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Novel activated carbon-based catalyst for the selective catalytic reduction of nitrogen oxide

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Abstract

A series of catalysts prepared with activated carbons, doped with some vanadium compounds including the ashes of a petroleum coke, have shown considerable activity in the reduction of NO in the presence of ammonia, at relatively low temperatures (100–300 °C). The presence of 10% (v/v) water vapour caused a considerable decrease in activity. The presence of 200 ppmv of SO_2 in the reactant gas mixture did not appear to cause any depletion of the NO reduction efficiency. Higher NO reduction efficiencies were measured for the catalysts prepared using pre-oxidised supports.

Keywords: Activated carbon; Selective catalytic reduction; Nitrogen oxide; Vanadium; Low temperature

1. Introduction

Selective catalytic reduction (SCR) in the presence of ammonia has become lately one of the most outstanding technologies for the removal of nitrogen oxides. This process has been widely studied, commercialized and successfully applied. However, intensive efforts are continuously being made in exploring catalysts durability, new active materials and reaction mechanisms [1,2].

The commercially available SCR processes use V_2O_5 supported over TiO_2 as catalytic system, which operates at temperatures higher than 350 °C [3,4]. Activated carbon has shown to be active at much lower temperatures, i.e. 100–250 °C [5–7]. In this way, SCR unit could be located at the end of the stack gas system, thus preventing many problems of catalyst deactivation and avoiding retrofitting in the boiler [8]. The main disadvantage of activated carbons is that, due to they low catalytic activity, they must be applied at high residence times. An important enhancement of the activity can be achieved by modifying activated carbon properties [9–11] or by doping it with an active phase like Cu [12,13], Fe [12], Mn [14–17] or V [18] oxides.

In our previous works [19,20], we reported the preparation of potential catalytic sorbents using a low-rank coal as the precursor of the carbonaceous support doped with different vanadium compounds. Among these precursors, the ashes of a petroleum coke were also employed. Metal capture and distribution, mineral and chemical composition, changes in surface area and surface chemical features, reactivity and redox properties were studied by means of a deep characterization of the materials. Those studies intended also to describe an optimum preparation procedure, which was found to be loading of metals on the previously steam activated char. The activity of these catalysts was in absence of ammonia as external reducing agent. In this case high NO removals were obtained but at temperatures higher than 350 °C. At these temperatures gasification of the carbonaceous support was found to be considerable. Thus, the reduction of NO in the presence of ammonia at low temperatures was also investigated. The catalysts prepared with the petroleum coke ashes (PCA) showed slightly less NO reduction efficiencies than similar catalysts prepared using model vanadium compounds (V_2O_5 and NH_4VO_3) [21]. The activity of the catalysts was improved by optimising the preparation of the activated carbon support. NO conversions up to 50% and high selectivity towards N_2 were obtained at 150 °C, especially for the PCA loaded improved activated carbon [22]. However, reduction tests in

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a wider temperature window were not already performed, and could yield interesting results. Moreover, the need to determine the activity of these materials in a set of conditions closer to their real potential use, led to the introduction of 10% water vapour and a residual concentration of SO_2 in the reactant gas mixture. Carbon support pre-oxidation was also tested as a way to improve catalyst efficiency. The results obtained have given yet a clear idea about the NO reduction reaction mechanism.

2. Experimental

2.1. Preparation of the carbon support

SAMCA coal from SAMCA mines in Teruel, Spain was used as carbon support precursor. This coal was pyrolysed at 800 °C in nitrogen. The obtained char was activated at 750 °C, with 20% of steam, at a total flow of 1200 l h^{-1} and with a residence time of 4 h. This activated carbon, named SCA750, was prepared in a preparative-scale unit with a batch-mode fluidised bed reactor.

Pre-oxidation of the carbon support SCA750 was performed either in liquid or in gas phase. Concentrated HNO_3, HNO_3 IN, H_2O_2 and air were used as oxidising agents. Table 1 shows the preparation of each of the oxidised carbon supports presented in this paper.

2.2. Petroleum coke ashes (PCA)

A coke from the Delayed Coke Unit in the REPSOL refinery in Puertollano, Spain, was used for the production of the 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 [19].

2.3. Catalysts production

The carbon support SCA750 was loaded with 3% (w/w) V using either V_2O_5 or NH_4VO_3 as the model vanadium compounds, and the PCA. A solution/suspension of each of these compounds in distilled water was stirred for 15 min at a temperature between 35 and 40 °C, before adding the correspondent amount of the activated carbon. The support was added stepwise in small charges while the suspension was continuously stirred. After stirring at ambient temperature for 4 h the temperature was raised to around 150 °C in order to evaporate most of the water in the suspension. Finally the catalysts were dried overnight in an oven at 108 °C. Table 2 shows a short description of the catalysts prepared.

Table 1
Pre-oxidised carbon supports

Sample	Description
SCAOX1	SCA750 + HNO_3 65%, ambient temperature, 4 h
SCAOX2	SCA750 + HNO_3 65%, 80 °C, 3 h
SCAOX3	SCA750 + H_2O_2 33%, ambient temperature, 4 h
SCAOX4	SCA750 + H_2O_2 33%, 80 °C, 3 h
SCAOX5	SCA750 in air, 200 °C, 3 h
SCAOX6	SCA750 in air, 300 °C, 3 h
SCAOX7	SCA750 in air, 200 °C, 6h
SCAOX8	SCA750 + HNO_3 1N, ambient temperature, 4 h

2.4. Catalysts characterization

Both the carbon support and the catalysts were physically and chemically characterised by means of different methods and techniques: Adsorption of N_2 at 77 K, O_2 and NH_3 chemisorption, and temperature programmed desorption (TPD).

Specific surface area was calculated from the N_2 adsorption isotherms applying the Brunauer–Emmett–Teller (BET) equation and yields important information about structural features.

As for the surface chemistry of the catalysts, oxygen chemisorption has proven to be very useful in evaluating the abundance of electron-donor sites on solid surfaces through a redox mechanism [23]. Ammonia, on the other hand, is one of the important reactants in SCR. It is adsorbed either on Bronsted acid sites through the formation of NH_4^+ ion or in Lewis sites through coordinative complexation. NH_3 and O_2 chemisorption were performed in a Micromeritics Pulse Chemisorb apparatus, using a flow of 30 mL/min of He on 600 mg of sample placed on a U tube. The sample was degasified at 125 °C for at least 15 min prior to chemisorption. During chemisorption the sample was heated at the corresponding temperature and the amount of NH_3 or O_2 not adsorbed by the sample was measured in a TCP integrated in the apparatus used.

TPD has become one of the most common techniques to characterise the functional groups on carbonaceous surfaces [24]. Acidic behaviour is associated with oxygen function-

Table 2
Description and preparation procedure of the catalysts presented in this work

Sample	Description
m200	SCA750 + 3% V, V_2O_5
m201	SCA750 + 3% V, NH_4VO_3
m202	SCA750 + 3% V, PCA
OX1PCA	SCAOX1 + 3% V, PCA
OX2PCA	SCAOX2 + 3% V, PCA
OX3PCA	SCAOX3 + 3% V, PCA
OX4PCA	SCAOX4 + 3% V, PCA
OX5PCA	SCAOX5 + 3% V, PCA
OX6PCA	SCAOX6 + 3% V, PCA
OX7PCA	SCAOX7 + 3% V, PCA
OX8PCA	SCAOX8 + 3% V, PCA

alities such as carboxyls, lactones and phenols while pyrones, chromenes, ethers and carbonyls are responsible for basic properties [25,26]. In general, it is considered that CO_2 peak results from carboxylic acids at low temperatures and lactones at higher temperatures, that carboxylic anhydrides originate both CO and CO_2 peaks and that phenols, ethers, carbonyls and quinones evolve as CO. TPD was performed heating 600 mg of sample at a constant rate (10 °C/min) from 150 to 1050 °C in a flow of 30 mL/min of He. Samples were collected in gas sample bags and CO and CO_2 were measured in a chromatograph equipped with a TCD.

2.5. Activity tests

The NO reduction efficiency of the catalysts was determined by passing a gas mixture containing 1000 ppmv of NO, 1500 ppmv of NH_3 and 3.5% (v/v) of O_2 in Ar through a fixed bed containing 0.4 g of sample. The residence time of the gas in the reactor was approximately 1.4 s. The tests were performed at different temperatures from 50 to 400 °C.

Activity tests in presence of water vapour and of both water vapour and SO_2 were also performed. The experiments were performed under the same conditions described before, adding to the reactant mixture 10% (v/v) of water vapour or 10% (v/v) plus 200 ppmv SO_2.

The composition of the gas exiting the reactor was continuously measured in a quadrupole mass spectrometer (Balzers 422) connected on-line.

The conversion of NO was calculated as follows:

$$\%\text{NO conversion} = 100 \times \left(\frac{C^{\text{i}}_{\text{NO}} - C_{\text{NO}}}{C^{\text{i}}_{\text{NO}}}\right)$$

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

3. Results and discussion

Table 3 shows the values of SSA, oxygen chemisorption ant 200 °C and the results of the TPD runs for the catalysts prepared with SCA750. Fig. 1 presents the amounts of ammonia chemisorbed at different temperatures for SCA750 and SCA750 loaded with V_2O_5 and with PCA (samples 200 and 202).

The values of SSA decrease a little with the loading either of the model vanadium compounds or of the PCA. Some pore blockage takes place that is even more noticeable for the PCA, probably due to the way they are loaded, more in the form of a suspension than of a solution.

The affinity towards oxygen increases when the vanadium compound is loaded in comparison with unloaded SCA750. This indicates probably an increase in the number of actives sites that are ready to be involved in a redox process. It is noticeable that the highest value is exhibited by sample m200 prepared with V_2O_5.

Table 3
Values of SSA, O_2 chemisorption and TPD results for SCA750, m200, m201 and m202

Sample	SSA (m^2/g)	O_2 chemisoption (cm^3/g)	TPD		
			cm^3CO/g	cm^3CO_2/g	CO_2/CO
SCA750	398	0.38	43.05	7.86	0.18
m200	385	1.01	46.22	9.91	0.21
m201	377	0.71	43.25	10.43	0.24
m202	344	0.82	52.74	17.23	0.32

The TPD results show an increase in the acidic features of the surface functionalities with the loading of the active phase, as deduced from the higher values of the ratio CO_2/CO. The increase is even more evident for the catalyst prepared with the PCA (m202). In general, the amounts of both CO and CO_2 evolved during the TPD runs are higher for the doped SCA750, as a consequence of the promotion by the presence of vanadium.

At the sight of the results of NH_3 chemisorption presented in Fig. 1 it seems, as could be expected, that the amount of NH_3 absorbed decreases as the temperature increases, both for loaded and unloaded SCA750. In general, over the entire range of temperatures, the sample that retains higher amounts of NH_3 is m200, the one prepared with V_2O_5. The unloaded SCA750 presents less affinity towards NH_3 than the vanadium loaded catalysts. This fact points out that the amount of surface active sites that are able to fix ammonia is greater in the catalyst prepared with V_2O_5, being less abundant in the unloaded carbon support. It seems that surface functionalities by themselves are not responsible for the whole NH_3 adsorption ability of the sample. Therefore, some NH_3 adsorption may be taking place also in V active sites.

With respect to the activity of the catalysts, Fig. 2 shows the behaviour of the three catalysts, m200, m201 and m202,

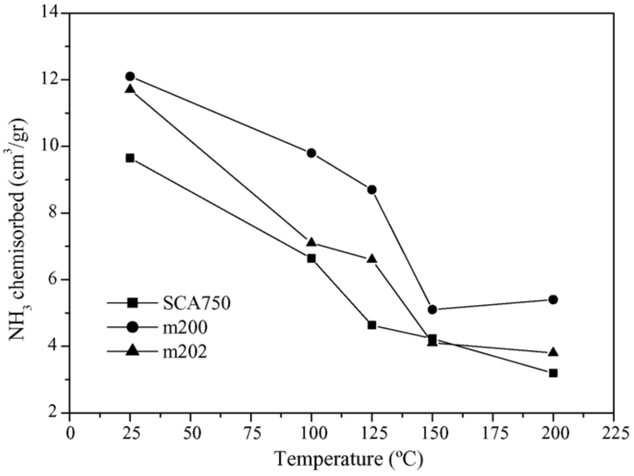

Fig. 1. Values of NH_3 chemisorption at different temperatures for SCA750, m200 and m202.

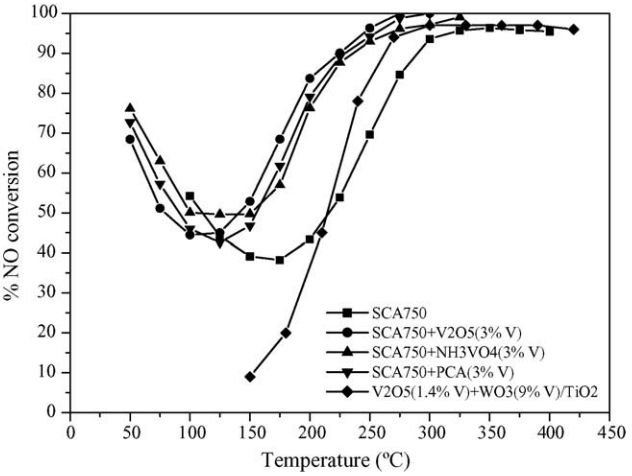

Fig. 2. NO conversion effectiveness with increasing temperatures for SCA750, m200, m201 and m202b (after 2 h time on stream).

and of unloaded SCA750 at different temperatures. NO conversion for these catalysts is compared with some data obtained for a commercial TiO_2-based catalyst presented in [27].

The four curves present similar appearance. Initially, the percentage of NO conversion decreases with the increase in the temperature up to 100, 150 or 175 °C. Then, the activity increases suddenly with the temperature reaching higher values at 300 °C. As these curves represent the activity, it can be said that unloaded SCA750 presents much lower NO reduction efficiency in the conditions tested. Loading of the vanadium compound leads in all cases to an important enhancement of the activity. It can be also observed, that the temperature of minimum NO conversion, is much lower for the vanadium doped samples than for the unloaded support. The first part of the curves could be attributed to the adsorption of the gases in the catalysts or in the activated carbon surface. However, some N_2 production is observed during reaction at low temperatures, thus indicating that although adsorption of NO on the catalyst surface might be occurring to some extent, a catalytic reduction of NO to N_2 may be taking place at the same time.

Finally, it can be clearly observed that the V_2O_5–WO_3/TiO_2 catalyst is less effective than the activated carbon-based catalysts, in the removal of NO in the temperature range between 150 and 250 °C.

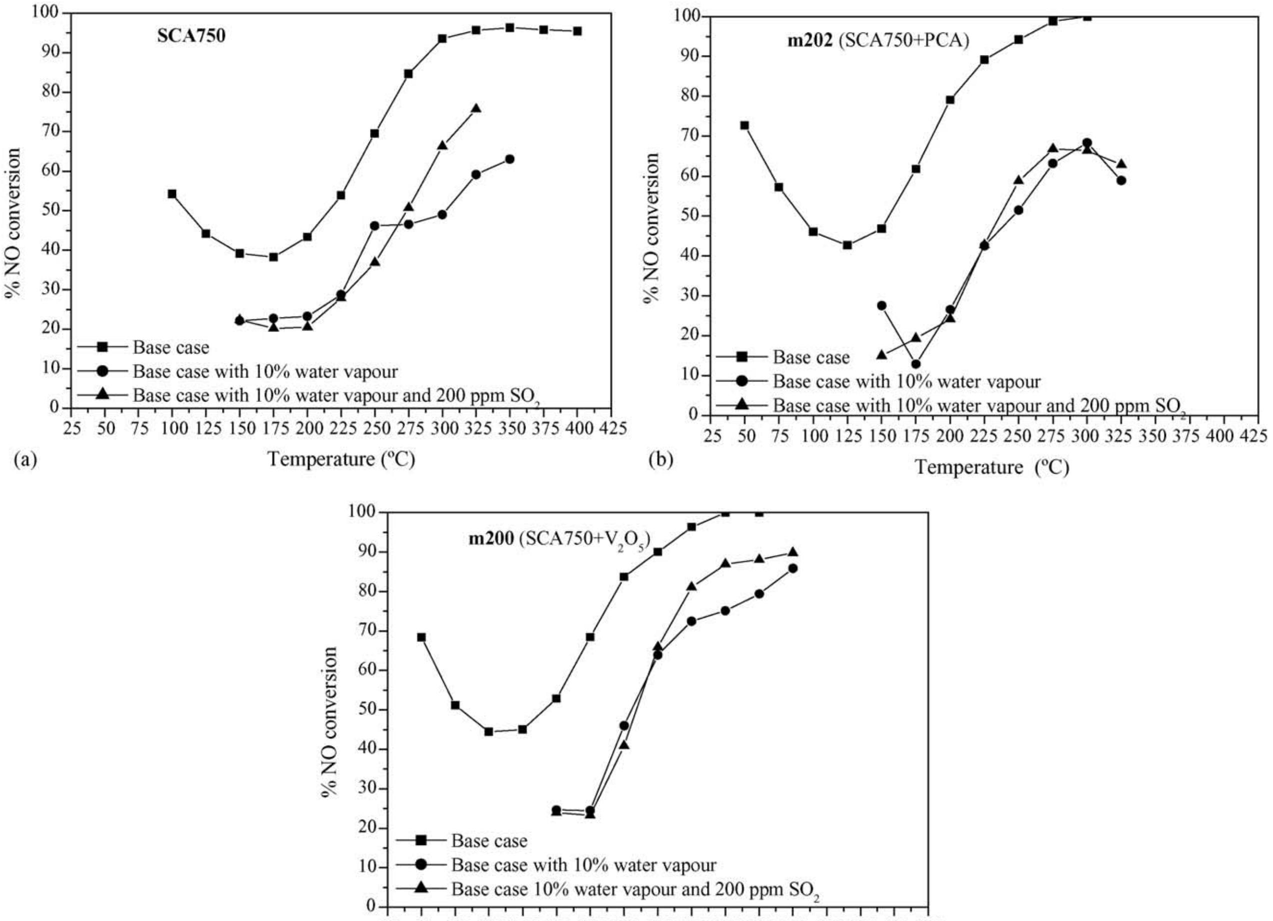

Fig. 3. (a–c) NO conversion curves after 2 h time on stream for SCA750, m200 and m202, respectively, in absence of water and SO_2, in presence of water and in presence of both water and SO_2.

Slightly higher NO reduction efficiencies are observed the one prepared with V_2O_5 in comparison with the one prepared with the PCA. Some authors agree that V_2O_5 could be more active than other vanadium species such as vanadates or polivanadates [2]. For Mn-loaded carbons it was reported than the highest NO reduction efficiency was achieved for the catalysts that contained the more oxidized phase of the manganese oxide [17]. Nevertheless, these differences become negligible at higher temperatures. Conversions even higher than 80% are obtained at a temperature of 200 °C for these catalysts, while unloaded SCA750 only reaches 43%. Thus, the catalytic effect of the introduced vanadium compound is demonstrated.

As for the behaviour of the catalysts in presence of water vapour and of both water vapour and SO_2 Fig. 3a presents the profiles obtained under such conditions for SCA750, Fig. 3b presents the same for m200 and Fig. 3c the ones corresponding to m202. A great depletion of the activity is observed when water is fed in the reactant gas mixture. Conversions rarely higher than 20% at 150 °C are obtained now, while in absence of water vapour 50% was reached. This decrease is well documented in literature for commercial and V_2O_5/TiO_2 or Al_2O_3-based catalysts [28,29] and is attributed to the competitive adsorption of water and NH_3. Authors agree that this negative effect becomes less important with increasing temperature and state that at temperatures higher than 250 °C starts becoming negligible.

Our work reveals undoubtedly a positive effect of temperature, but the conversions obtained at the same temperature in absence and in presence of water vapour can not be compared. For example, in absence of water at 250 °C, sample m200 yielded a conversion over 95% while less than 75% was measured when water was fed. The same happens for the sample prepared with the PCA (sample 202) and also for unloaded SCA750.

Some authors [30] have reported for V_2O_5 doped activated carbons higher activities in NO conversion in the presence of ammonia when SO_2 was present in the reactant gas mixture. They claim that the formation of sulphate species on the catalyst surface might be responsible for this. In our work, much difference is not appreciated between the behaviour in absence or in presence of SO_2, only with the exception of some cases at temperatures higher than 225 °C (samples SCA750 and m200). However, those authors employ higher concentrations of SO_2 and they operate in absence of water vapour. Under such conditions the formation of sulphates would be much more noticeable. These same authors have recently reported [31] some kind of deactivation due to SO_2 in the presence of water. Any case, what is remarkable is the fact that for this type of activated carbon-based catalysts, the presence of SO_2 does not seem to cause any deactivation as it has been widely reported for commercial, TiO_2- and Al_2O_3-based catalysts. This problem of deactivation has become a subject of major concern [2,32] that seems to be solved when using this kind of carbon-based materials.

Table 4
NO conversion at 150 °C after 2 h time on stream measured for the catalysts prepared with the pre-oxidised supports

Sample	% NO conversion
SCA750	34
m202	46
OX1PCA	88
OX2PCA	86
OX3PCA	52
OX4PCA	70
OX5PCA	40
OX6PCA	53
OX7PCA	38
OX8PCA	72

Table 4 shows the values of NO conversion achieved when using those catalysts prepared with the oxidised carbon supports loaded with the PCA. With the exception of those catalysts prepared with the supports oxidised in air at 200 °C, the NO conversions are generally higher than the ones measured for the catalysts prepared with the non-oxidised carbon support. This could be indicating that the new surface functionalities created during the oxidation of the carbon support may have led on one hand to stronger interactions between the active phase and the support and on the other they could be favouring ammonia chemisorption acting as reservoir for the reduction reaction. The higher activities are shown by the catalysts prepared using the HNO_3-pretreated SCA750.

4. Conclusions

Activated carbon catalysts prepared from a low-rank coal doped with several vanadium precursors, including the ashes of a petroleum coke, have demonstrated their activity in the reduction of NO in the presence of NH_3 at low temperatures. In all cases a significant promotion of the activity was obtained by doping the activated carbon with an active phase.

The NO reduction efficiency decreases initially with increasing temperature up to a point where it increases markedly. This point could be indicating the change from a simple adsorption of the reactants to real chemical reaction.

A considerable depletion of the activity is observed when water vapour is added to the reactant mixture. This effect becomes less important with increasing temperatures. However, such high conversions obtained in absence of water are not obtained. The presence of SO_2, together with water vapour, does not seem to affect the activity either positively or negatively. This would imply an important advantage with respect to commercial TiO_2-based catalysts.

Previous oxidation of the carbon support, concretely using HNO_3 and H_2O_2, led to the production of more active catalyst, due to the positive effect of the new oxygen-containing groups created.

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