation of these relative effects on the response variables can be corroborated by means of a statistic tool as the Pareto diagram. These data are not shown for the sake of clarity, however, it is worth noticing that all experiments presented in this study have at least a degree of certainty of $\alpha = 0.95$ except for the NH_3-slip values. This degree of certainty is usually considered high enough to ensure that the model fits the experimental values. We can observe that the effect of higher significance is the temperature. Temperature has a strong influence in all the samples and all the response variables.

NO conversion is equally greatly effected by spatial velocity, showing that an increase in this variable causes a decrease in the NO conversion. Finally, the molar ratio has a less significant effect and in some cases it does not have an effect as a single variable, but in interaction to another one.

Comparing the as-prepared four catalysts, we can observe that the constant parameter is related to the NO conversion reached by them. At a sight of the results, we can observe that the catalysts doped with a commercial precursor reached a higher conversion that the catalysts doped with PCA. Equally catalysts doped with 3% V reach a higher conversion than catalysts doped with 5% V. This fact can be due to a partial pore blockage produced while impregnation the carbon support. Table 4 shows the data of SSA and micropore volume for all samples. As observed, the micropore volume of 3% V doped catalysts is slightly higher that those values of 5% V catalysts. According

Table 3
Mathematical modelling for the catalysts prepared

Catalyst	Constant	T	GSVH	NH_3/NO	NH_3/NO*T	NH_3/NO*GSVH	T*GSVH	NH_3/NO*GSVH*T
% NO conversion								
5% NH_4VO_3/C	63.50	8.17				2.60		
3% NH_4VO_3/C	62.13	12.99	−5.77	4.33				
5% PCA/C	54.70	15.30	−6.57	4.18	4.30		6.30	
3% PCA/C	56.50	14.11	−5.60		4.60			
% N_2 selectivity								
5% NH_4VO_3/C	82.81	16.04	11.54				12.25	
3% NH_4VO_3/C	80.22	15.43	−11.00		11.64			
5% PCA/C	82.23	16.50		−1.27		−4.31		−3.44
3% PCA/C	81.10	17.52	−2.90		2.75			
Ammonia-slip								
3% NH_4VO_3/C	12.99	9.90				−12.99		−9.90
5% PCA/C	22.63	−3.19	9.36	11.60				6.78
3% PCA/C	6.05	6.02	6.05				6.05	

Table 4
SSA, volume of pore, TPD and NH$_3$ chemisorption results

Catalyst	S_{BET} (m^2/g)	$V_{micro\ total}$ (cm^3/g)	$V_{micro\ (<0.7\ nm)}$ (cm^3/g)	$V_{micro\ meso}$ (cm^3/g)	V_{meso} (cm^3/g)	TPD experiments			NH$_3$ chemisorption (cm^3/m^2 g)
						cm^3 CO/g	cm^3 CO$_2$/g	cm^3 CO + CO$_2$/g	
5% NH$_4$VO$_3$/C	29.15	6.48	4.11	2.37	0.026	11.1	3.9	15	5.22
3% NH$_4$VO$_3$/C	34.19	8.41	6.86	1.55	0.025	8.5	3.3	11.8	5.24
5% PCA/C	47.64	5.82	1.16	4.65	0.047	8.2	3.3	11.6	2.14
3% PCA/C	31.65	5.82	1.47	4.35	0.039	7.8	3.4	11.2	3.16

to previous studies [39] the presence of micropores and mesopores is of key importance to get high NO conversion since micropores enhance the dispersion of the catalyst and mesopores guarantee the accessibility to catalyst precursor and reactants to the carbon coating inside the macropores of cordierite wall. Moreover, according to the literature [39] the impregnation with V_2O_5 can cause some narrow micropore clogging when they are deposited at the entrance of the pores since its diameter is in the range of narrow microporosity. This fact seems to be the reason why higher vanadium-loaded monoliths get lower NO conversion.

At the sight of the results presented in Table 4, it can be observed that the amount of CO and CO$_2$ evolved during TPD runs increases for the higher vanadium-loaded catalysts, and therefore vanadium could be responsible for this increase. Moreover, according to the deconvolution of TPD runs carried out by ORIGIN, for both higher vanadium-loaded catalysts there is a higher amount of phenol groups as well as lower amounts of carbonyl, quinone and carboxyl groups. For the PCA-loaded catalysts, lower amounts of phenol and carboxyl groups as well as higher amounts of carbonyl and quinine groups can be observed. Making a correlation between oxygen surface groups and catalytic activity, it could be proposed that a higher amount of carboxyl groups can favour the SCR reaction with NH$_3$ on carbon-based catalysts.

For all samples, ammonia chemisorption considerably increases after loading of the vanadium compounds. But the ammonia adsorption depends on the loading and active phase precursor. In the case of catalysts prepared with NH$_4$VO$_3$ as precursor of the active phase, the amount of ammonia adsorbed is higher than that in the case of catalysts prepared with PCA. This fact shows a close relationship between the SCR activities. In the same way, the higher the loading the lower the ability to adsorb ammonia what once more seems to be in a close correlation to the SCR activity. These results confirm the theory that the ammonia adsorption during the SCR reaction plays a key role on the activity and therefore a high ammonia adsorption enhances the SCR activity of this kind of catalysts [41].

Apart from the influence of temperature, selectivity towards N$_2$ is greatly influenced by the spatial velocity and to a certain extent by the interactions between variables, mainly the interaction between the molar ratio and another one. On the contrary to the NO conversion, the catalysts doped with a higher amount of vanadium show a higher selectivity towards N$_2$ and there is no difference between the selectivity of PCA and NH$_4$VO$_3$-doped catalysts.

The ammonia-slip is little influenced by none of the studied variables and therefore the mathematical modellings were obtained taking into account those parameters which shown a higher influence regardless the *p*-value. The higher influence belongs to the temperature. This result agrees with the fact that the higher the temperature is, the higher the NO conversion and therefore there should be a higher consumption of NH$_3$, causing a reduction of the ammonia-slip. Comparing PCA-doped catalysts we can observe that they give out generally higher values of ammonia-slip in the outlet gas in comparison with the catalysts prepared using NH$_4$VO$_3$, what agrees with the experiments carried out by other authors [21,23,40] and what may be due mainly to its lower catalytic activity.

4. Conclusions

In this study vanadium-loaded carbon-coated monolithic catalysts have been prepared for testing their activity under laboratory conditions close to real lean-burn on-board ones. The influence of several parameters: temperature, gas velocity and NH_3/NO ratio were studied on NO conversion, N_2 selectivity and NH_3-slip. Taking into account the results obtained carbon-based catalysts should be considered as a candidate of on-board NO reduction as they show a considerable NO reduction activity.

Vanadium-loaded carbon-based monolithic catalysts showed considerable activity, high selectivity towards N_2 and low ammonia-slip values in the reduction of NO in the presence of NH_3 and O_2 at relatively low temperatures. Catalysts were doped with two different precursors of active phase, NH_4VO_3 or PCA, showing in both cases a similar NO reduction behaviour. The activity reached by PCA doped catalysts is slightly lower, the selectivity is comparable and finally the ammonia-slip is little higher than those to the one measured for the catalysts prepared with model vanadium compounds such as NH_4VO_3.

The influence of single parameters on the above response variables was previously tested. Generally speaking, the higher the temperature the lower the spatial velocity and the higher the molar ratio are, the higher the NO conversion becomes. However, temperature should be maintained below 400 °C to avoid carbon support gasification and molar ratio should be lower than 0.65 to minimize ammonia-slip in the outlet gas.

The influence of interaction parameters was evaluated, thanks to an experiment design. The statistical analysis shows that temperature and GSVH have a significant impact on NO conversion and selectivity towards N_2 while molar ratio of NH_3/NO shows its effect mainly in the interaction with other parameters. Surprisingly these parameters do not show a high influence on the amount of ammonia-slip which varies according to the NO conversion.

The physical and chemical features of the carbon catalysts employed played a key role in the catalytic activity. The presence of higher amounts of carboxyl and lactone groups favours the NO conversion reached by the catalysts. This presence is favoured in the catalysts doped with NH_4VO_3 as a precursor of the active phase and lower amounts of vanadium loading. Moreover, it was observed that amounts of vanadium loading higher than 3% wt seem to produce a little decrease of surface area as well as a small micropore blocking which could be the cause of their slightly lower catalytic activity.

Finally, the apparent activation energies calculated for these catalysts are similar to the values presented in the literature for other carbon-based catalysts, and all of them are considerably lower than the one corresponding to a TiO_2-based catalyst, which confirms the higher activity of carbon-based catalysts in the lower temperature range.

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