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Novel carbon based catalysts for the reduction of NO: Influence of support precursors and active phase loading

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Abstract

Carbon-supported catalysts in the form of powder, briquettes and monolitos have been prepared. Powder and briquette samples have been obtained using a Spanish low-rank coal as raw material for carbon support through a pyrolysis process whereas monoliths were prepared by coating cordierite monoliths with a blend of two polymers. Vanadium was chosen as active element and impregnated by equilibrium adsorption from 1 to 8 wt% on the surface of as-prepared supports. All samples were tested in the selective catalytic reduction of NO with NH_3 as reducing agent at low temperature (150 °C), demonstrating a considerable efficiency which was enhanced mainly by oxidation treatments and an increase of vanadium loading up to vanadium agglomerates formation. The nature of carbon precursor determines the porosity development and surface chemistry of supports, what results in a different dispersion and fixation of active phase. An enhancement of NO efficiency is achieved by increasing microporosity and the amount of surface oxygen groups in pyrolysed coal whereas in polymer blend, mesoporosity and just a certain amount of surface oxygen groups should be promoted. An excess in vanadium loading decreases NO reduction efficiency because of a pore blockage and the formation of vanadium agglomeration what makes to expose a lower vanadium surface to the reactants.

Keywords: Carbon based catalysts; Vanadium loading; SCR-NH_3

1. Introduction

The removal of nitrogen oxides from outgases is one of the most challenging problems of 21st century. Until now, the most efficient method of NO_x removal from stationary sources used on industrial scale is selective catalytic reduction (SCR) with ammonia. The most frequently used catalyst is $V_2O_5/WO_3/TiO_2$ prepared in the form of a monolith [1]. The catalyst performance is, however, far from an ideal one since: a higher activity at either low (<250 °C) or high (>400 °C) temperature range, broader temperature window, higher resistance to water and SO_2, and last, but not least, reducing production and operational costs are required. These properties are highly dependent on the support material and consequently a large number of materials have been tested. Among them coal is one of the most promising due to its abundance a potentially lower cost, possibility of obtaining samples with proper geometry, good mechanical resistance [2]. Apart from these characteristics, one of the main advantages is the possibility to tailor their properties, both textural and chemical (acidity, redox properties, etc.) by means of the preparation procedure that consists of several steps, such as: pyrolysis, activation, acidic pretreatment and impregnation [3].

According to the carbon precursor election, there are many types of materials which can be used as carbon based supports, but nowadays the most important ones are those coming from coals and polymeric blends. Each precursor presents a series of advantages and drawbacks. On one hand, coals are known to be easily available and depending on their rank they could be a really low-cost raw material. Low-rank coals have a high amount of ashes what can be considered as an additional advantage since previous investigations indicated that could have a catalytic effect on NO reduction [4–7]. Catalytic effect for the NO reduction of coal-supported catalyst is mainly attributed to alkaline and alkaline earth metals [8–12] and some first-series transition metals (Fe, Cu, Cr, Co, Ni) [13–17].

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However, other authors argue that the incorporation of an additional active phase on the coal surface is required to enhance their NO removal activity [18,19].

Polymer blends are usually considered a good option because they do not involve using mineral matter and consequently can get a higher selectivity towards nitrogen, since no side-reactions are catalyzed. Polymer characteristic promotes the application of carbon blends as catalyst washcoats when they are supported on structures such as monoliths since the development of meso and microporosity ensures a good contact between reactants and the active phase [20].

As commented before, each preparation step has an influence on carbon support. Pyrolysis provides a possibility of tailoring porous structure, through the opening of constrictions in the char porosity and the development of new interconnecting pores [21]. Activation results depending on the activation agent, temperature and residence time, in the formation of either micro or mesoporosity. Moreover, activation causes a change on the chemistry surface of carbon materials. All literature studies unanimously show that the catalytic activity of activated carbons for NO conversion increases with the oxygen concentration on the carbon surface [4–9]. However, there are still several unanswered questions concerning the effect of anchoring active phase and if the presence of determined oxygen groups could influence the formation of the aggregates on the surface.

Active phase impregnation may be introduced as the last step of the preparation. The influence of the nature of precursors, loading and impregnation method was also studied [4–5,15]. Marbán et al. [15] found that NO reduction increases with higher active phase loading up to a maximum where dispersion of this component starts to drop off. Vanadium is without any doubt the most common active element for SCR reactions [22]. When it is used supported on carbon based catalysts they can enhances NO reduction at low temperatures being this fact considered as one of the most outstanding properties of vanadium loaded carbon-supported catalysts.

In this work, the results of catalytic tests for carbon samples in the form of powder, briquettes and monoliths are presented. Samples were prepared with two different carbon precursors modified by means of various activation and oxidation procedures and containing different amounts of active phase precursors. These catalysts have been characterized by means of a series of physical–chemical methods like N_2 adsorption, TPD, SEM and AFM techniques showing that the preparation steps as well as active phase precursors have a great influence on their whole performance.

2. Experimental

2.1. Catalyst preparation

Three kinds of carbon based catalysts under different forms and compositions have been prepared. Firstly, powder catalysts with a particle size between 0.2 and 0.5 mm was obtained from a low-rank coal from SAMCA coal mining company in Teruel (Spain). This coal was pyrolysed in N_2 at 800 °C, activated with 20% steam in N_2 and finally oxidized with HNO_3 as described in detail elsewhere [19]. Secondly, briquette carbon support was obtained from the above mentioned pyrolysed coal and commercial pitch. Briefly, the preparation process consists in coal pyrolysis, blending with the ground commercial tar pitch, briquetting process by pressure performed in a device specially designed to this purpose, curing in an electric furnace with air, pyrolysis of briquettes under N_2, activation either with 20% of water vapour in N_2 or CO_2 at different temperatures and oxidation with HNO_3 (1N). The activation as well as the pyrolysis, were conducted in a fixed-bed reactor as described in more detail elsewhere [23]. Finally, carbon coated cordierite monolith supports were prepared. In this case cordierite monoliths were coated with a carbon layer by means of the dipcoating method as described in details elsewhere [20]. Briefly, it consists in dipping the cordierite monolith (400 cpsi, 1 cm diameter and 5 cm length) into a liquid polymer that is subsequently cross-linked and carbonized. To coat the monoliths two carbon precursors were used polyethyleneglycol (PEG) 6000 mol wt (Sigma–Aldrich) and Furan resin (Huttenes-Albertus). After dipcoating, the sample was cured, carbonized in Ar, activated with CO_2 and treated with 2N and 4N HNO_3 at room temperature to created superficial oxygen groups [25].

In all cases, after carbon support preparation, catalysts were loaded with 1, 3, 5, 6 or 8% (w/w) V by equilibrium adsorption using commercial vanadium compounds provided by Aldrich (either V_2O_5 or NH_4VO_3) as active phase precursor. A solution/suspension of each of these compounds in deionized water was stirred and the sample was introduced inside for 3 h. In the case of NH_4VO_3 solution in distilled water was improved by adding around 10 mg of oxalic acid. After stirring samples were rinsed and dried overnight. Just in order to clarify the used abbreviation, it is worth including in this section a short description of all of them. Samples structured as powder were named as follows: SCA750/PV/1%/AD/E where SCA accounts for the carbon support prepared from the low-rank coal, as stated before, 750 is the temperature of activation used, when AC appears instead of SCA this indicates that in that case the catalyst was prepared using a commercial activated carbon as support, PV is commercial vanadium model, PCA is ashes of a petroleum coke, 1, 3 or 5% is the vanadium loading, AD is adsorption equilibrium and finally E means that the excess of dispersant was removed by means of evaporation. In the case of briquettes samples, they were named as follows: Br/AC/750/2 h/H_2O + PCA where Br means briquette, AC is activated carbon and P pyrolized, 750 is the activation temperature in °C, 2 h is the activation time and H_2O or CO_2 are the activation agent, PCA is the active phase precursor used that always provides a loading of 3 wt%. Finally monolith samples were named as 1% V_2O_5/AC where 1% is the loading and V_2O_5 the active phase precursor used. 30PEG or 50PEG mean the quantity of PEG used, respectively, and ACN for carbon activated and subsequently oxidized with HNO_3 (2N).

2.2. Catalyst characterization

Carbon support and catalysts were physically and chemically characterized by means of two different methods and techniques: Adsorption of N_2 at 77 K and temperature programmed desorption (TPD). Specific surface area was calculated from the N_2 adsorption isotherms applying BET equation in an ASAP-2000 apparatus. On the other hand, TPD tests were performed heating 600 mg of sample at a constant rate (10 °C/min) from 150 to 1050 °C in a flow of 30 ml He/min. Samples were collected in gas samples bags and CO and CO_2 were measured in a chromatograph equipped with a thermoconductivity detector.

Two techniques (SEM and AFM) have been used for the optical characterization of the active phase. SEM pictures were obtained in a SEM EDX Hitachi S-3400 N using backscattered electrons detection. The AFM apparatus was operated in a dynamic mode, where the cantilever is oscillated at its eigenfrequency (72 kHz). Topographic image and height data were collected simultaneously.

2.3. Activity tests

The NO reduction efficiency of the catalysts was determined at 150 °C 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 in the case of powder and briquette samples or just a single monolith for cordierite support. The low rate of powder and briquette catalysts was 22 ml/min while monoliths permit a flow rate of 100 ml/min. The composition of the gas exiting the reactor was continuously measured in a quadropole mass spectrometer (Balzers 422) connected on-line. The conversion of NO was calculated as follows:

$$\%\mathrm{NO\,reduction} = \frac{(C^{\mathrm{i}}_{\mathrm{NO}} - C_{\mathrm{NO}})}{C^{\mathrm{i}}_{\mathrm{NO}}} \cdot 100 \tag{1}$$

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

3. Results and discussion

3.1. Influence of support nature and thermal preparation steps on the NO reduction efficiency

Carbon support characteristics have shown to be a key factor in the NO reduction efficiency of the catalysts prepared. At the sight of the results presented in Tables 1a and 1b, both mineral and polymer blend carbon catalysts show efficiencies in the NO reduction in the range of 28 and 88%. The large difference between these values could be due to either the nature of the supports as well as the conditions used in the preparation steps that can modify the chemistry and porosity of catalysts and consequently their NO reduction efficiency.

Regarding to the activation step, all supports achieved a porosity development by an increase in temperature and residence times of activation. Especially in coal supports (powder and briquette samples) the activation process results in an increase of porosity due to the opening of constrictions in the char porosity and the development of new interconnecting pores [21]. The activation step was carried out under several conditions, steam or CO_2 activation agent and several temperatures showing that the use of CO_2 as activation agent provides a larger microporosity. This fact agrees with other authors [26–28]. In those works, authors studied the different effect of the activating agent (CO_2 or steam) in the development of porosity of a char obtained from the pyrolysis of an organic carbon. After the studies, they concluded that the CO_2 produces an opening, followed later by widening of narrow microporosity whereas steam widens the microporosity from the early stages of the activation process and consequently microporosity is favoured by CO_2 activation while meso and macroporosity are both favoured by steam activation.

Generally speaking, coal supports have mainly a microporous structure whereas monoliths are mainly mesoporous. Monoliths prepared with a polymer blend were activated under CO_2 at different temperatures. In these cases, activation process causes an increase in the microporous structure although the microporous volume adsorption did not reach the mesopority, being considered on the whole such as mesoporous materials. Porous structure of samples seems to have a great influence on the NO reduction activity reached. In the case of coal catalysts an increase in the porous structure causes an increase in the NO reduction activity although it does not seem to be a mathematical relationship between them but a threshold around 100 m^2/g that should be overcome to avoid pore blockage. On the other hand, polymer blend based catalysts show a higher dependence to the structural development. A well-developed mesoporosity is essential to favour a high amount of oxygenated surface groups that can be responsible for dispersion and fixation of active phase whereas narrow microporosity developed by CO_2 activation does not seem to play a significant role in the improvement of the catalyst prepared [27].

On the other hand, activation procedures and especially oxidation ones have a great effect on the surface chemistry. Surface chemistry plays an important role on the NO reduction. Oxidized coal supports have an average increase of 25% in the surface oxygen groups evolved such as CO or CO_2 in the TPD runs in comparison to non-oxidized samples. This enhancement is expected to be a consequence of HNO_3 treatment where new oxygen groups are created (Table 1b). The activity increases notably when subjecting the briquette to the HNO_3 oxidizing treatment prior to its impregnation. This fact could be indicating that the surface oxygen functionalities created upon HNO_3 treatment can probably favour both the fixation of the active phase and the adsorption of some reactant, likely NH_3, during the reaction, thus resulting in an increased catalytic activity. However, and although it is not shown, oxidation process of coal supports causes an important decrease in porosity what is likely due to a demineralization and redistribution of the mineral matter in coal. That matter could be displaced to the outer or inner walls of microporous what

Table 1a
Reduction of NO at 150 °C, textural and surface chemistry parameters of catalysts prepared without oxidation step

Sample	NO red (%)	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	CO (cm^3/g)	CO_2 (cm^3/g)
Powder samples						
SCA600/PV/3%/AD/E	33	8	0.04	0.010	31	13
SCA600/VA/3%/AD/E	32	6	0.04	0.011	38	11
SCA600/PCA/3%/AD/E	28	8	0.05	0.016	43	10
SCA750/PV/3%/AD/E	56	385	0.26	0.24	44	19
SCA750/VA/3%/AD/E	46	377	0.23	0.18	51	17
SCA750/PCA/3%/AD/E	46	344	0.23	0.20	53	17
Briquette samples						
Br/AC/600/2 h/H_2O + PCA	34	3	0.10	–	25	49
Br/AC/750/2 h/H_2O + PCA	52	278	0.12	–	9	32
Br/AC/750/2 h/H_2O + V_2O_5	47	285	0.21	–	9	32
Br/AC/750/2 h/CO_2 + PCA	42	106	0.05	–	16	49
Br/AC/800/1 h/CO_2 + PCA	50	182	0.08	–	13	41
Br/AC/800/2 h/CO_2 + V_2O_5	54	197	0.08	–	13	41
Monolith samples						
30PEG-AC	–	406	0.13	0.64	–	–
50PEG-AC	–	473	0.11	0.96	–	–
50PEG-ACN	72	–	–	–	–	–
AC	10	836	0.22	1.57	3.5	0.4

blocks or reduces their capacity [29]. Despite this fact, it could be observed that the loss of textural properties due to demineralization does not affect in the catalytic activity or at least, it is not as important as the influence of the surface oxygen groups formed by the oxidation process.

In the case of monolith catalysts two oxidation process where carried out by using 2N and 4N HNO_3, respectively. Comparing both samples, it is observed that increasing the severity of HNO_3 treatment entails some decrease of micro–mesopore surface area while the variation of pore volume has little significance. It could be explained by the collapse of pore walls and the ensuing widening of the pores [30]. As a consequence of this decrease in surface area, the more severe oxidized sample seems to adsorb a lower amount of vanadium and therefore reaches a lower catalytic activity.

Support nature and thermal treatments also influence in the catalysts stability. Carbon supports are known to suffer from gasification when temperature rises. In order to determine the maximum temperature at which carbon supports were stable TGA runs were performed. According to the results shown in more detail in [35,36] coal supports reach a maximum temperature around 350 °C while polymer blend supports permit a higher temperature around 400 °C. In both cases, the impregnation with vanadium results in a slightly decrease of stability that mainly depends on the active phase precursor and oxidation treatment. Time-on-stream conversion was also examined in [35] showing that catalysts resist more than 24 h without any sign of desactivation.

Finally, carbon based catalysts, both coal and polymer blend-supported catalysts have been tested in a large range of

Table 1b
Reduction of NO at 150 °C, textural and surface chemistry parameters of catalysts prepared with oxidation step

Sample	NO red (%)	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	CO (cm^3/g)	CO_2 (cm^3/g)
Podwer samples						
SCA750/PV/3%/AD/E (HNO_3 65% w/w, Troom)	86	290	0.12	0.23	41.6	51.7
SCA750/PV/3%/AD/E (HNO_3 1N, Troom)	87	300	0.15	0.22	41.6	51.7
SCA750/PCA/3%/AD/E (HNO_3 65% (w/w), Troom)	88	267	0.13	0.19	21.3	24.8
SCA750/PCA/3%/AD/E (HNO_3 1N, Troom)	72	275	0.12	0.22	21.3	24.8
Briquette samples						
Br/AC/600/2 h/H_2O + PCA (HNO_3 1N, Troom)	28	1	–	–	34	44
Br/AC/750/2 h/H_2O + PCA (HNO_3 1N, Troom)	42	189	0.08	–	27	27
Br/AC/750/2 h/H_2O + V_2O_5 (HNO_3 1N, Troom)	48	181	0.06	–	27	27
Br/AC/750/2 h/CO_2 + PCA (HNO_3 1N, Troom)	71	70	0.03	–	31	31
Br/AC/800/1 h/CO_2 + PCA (HNO_3 1N, Troom)	67	183	0.07	–	31	31
Br/AC/800/2 h/CO_2 + V_2O_5 (HNO_3 1N, Troom)	79	113	0.05	–	28	31
Monoliths samples						
V_2O_5/AC + HNO_3 2N	43	825	0.18	0.78	65.0	49.0
V_2O_5/AC + HNO_3 4N	40	775	0.20	1.48	60.5	29.1
V_2O_5/AC + conc HNO_3	37	363	0.18	0.27	66	51

Table 2
Influence of vanadium loading on activity and textural properties

Sample	NO red (%)	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
Powder samples				
SCA750/0%PCAorPV	28	–	–	–
SCA750/PV/1%/AD/E	52	347	0.18	0.25
SCA750/PV/3%/AD/E	55	384	0.26	0.22
SCA750/PV/5%/AD/E	42	302	0.15	0.22
SCA750/PCA/1%/AD/E	45	373	0.18	0.26
SCA750/PCA/3%/AD/E	46	344	0.23	0.20
SCA750/PCA/5%/AD/E	50	324	0.15	0.22
Monolith samples				
0% V_2O_5/AC + HNO_3 (2N)	12	617	0.18	0.78
3% V_2O_5/AC + HNO_3 (2N)	43	620	0.23	0.61
4% V_2O_5/AC + HNO_3 (2N)	56	629	0.23	0.63
6% V_2O_5/AC + HNO_3 (2N)	68	607	0.20	0.70
8% V_2O_5/AC + HNO_3 (2N)	67	529	0.16	0.61

temperature (75–350 °C) and their activity has been compared to other commercial catalysts activity found in the literature [36,37]. As shown in these studies, carbon based catalysts present a higher activity at lower temperatures than commercial catalyst what can avoid the need of gas reheating in an industrial facility.

3.2. Influence of vanadium loading on the NO reduction efficiency

As described previously, all samples were loaded with vanadium by means of equilibrium adsorption method. It is known that in the preparation of supported catalysts by impregnation, the sorption of metal ions in solution is influenced by the physical–chemical properties of the support, pH of impregnation, and nature of the solvent. When the pH of impregnation solution is higher than the point zero charge (PZC), the surface of the support will become negatively charged, and the adsorption of cations is favoured [31]. The main goal of the oxidation with HNO_3 is to obtain a more hydrophilic surface with a relatively large number of surface oxygen groups, hence decreasing the PZC. However, if carbon based supports have been prepared under the same preparation procedure, both the nature of precursor and the loading of vanadium have a great influence on the catalytic behaviour of the samples.

An increase of vanadium loading leads in all cases to an enhancement of the activity until a certain extend where a drop off in catalytic activity starts. As shown in Table 2 an increase in loading leads to an important increase in the catalytic activity. When polymer blend are tested the activity increases up to a 6% of vanadium whereas coal based catalysts show a higher activity but only up to a 5% in vanadium. This fact could be attributed to a possible pore blockage together with agglomeration leading to poor dispersion of the active phase, when an excess of vanadium precursor is used. According to literature the amount of active phase that can find place on the catalysts surface depend on the structural and surface chemistry of supports [15]. Comparing both supports, coal based catalysts present a lower surface area what can restrict the dispersion of active phase on the catalyst surface inducing the formation of vanadium aggregates and consequently a decrease in the catalytic activity. This fact was characterized by means of N_2 adsorption and SEM pictures show in Table 2 and Fig. 1, respectively. At the sight of results, from a 5% of vanadium loading on there is a decrease in the total volume adsorbed an especially in those related to the micropore and mesopore

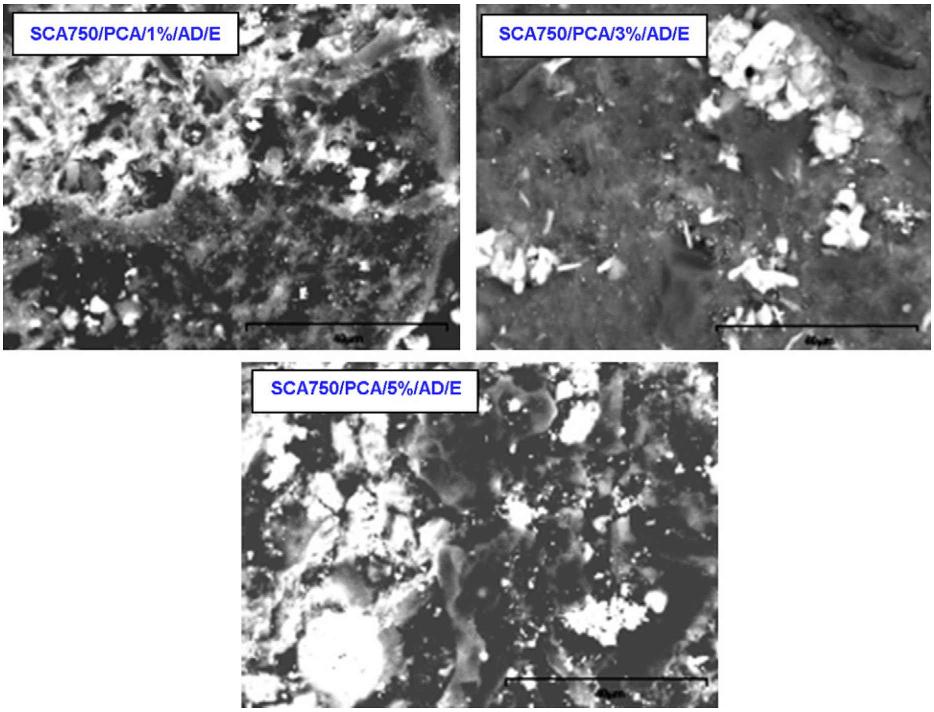

Fig. 1. SEM picture of the vanadium agglomeration on powder samples.

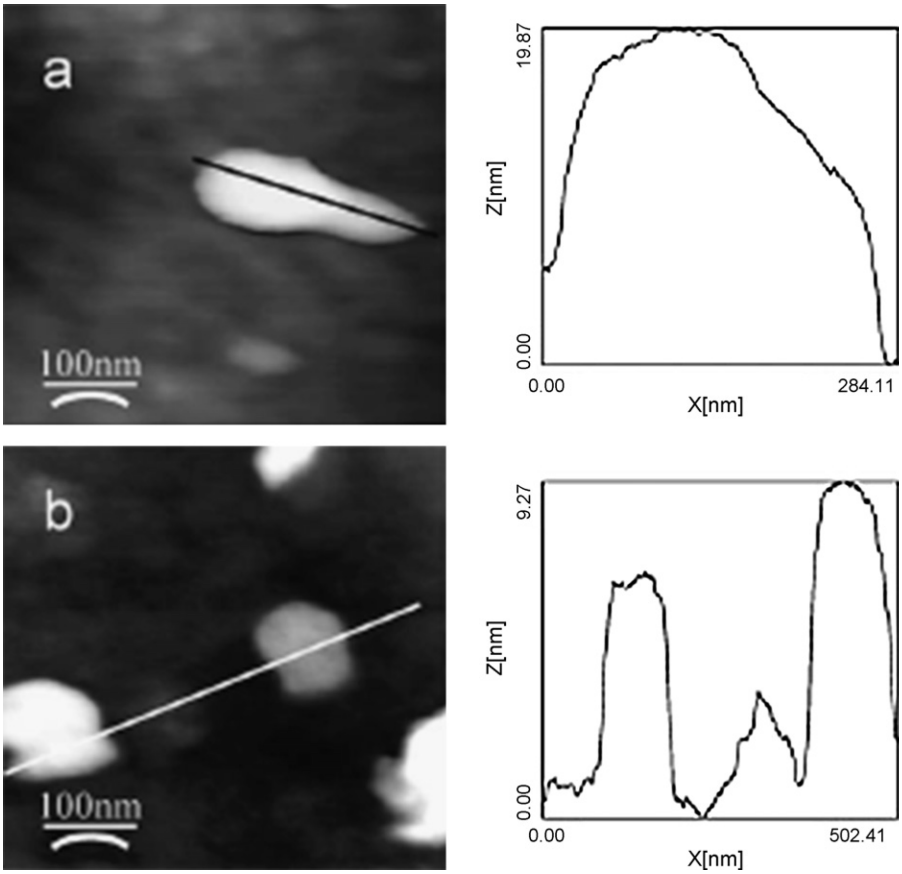

Fig. 2. AFM picture of vanadium agglomeration on monolith samples. Samples with 8% vanadium. Left AFM top view, right profile along the line in the top view [27].

volume what can point out a pore blockage due to the higher amount of active phase incorporated. Moreover, SEM pictures of 5% vanadium loaded catalyst show evidence of agglomeration of metals (left lower corner) that cannot be observed on the 1 and 3% of vanadium pictures.

Polymer blend carbon catalysts equally show a vanadium loading limit from which the catalytic activity no longer increases. However, this limit seems to be slightly higher. The characterization of vanadium dispersion was carried out by means of two microscopy techniques such as SEM and AFM. AFM pictures are shown in Fig. 2. The different contrast between the features and the support in the phase-shift image enables us to state that the features in the picture have a different chemical composition than the carbon support; i.e. theses crystallites can be unambiguously ascribed to vanadium compound. According to Fig. 2 (at the left there is a top view image and at the right there is the profile in nanometers along the line drawn in the top view) the higher the vanadium loading the higher the agglomeration of the active phase on the surface and consequently the worse the dispersion of vanadium causing a decrease in the NO reduction efficiency. Moreover, it should be taken into account that with this technique there is impossible to characterize vanadia aggregates smaller than 4 nm since they cannot be discerned from the roughness of the support [24].

From the catalytic experiments a relationship between the morphology of vanadium compound and the catalytic behaviour arises. The catalytic activity is increasing up to the monolayer coverage but drops in samples where crystallites are formed because of the amount of inactive vanadium and the reduction of vanadium surface which is exposed to the gas phase. Furthermore, the decrease in BET surface area of these samples suggests that some vanadium can be buried in the micropores.

From all the above, the dispersion of vanadium is crucial for both the efficiency and the selectivity of the catalysts. This is consistent with most of the results in the literature for the SCR of NO at higher temperatures in which vanadium is supported on metal oxide [32–34]. All these authors emphasize the necessity of well-dispersed vanadium overlayers, regardless the reaction mechanism that they suggest.

4. Conclusions

In this work, carbon based catalyst in powder, briquette and monolith samples have shown to be considerably active for the NO reduction with the addition of ammonia at low temperature (150 °C). The nature of carbon support as well as the preparation procedure influence greatly on the catalytic activity. On one hand, powder and briquette catalysts have been prepared from a low-rank coal. These catalysts have demonstrated that the porous structure, as determined from N_2 adsorption isotherms at 77 K, plays an important role in high catalytic activities. It could be said that the total volume increases with the severity of the activation and reduces with oxidation treatment, thus a proper development of the porous structure is fundamental in order to avoid pore blockage, but the presence of surface oxygen functionalities is even more important since it provides an adequate distribution and fixation of the active phase. The presence of these groups may contribute also to the adsorption of the reactants during the NO reduction reaction.

On the other hand, polymer blend based catalysts show a higher dependence to the structural development. A well-developed mesoporosity is essential to favour a high amount of oxygenated surface groups that can be responsible for dispersion and fixation of active phase whereas narrow microporosity developed by CO_2 activation does not seem to play a significant role in the improvement of the catalyst activity. In this way, an increase in the severity of HNO_3 treatment entails some decrease of micro–mesopore surface area allowing a lower amount of vanadium adsorbed on the surface and consequently a lower catalytic activity.

An increase of vanadium loading leads in all cases to an enhancement of activity, until a certain extend where vanadium agglomeration starts and activity drops off. This fact could be attributed to either a possible pore blockage or the formation of crystallites on the surface, decreasing the total active vanadium as well as the global vanadium area exposed.

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