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A study of the mechanisms of NO reduction over vanadium loaded activated carbon catalysts

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Abstract

The kinetics of the selective catalytic reduction of NO in the presence of vanadium loaded carbon-based catalysts has been studied, by means of different techniques, such as transient response analysis, temperature programmed desorption and DRIFT spectrometry. The results point out to a reaction mechanism involving adsorbed species of ammonia, which react with the NO from the gas phase. The role of oxygen will be the regeneration of the spent catalytic sites. Finally, the Mars van Krevelen kinetic model was successfully used to fit the experimental data.

Keywords: Selective catalytic reduction; Carbon-based catalysts; Mars van Krevelen kinetics

1. Introduction

In the last years, selective catalytic reduction (SCR) has become one of the most outstanding technologies for controlling the emission of nitrogen oxides from stationary sources [1]. The commercial V_2O_5/TiO_2 type catalysts are successfully employed at temperatures above 300 °C. However, carbon-based catalysts represent an interesting alternative to TiO_2-based ones, as they can operate efficiently at considerably lower temperatures, between 100 and 250 °C [2]. Thus, the catalytic bed could be located downstream of the desulphurization device, bypassing the need of reheating the flue gas and avoiding retrofitting of the equipment in an existing boiler. In addition, it has been recently reported that carbon catalysts are less sensible to SO_2 poisoning, one of the main drawbacks of the use of TiO_2-based catalytic systems [3,4].

Further understanding of the operation and application of these catalysts can be gained through a deeper knowledge of the mechanism and kinetics of the NO reduction reaction in their presence. A great number of studies dealing with this subject have been published in recent years, for a wide variety of catalysts and under different reaction conditions. However, no general agreement has been attained and there are some aspects that remain already not fully clarified [1,2,5].

In the presence of NH_3 as a reductant, it is generally admitted that this compound reacts from an adsorbed state on the catalyst's surface. However, there is more controversy about the active centres involved, as NH_3 can be adsorbed either as NH_4^+ on Brønsted sites or via coordinative adsorption on Lewis sites. Some authors claim that both kinds of active sites are necessary [6,7], while some others state that NH_3 reacts, in the form of amides, adsorbed only in Lewis type sites [8,9].

Soyer et al. [10] concluded from a quantum chemical study of SCR on V_2O_5 catalyst that the SCR reaction on (0 1 0) vanadium oxide surface is initiated favourably by the Brønsted acidic ammonia adsorption. The second part of the SCR reaction consists of the interaction of nitric oxide with the pre-adsorbed ammonia species to eventually form nitrosamide species. These species leave the ammonia adduct and then re-adsorbed on a new Brønsted acidic site of V_2O_5 when decompose by means of a push–pull hydrogen transfer mechanism between the active V=O and V-OH groups.

The role of NO in the reaction is also a subject of diverse opinions. Some authors have reported that NO reacts from an adsorbed state [11,12], while others argue that it reacts directly from the gas phase [6,13,14] or even weakly adsorbed [15–17]. Thus, two types of mechanisms can be proposed, an *Eley–Rideal* type one that considers NO reacting from the gas phase and NH_3 strongly adsorbed or a *Langmuir–Hinselwood* like mechanism

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where NO and NH_3 are considered to react both adsorbed on the catalyst surface.

This debate extends also to carbon-based catalysts. Richter et al. [18], Singoredjo et al. [19] and Teng et al. [20] have reported that the reaction takes place between adsorbed NO and NH_3 while Marbán et al. [21] claim that NO reacted from the gas phase via the formation of a nitrosamidic intermediate and they observed that the formation of nitrates resulted in a partial deactivation of the catalysts at temperatures below 230 °C [22].

Oxygen, either present in the reactant mixture or as a heteroatom on the catalyst's surface, is also involved in the SCR reaction. It is generally accepted that oxygen is mainly involved in the re-oxidation of the catalytically active phase after reaction [19,5], but it has been also suggested that its presence favours NO adsorption on the catalyst's surface [19], and that it is responsible for the abstraction of one atom of hydrogen from adsorbed NH_3, in the first step of nitrosamide formation [12].

In previous works, we have studied the activity of novel activated carbon catalysts prepared using different V compounds as active phase [23,24] for SCR at low temperature. One of these V compounds was the ash obtained by calcination of a petroleum coke, designed as petroleum coke ash (PCA), which contain up to 23% of V. The catalysts showed interesting activities in the reduction of NO in the presence of NH_3 and O_2, with almost 100% selectivity towards N_2, even at temperatures as low as 150 °C. For future scaling up of the catalytic system, the need of performing an investigation of the SCR reaction mechanisms was identified.

At present there is not any mechanistic study on this kind of catalyst. It should be noted that the active phase present in PCA is very complex [25] and other vanadium species besides V_2O_5 have been identified. This paper presents the main results of the study carried out for the elucidation of the reaction mechanisms of SCR over PCA loaded activated carbon catalysts. The transient response method was applied to the reaction system and Temperature Programmed Desorption of NH_3 and *in situ* DRIFTS studies were also performed. Finally, experimental data of activity were successfully fitted to a *Mars van Krevelen*-type kinetic model.

2. Experimental

2.1. Activated carbon supports

For the preparation of the activated carbon support, a low-rank coal from SAMCA mines in Teruel, Spain, was used as precursor. Previous results obtained in a deep study of the influence of the different activation conditions on the physical and chemical characteristics of the resulting materials [26], showed that the surface area and micropore volume increased with the severity of the activation. It was observed that an activation temperature over 750 °C and a residence time of more than 4 h led to an activated carbon with an adequate surface area with an important contribution of wide micropores and mesopores, together with an oxygen group enriched surface chemistry. Based on these results, an activated carbon, SCA750, was prepared in a batch-mode fluidized bed.

Table 1
Description of the catalysts studied

SCA750	Activated carbon support
SCA750 + V_2O_5	Carbon support loaded with 3% V, V_2O_5 in water
SCA750 + PCA	Carbon support loaded with 3% V, PCA in water
SCAOX + PCA	Oxidized carbon support loaded with 3%V, PCA in water

With the main aim of increasing the concentration of oxygen functionalities on its surface, the activated carbon SCA750 was subsequently submitted to oxidation with concentrated HNO_3 at room temperature during 4 h. The oxidized activated carbon obtained is referred as SCAOX. A more detailed description of the preparation method can be found in Gálvez et al. [24].

2.2. Active phases

A coke from the Delayed Coke Unit in the REPSOL refinery in Puertollano, Spain, was used for the production of the petroleum coke ashes (PCAs), by combustion under air at a temperature up to 650 °C. This PCA contains 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 complete description of PCA components can be found in [25]. Commercial V_2O_5 (Aldrich) was also used as a model vanadium compound for the preparation of some of the catalysts.

2.3. Catalysts preparation

The carbon supports were loaded with 3% V (w/w), nominal, using either V_2O_5 or PCA. A 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 corresponding amount of char. The char was added stepwise in small charges while the suspension was continuously stirred. After stirring at ambient temperature for 4 h the temperature was raised in order to evaporate most of the water in the suspension. Finally, the catalyst was dried overnight in an oven at 108 °C. Table 1 shows a short description of the preparation procedure for the catalysts presented in this paper.

2.4. Catalysts characterization

Both the carbon supports and the catalysts were physically and chemically characterized by means of N_2 adsorption at 77 K (Micromeritics ASAP 2000), chemisorption of O_2 and NH_3 (Micromeritics Pulse Chemisorb 2700) and temperature-programmed desorption of carbon oxides and ammonia. For the TPD of carbon oxides, 0.6 g of sample was placed in a U tube and heated in He flow from 150 to 1050 °C ($10\,°C\,min^{-1}$) and the amounts of CO and CO_2 evolved were measured by means of gas chromatography. For the Temperature Programmed Desorption of ammonia, 0.4 g of catalyst was placed in a cylindrical quartz reactor of 7 mm internal diameter. A flow of $25\,cm^3\,min^{-1}$ of 1700 ppm of NH_3 in Ar was fed for 2 h at150 °C. Then the reactor was heated up from 150 to 1050 °C at $10\,°C\,min^{-1}$ in a flow of

Table 2
NO reduction efficiency, selectivity, SSA, O_2 and NH_3 chemisorption and TPD results

Catalysts	% NO reduction	% Selective N_2	SSA (m^2/g)	Chem. NH_3 (cm^3/g)	TPD experiments		
					cm^3CO/g	cm^3CO_2/g	CO_2/CO
SCA750	34	92	398	3.7	43	8	0.18
SCA750 + V_2O_5	56	92	385	5.8	46	10	0.21
SCA750 + PCA	46	91	344	4.4	53	17	0.21
SCAOX + PCA	88	87	286	7.1	42	52	1.23

25 $cm^3 min^{-1}$ of Ar, and the amount of NH_3 desorbed was measured by means of a mass spectrometer (Balzers 422) connected on-line (*m*/*z* 17).

2.5. Activity measurements

The NO reduction efficiency of the catalysts was determined by passing a flow of 22.2 $cm^3 min^{-1}$ containing 1000 ppmv 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 (0.2–0.5 mm particle size) at a temperature of 150 °C and 1.4 s of residence time. The gases were dosed by means of mass flow meters and fed to the cylindrical quartz reactor of 7 mm internal diameter, heated by an electric oven. Before reaching the sample, the gases were forced to pass through a bed of Al_2O_3 crystals acting as mixing chamber. A blank test showed no de-NO_x activity for these Al_2O_3 crystals under reaction conditions. 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 online. The mass spectrometer was calibrated using mixtures of 2000 ppmv of NO in Ar, 3000 ppmv of NH_3, 7% (v/v) of O_2 in Ar, 1000 ppmv of N_2 in Ar and 1000 ppmv of N_2O in Ar. The NO conversion and selectivity towards N_2 were calculated as described elsewhere [27].

2.6. Transient response experiments

Transient response experiments were carried out in the same installation used for the activity tests, using 0.4 g of catalyst and a total flow of 22.2 $cm^3 min^{-1}$, at a temperature of 150 °C. Initially, a mixture of 1000 ppmv NO, 1500 ppmv of NH_3 and 3.5% (v/v) of O_2 in Ar was fed into the reactor until a stationary state with a constant composition of the gas leaving from the reactor was reached. Then, the variations of the gas composition when one or a combination of reactants was eliminated from the fed mixture were measured for 2 h. Finally, the complete reaction mixture was restored and the system was left for stabilization until the steady state was reached again. All the results obtained were checked against the corresponding blank experiments performed in absence of catalytic bed.

2.7. In situ DRIFTS studies

For the acquisition of the DRIFT spectra, a catalytic chamber (Spectra-Tech 0030-102) was employed attached to a diffuse reflectance device (Spectra-Tech Collector) and situated inside a Nicolet Magna-IR Spectrometer 550. The temperature inside the catalytic chamber was controlled by means of a Spectra-Tech Temperature Controller 0019–022 and maintained at 150 °C. Inside the ceramic sample holder, 200 mg were placed and a flow of 50 $cm^3 min^{-1}$ of reactant gas containing 1000 ppm of NO, 1500 ppm NH_3 and 3.5% of O_2 in He, 3000 ppm of NH_3 and 7% of O_2 in He, or 2000 ppm of NO in He, was fed to the chamber. Prior to reaction, the sample was degasified in He atmosphere at 200 °C during 30 minutes. The background spectrum was taking after the first 15 minutes in He atmosphere and at 150 °C, and was automatically subtracted from the rest of the spectra.

2.8. Fitting of the kinetic model

Solver tool from Microsoft Excel was employed for the mathematical fitting of the data to the kinetic model.

3. Results and discussion

3.1. Catalytic activity and catalyst characterization

Table 2 shows the catalytic activity measured at a constant temperature of 150 °C, for the different catalysts presented in this paper. Values of BET surface area, NH_3 chemisorption and the CO and CO_2 evolved during TPD tests. NO conversions around 50% were obtained for the catalysts prepared with the non-pre-oxidized carbon support, SCA750, while a conversion up to 88% was determined for the catalyst prepared using the carbon support treated with HNO_3, SCAOX.

Specific surface area of catalyst decreases when the active phases are loaded on the carbon support. Chemisorption of ammonia as well as the amount of CO_2 evolved during TPD, are significantly higher for the catalyst prepared using the pre-oxidized support, SCAOX. Acidic surface functionalities, such as the carboxylic groups created after the treatment with HNO_3, can adsorb ammonia, acting as Brønsted acid sites. At the same time, this catalyst, SCAOX + PCA, is the one that showed the highest NO reduction efficiency. Chemisorption of NH_3 also increases when both V_2O_5 and PCA are loaded on the carbon support. This means that both compounds are able to provide Lewis acid sites where ammonia can be adsorbed. The lower capacity of PCA is attributed to the presence of vanadium species different from V_2O_5, such as iron vanadate, [25] which has a lower acid character. It seems that catalytic activity is mainly related to the ability of the catalyst to adsorb ammonia on the surface.

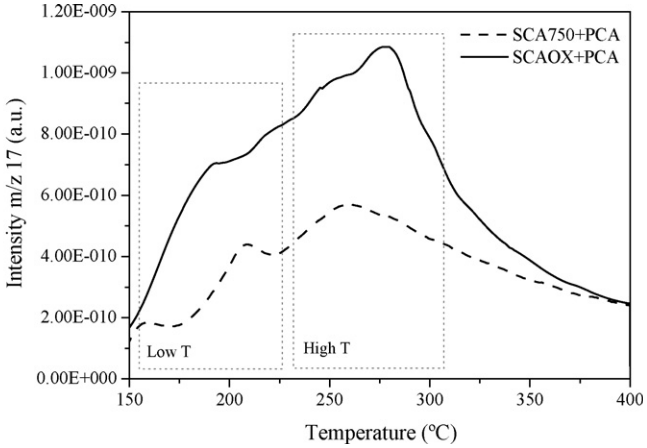

Fig. 1. Temperature programmed desorption after saturation with NH_3.

Further evidence of NH_3 adsorption was obtained from the Temperature Programmed Desorption of NH_3 after saturation of the catalyst surface. Fig. 1 shows the amount of ammonia desorbed as a function of the temperature for the catalysts SCA750 + PCA and SCAOX + PCA. In both cases it can be observed that NH_3 desorption begins at temperatures around 150 °C. The evolution of ammonia presents a broad peak that extends up to a temperature of 350 °C, indicating the presence of several adsorbed forms of ammonia with different thermal stability. Kijlstra et al. [9,12] have previously reported the same observation for MnO_x/Al_2O_3 catalyst. Teng et al. [20] also observed ammonia desorption from 125 to 325 °C. Furthermore, they claimed that the amount of NH_3 adsorbed was directly related to the activity of the catalysts, and that the SCR reaction rate was controlled mainly by this amount of ammonia adsorbed on the catalyst's surface sites.

This broad peak of ammonia desorption can be divided mainly in two important contributions, as suggested by Zhu et al. [28]. The first of this two contributions is centred at a temperature of 175–200 °C, while the maximum of the second one can be located at about 250–275 °C. Just as suggested by Zhu et al. [28] these two contributions can be ascribed with the NH_3 adsorbed on two different kinds of surface sites, as NH_4^+ on Brønsted sites, i.e. oxygen surface groups, and coordinatively on Lewis sites, i.e. V sites.

It can be observed in Fig. 1 that the highest amount of ammonia desorbed corresponds to the catalyst SCAOX + PCA. This is due to the higher number of oxygen surface groups with acidic character that will favour NH_3 adsorption acting as Brønsted sites. These results agree with the ones shown in Table 2 and confirm that catalytic activity is related to ammonia adsorption capacity, since the catalyst SCAOX + PCA presents the highest efficiency in NO removal.

3.2. Transient response experiments

The transient response technique, TR, evaluates the evolution of the catalytic reactions under non-stationary conditions. This method has been used in literature to gain information on the role of the different species involved in the SCR reaction [21,22,29,30]. The experimental procedure mainly consists of studying the evolution of the catalyst behaviour when some of the components of the reactive

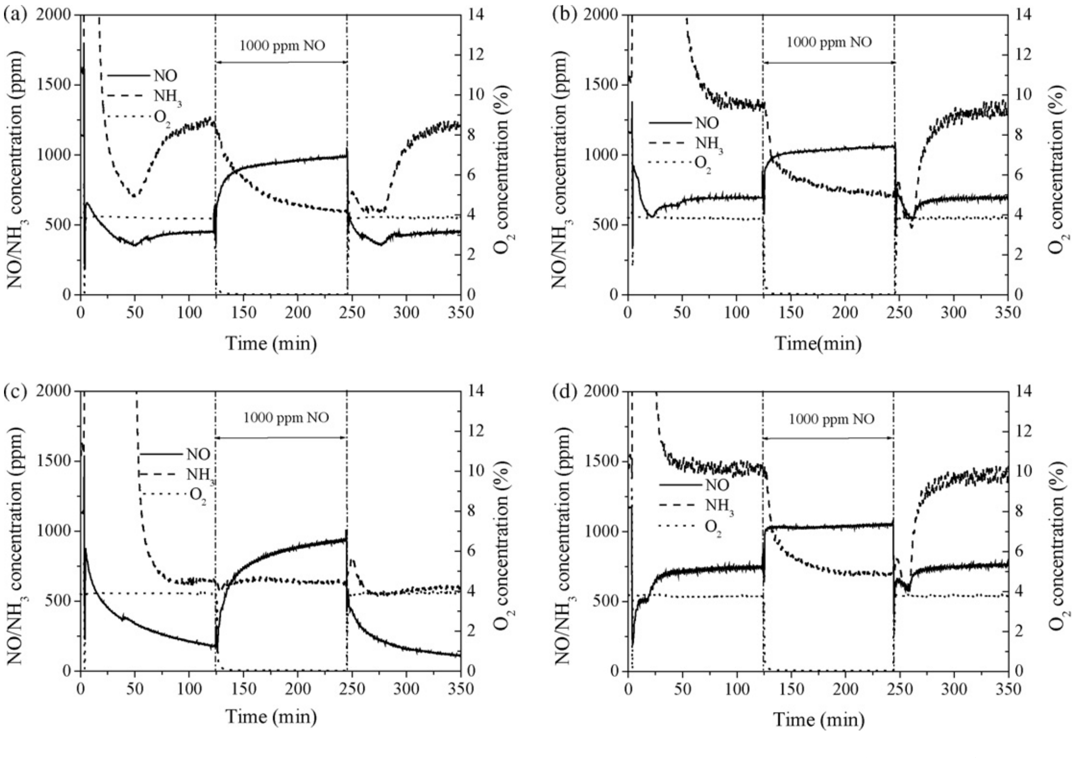

Fig. 2. Transient response experiments where NH_3 and O_2 where removed and subsequently added to the reaction mixture, for (a) SCA750 + V_2O_5; (b) SCA750 + PCA; (c) SCAOX + PCA and (d) unloaded carbon support SCA750.

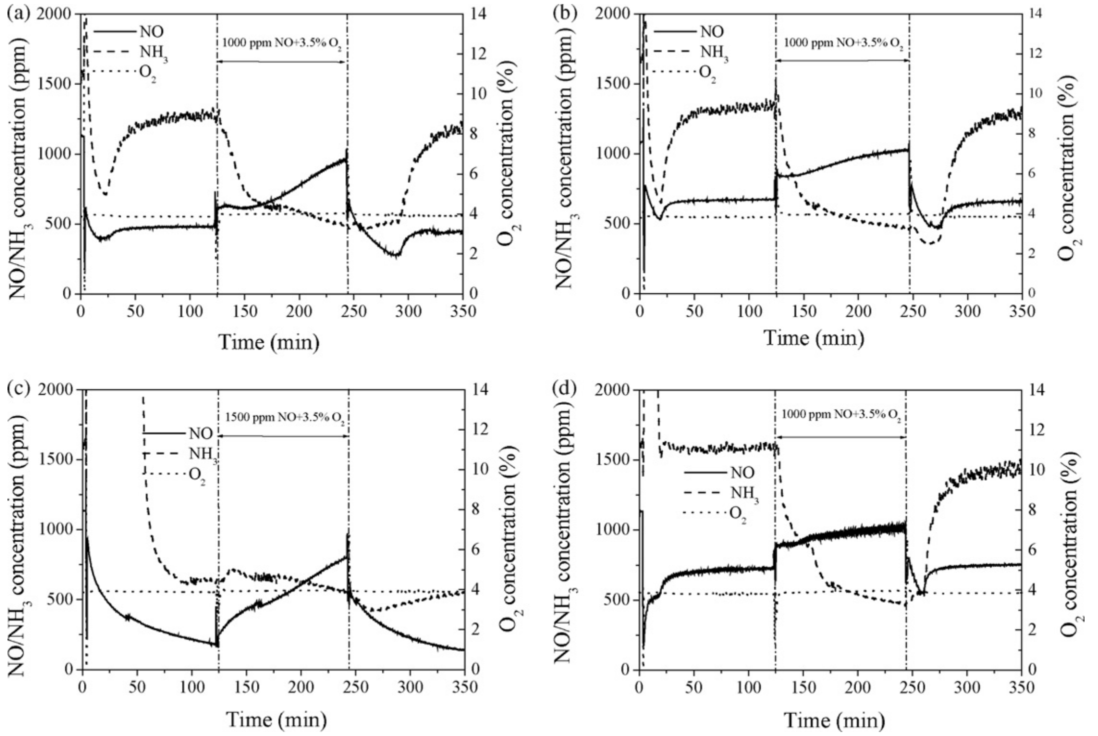

Fig. 3. Transient response experiments where NH_3 was removed and subsequently added to the reaction mixture, for (a) SCA750 + V_2O_5; (b) SCA750 + PCA; (c) SCAOX + PCA and (d) unloaded carbon support SCA750.

mixture are alternatively removed and replaced. Figs. 2–5 show the concentration profiles for NO, NH_3 and O_2 before and after introducing several changes in the reactant gas. N_2 concentration profile follows exactly the opposite trend observed for NO, but was not presented for the sake of clarity.

Fig. 2a–d shows the gas composition in TR when NH_3 and O_2 were removed and subsequently put back to the reaction

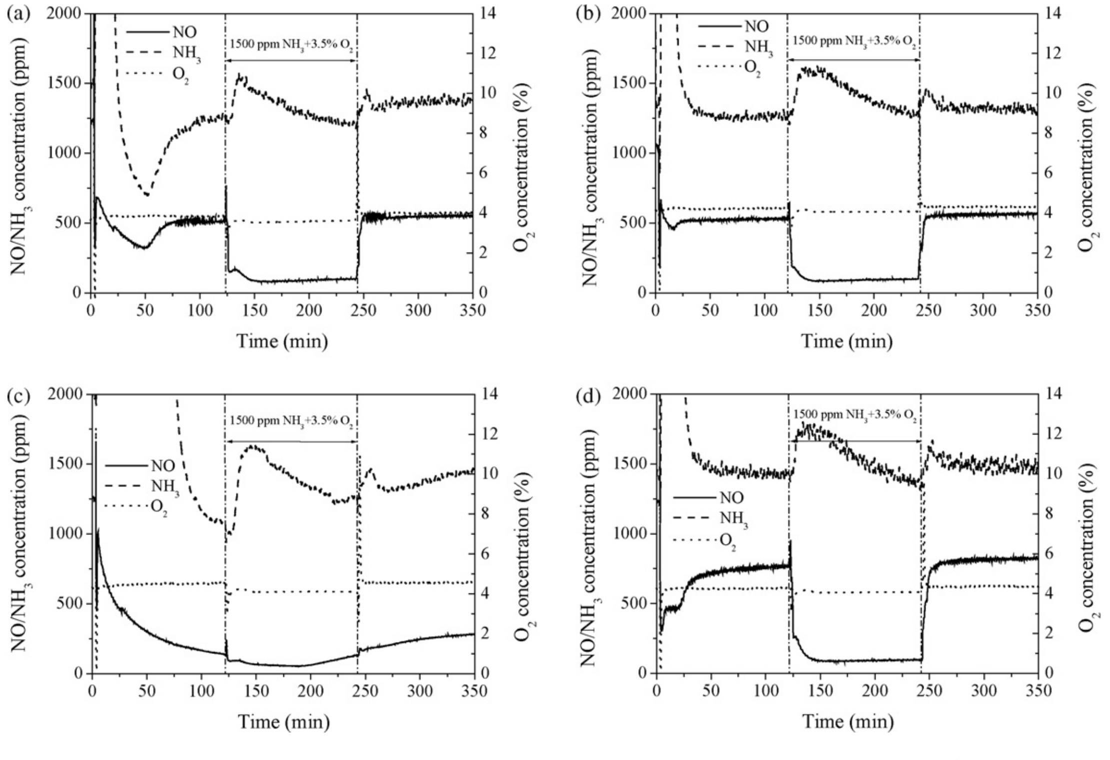

Fig. 4. Transient response experiments where NO was removed and subsequently added to the reaction mixture, for (a) SCA750 + V_2O_5; (b) SCA750 + PCA; (c) SCAOX + PCA and (d) unloaded carbon support SCA750.

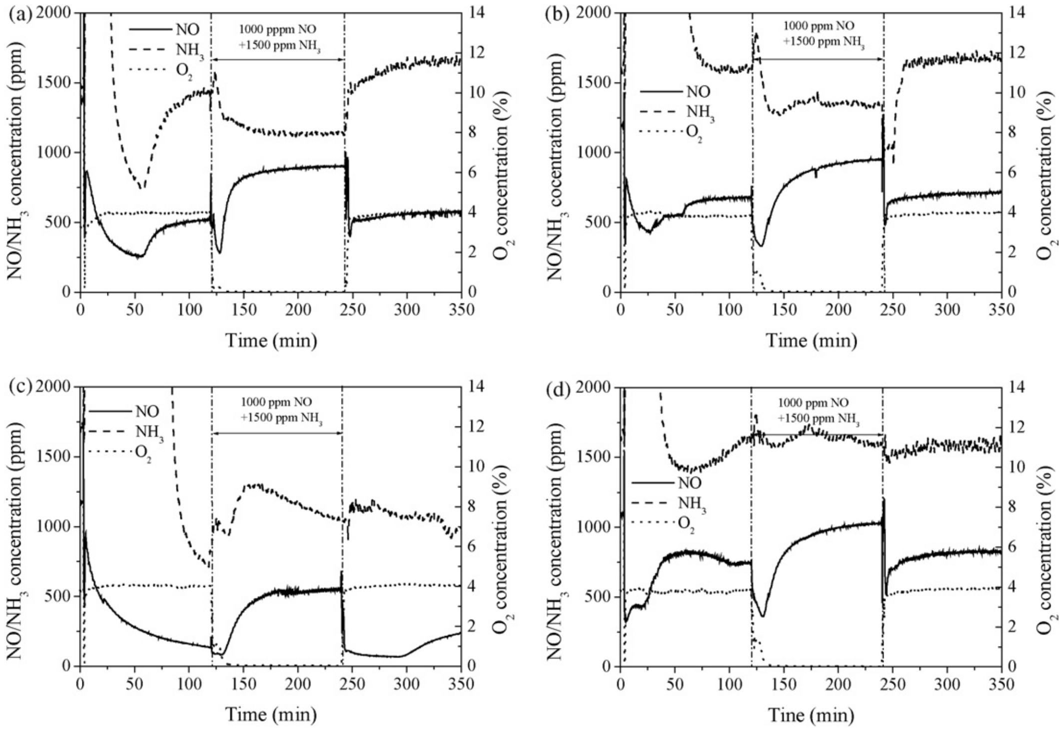

Fig. 5. Transient response experiments where O_2 was removed and subsequently added to the reaction mixture, for (a) SCA750 + V_2O_5; (b) SCA750 + PCA; (c) SCAOX + PCA and (d) unloaded carbon support SCA750.

mixture, for the three catalysts and the carbon support. The TR patterns for SCA750 + V_2O_5 and SCA750 + PCA are similar. At the steady state, a slightly lower ammonia concentration and a higher NO concentration (lower conversion) are observed for SCA750 + PCA, which agrees with the results on ammonia adsorption and catalytic activity presented in Table 2. After the removal of these reactants, a gradual diminution of the concentration of NH_3 can be noticed, while a sharp decrease in the concentration of O_2 is observed. NO concentration increases, indicating that reaction stops when removing NH_3 and O_2 from the gas mixture.

In contrast, a different TR pattern is observed for the catalyst SCAOX + PCA prepared using the pre-oxidized carbon support. The concentration of NH_3 is quite low even before its withdrawal from the stream, due to increased adsorption of this reactant on the surface. This low concentration remains nearly constant after removal of ammonia. After removing of NH_3 and O_2, the increase of the NO concentration observed for SCAOX + PCA

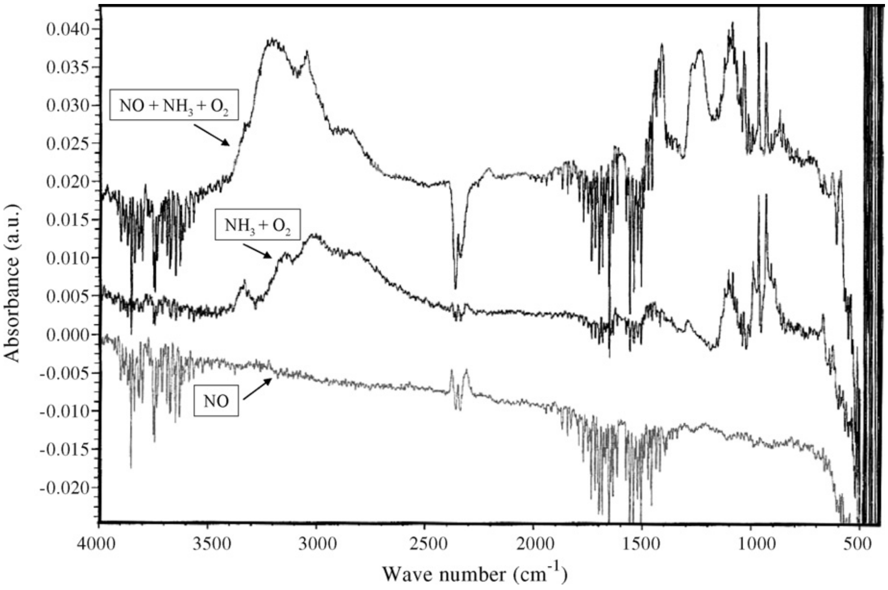

Fig. 6. DRIFTS spectra obtained for the catalyst SCA750 + V_2O_5, exposed to three different reaction atmospheres: (1) NO + NH_3 + O_2 in He; (2) NH_3 + O_2 in He; (3) NO in He.

is more gradual than for the catalysts prepared using the non-oxidized supports. This fact points out that in this case the adsorbed NH_3 can be still reacting with NO, even in absence of O_2 in the gas phase, with the aid of the oxygen coming from surface functionalities.

Fig. 3a–d shows the TR results when only NH_3 was removed from the reactant mixture. NO concentration increases now more slowly after removal of NH_3 than in the previous set of TR experiments, when both NH_3 and O_2 were removed form the gas phase, in particular for $SCA750 + V_2O_5$ and SCAOX + PCA. This result shows that presence of oxygen is of key importance for the NO reduction. Another important fact is that this gradual increase in the concentration of NO after removing NH_3 is not observed in the case of the unloaded carbon support, what means that in absence of an active phase, the reaction between adsorbed ammonia and NO does not proceed.

Fig. 4a–d shows the evolution of the concentrations of the reactants for the transient response experiments where NO was removed from the mixture. A stepwise decrease in the concentration of NO is observed in all cases, what denotes that NO reacts probably from the gas phase or from a weakly adsorbed state.

Fig. 5a–d presents the TR curves obtained when removing only O_2 from the reactant mixture. In this case it is important to point out the fast recovery of the conversion of NO after O_2 is replaced within the reactants. This fact further indicates that O_2 reacts directly from the gas phase, confirming what was observed also in the other TR experiments. When O_2 is removed from the reactant mixture, the concentration of NO increases, what substantiates the importance of this reactant in the SCR reaction.

All these observations indicate that: (1) ammonia reacts absorbed on the catalyst surface; (2) oxygen is needed for SCR and (3) the reaction occurs on V-active sites of PCA. The role of oxygen may be the regeneration of the metal sites after reaction, bringing them back into the highest oxidation state. These facts point out that SCR on the catalysts presented in this paper proceeds via an *Eley–Rydeal* type kinetics, with NO reacting from the gas phase, and not following a *Langmuir–Hinselwood* type, which would imply reaction between adsorbed species of both NO and NH_3.

3.3. *In situ FTIR spectroscopy*

FTIR Spectroscopy has been widely used in literature to identify the species adsorbed on the surface of a catalyst [9,6,16,22,31,32]. In particular, diffuse reflectance infra-red spectroscopy (DRIFTS) can be used to observe the evolution of the adsorbed species as the catalytic reaction proceeds with the aid of a catalytic chamber [33–38]. All the studies reported in literature have been performed for catalysts supported on materials such as TiO_2, SiO_2 or Al_2O_3. For carbon-supported materials, some studies can also be found in the literature [39–42].

Fig. 6 shows the DRIFTS spectra obtained for the catalyst $SCA750 + V_2O_5$, exposed to three different reaction atmospheres: (1) $NO + NH_3 + O_2$ in He; (2) $NH_3 + O_2$ in He; (3) NO in He. In the presence of the complete reaction mixture, several peaks at different wave numbers can be observed. This confirms that this method can provide useful information about the different species adsorbed during SCR in the presence of carbonaceous catalysts.

Two regions can be appreciated in the three spectra, with well-defined peaks that have been ascribed to different adsorbed species in the literature. The first group of peaks appear at wave numbers between 3500 and 2500 cm^{-1}, while the second group is placed in the region 1500–950 cm^{-1}. The spectrum obtained in the presence of NO, NH_3 and O_2 presents peaks at 3200, 3050 and 2825 cm^{-1} which have been attributed to NH_3 adsorbed in the form of NH_4^+ in Brønsted sites of the catalyst surface [33–36]. In the region between 2250 and 2400 cm^{-1} two peaks with negative absorbance are observed. These peaks correspond to V=O bond and have been ascribed to the reduction of the metallic centres on the surface of the catalyst [33]. Less agreement can be found in literature for the peaks that appear from 2000 to 900 cm^{-1}. The peak observed at 1600 cm^{-1} has been equally assigned to NH_3 adsorbed coordinatively on Lewis metallic sites [35,38] and to nitrates [35], or even to NO_2 adsorbed on the catalyst's surface [36]. Afterwards, several peaks appear between 1400 and 1250 cm^{-1}, that have not been clearly ascribed to any particular species, and that appear assigned in literature to different forms of adsorbed NO and NH_3 [33,38]. Finally, one band at 1100 cm^{-1} and two narrow peaks, centred at 980 and 942 cm^{-1}, which have not been reported in literature are observed.

The spectrum corresponding to reaction in the presence of NH_3 and O_2, shows also the well-defined bands between 3200 and 2800 cm^{-1}, associated to the presence of NH_4^+. Furthermore, a band at 3325 cm^{-1} can be observed that has been assigned to NH_3 adsorbed on Lewis sites [38]. The peaks at 1100, 980 and 942 cm^{-1} appear also in this spectrum, which can be due to different forms of ammonia adsorbed on the catalyst's surface. However, bands at 1400 and 1250 cm^{-1} that appeared in the spectrum taken in the presence of the whole reaction mixture are missed. It seems that some kind of adsorbed species is formed in the presence of NO, NH_3 and O_2 that is not present when the reaction mixture contains only NH_3 and O_2.

Adsorbed species have not been observed in the DRIFTS spectrum taken in presence of NO as indicated by the absence of absorbance bands in all the range of wavelength tested. The only two peaks that appear are those corresponding to the V=O bond in the middle part of the spectrum. This fact confirms that NO reacts most probably from the gas phase. Ramis et al., however, suggested the formation of a nitrosamidic intermediate, where adsorbed NH_3 was slightly bonded to NO [16]. The presence of the bands at 1400 and 1250 cm^{-1} that are observed only when the whole reactant mixture is fed may be an indication of the formation of this kind of nitrosamidic intermediate, and, so, it could be considered that NO reacts once this complex is formed and not directly from the gas phase.

3.4. *SCR mechanism*

At the sight of the results provided in the previous sections, the mechanism proposed for SCR over the catalyst studied

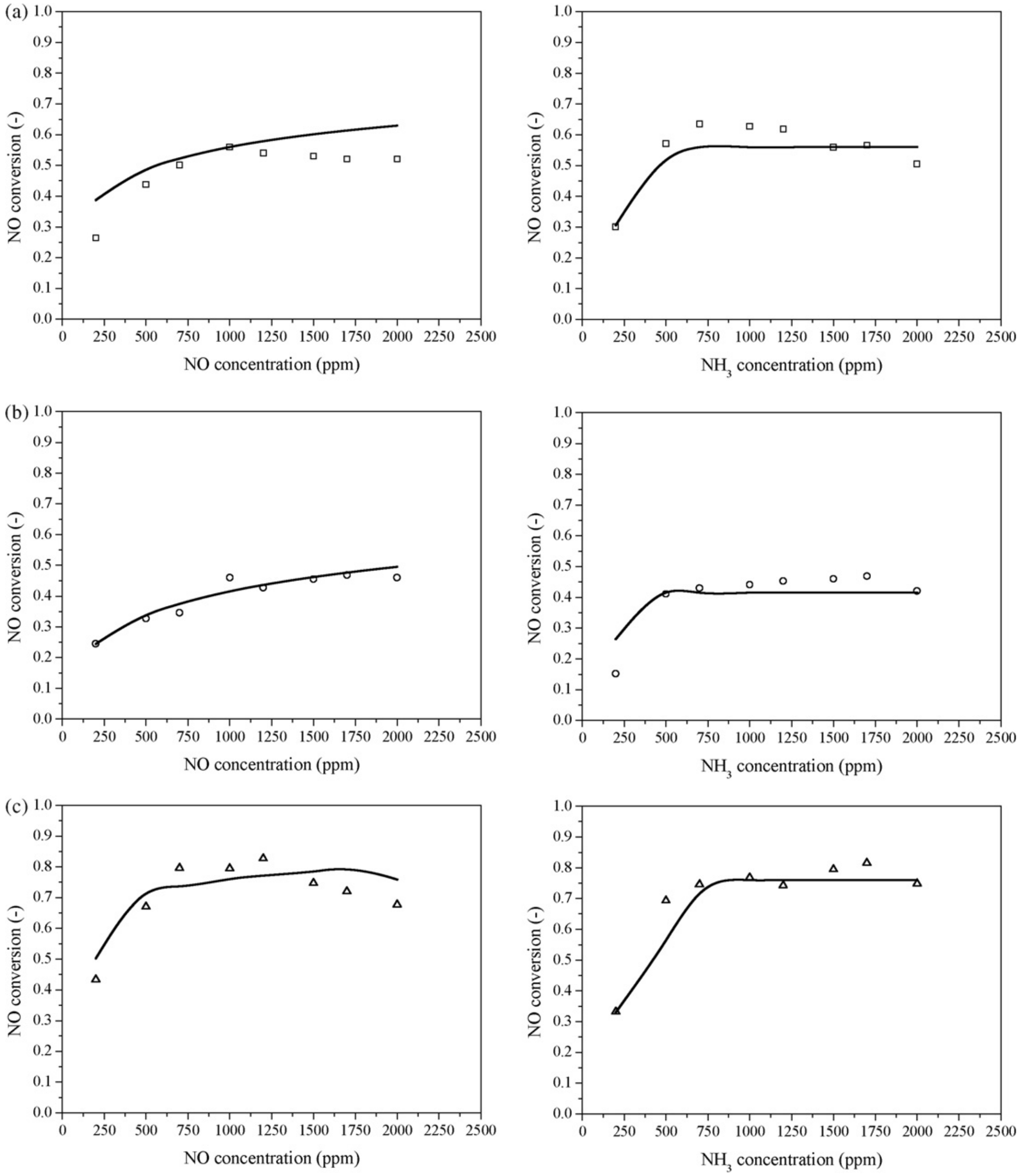

Fig. 7. Experimental data fitting to the Mars van Krevelen model for CA750 + V_2O_5; (b) SCA750 + PCA; (c) SCAOX + PCA; markers indicate experimental data, continuous line represents the conversion predicted by the model.

here must accommodate the following experimental evidences: (1) ammonia reacts from a strongly adsorbed state on catalyst surface; (2) NO reacts from the gas phase, most probably through the formation of a nitrosamidic intermediate, but it is not adsorbed itself directly on any surface site; and (3) O_2 is in charge of the re-oxidation of the catalyst's spent sites.

NH_3 will react adsorbed on Lewis type sites, i.e. V-sites, but migration from oxygen surface groups – Brønsted sites – is bound to occur, thus resulting in an increase in the reaction rate. On the other hand, oxygen surface groups can also provide the oxygen needed for the regeneration of the metallic sites after reaction. In this case, O_2 in the gas phase will regenerate these surface functionalities instead of regenerating directly the metallic site.

$$\mathrm{NH_3(g)} + \mathrm{O_3V{=}O} \Leftrightarrow \mathrm{HO_3V{=}O : NH_2} \times (\mathrm{NH_3 adsorptiononactivesites}) \tag{A}$$

$$\mathrm{HO_3V{=}O : NH_2} + \mathrm{NO} \Leftrightarrow \mathrm{HO_3V{=}O : NH_2 : NO} \times (formationofthenitrosamidiccomplex) \tag{B}$$

$$\mathrm{HO_3V{=}O : NH_2 : NO} \Leftrightarrow \mathrm{HO_3V{=}O} + \mathrm{N_2} + \mathrm{H_2O} \times (decompositionofthenitrosamidiccomplex) \tag{C}$$

$$HO_3V{=}O + \tfrac{1}{4}O_2 \Leftrightarrow O_3V{=}O + \tfrac{1}{2}H_2O \times \text{(active site regeneration)} \qquad \text{(D)}$$

3.5. Kinetic modelling

In a first trial, mechanistic kinetic equations were obtained from the proposed mechanism using the chemical equilibrium approach and considering several reaction steps as rate controlling. However, no good fitting to the experimental data was obtained for any of the kinetic equations deduced, in particular, when trying to reproduce the influence of NO concentration in the catalytic activity. This lack of fitting to the mechanistically derived kinetic equations can be due to the implicit consideration made within this approach which assumes that the reaction takes place over one isolated active site. Thus, the application of a more bulk-type model as the *Mars van Krevelen* model was considered.

It is a matter of fact that the selective catalytic reduction of NO implies some kind of electron transfer. In this transfer, one of the species involved is reduced while others are oxidized. In the presence of a catalyst, it is generally admitted the process of electronic transfer takes place between reactants and the catalytically active phase [5]. When trying to understand this interaction between reactants and active phase, *Mars van Krevelen*-type mechanisms consider that after the electronic transfer some of the products leave the catalyst's surface containing one or more of the atoms from the catalyst's matrix [43]. In the case of the SCR of NO in the presence of NH_3 and O_2, products leaving the catalytic surface may contain one or more O-atoms from the catalyst's surface, and thus an interaction of this kind can be proposed:

$$NH_3 + \text{oxidized active site} \rightarrow \text{reduced active site} + \text{products} \qquad (1)$$

$$NO + \text{reduced active site} \rightarrow \text{oxidized active site} + \text{products} \qquad (2)$$

Furthermore, this process can take place over one isolated active site, but can also involve several reaction sites at the same time, also of different kind, i.e. Lewis and Brønsted sites. This explains also the positive influence of the presence of oxygen surface groups as they can be directly involved in the O-transfer. In any case, it is generally supposed that the adsorption of the reactants and the migration of the atoms on the surface of the catalyst are fast enough in comparison with the red-ox reaction itself. The role of O_2 in the gas phase remains the same, which is the regeneration of the spent catalytic site after reaction.

Several authors have reported the use of this kind of kinetic models to fit the experimental data obtained in the catalytic reduction of nitrogen oxides, using different catalytic systems. Coq et al. [44] found out that the kinetics of N_2O reduction in the presence of NH_3 and employing a Fe-β-zeolite as catalyst, obeyed a *Mars van Krevelen*-type mechanism, where they introduced an additional term that accounted for the strong adsorption of NH_3 on catalyst's active sites. Delahay et al. [45] also applied a *Mars van Krevelen* model to fit the experimental data of the reduction of NO with NH_3 using a Cu-doped faujasite. Hsu and Teng [46] observed that a mechanism of this type adequately described the kinetics of NO reduction in the presence of NH_3 over Cu and Fe doped activated carbons. Liu and Teng [47] employed the same kinetic model to fit the data obtained in the SCR of NO in the presence of Cu/MCM-41 catalysts. Therefore, for the reaction that is being considered herein, the kinetic equation can be written as:

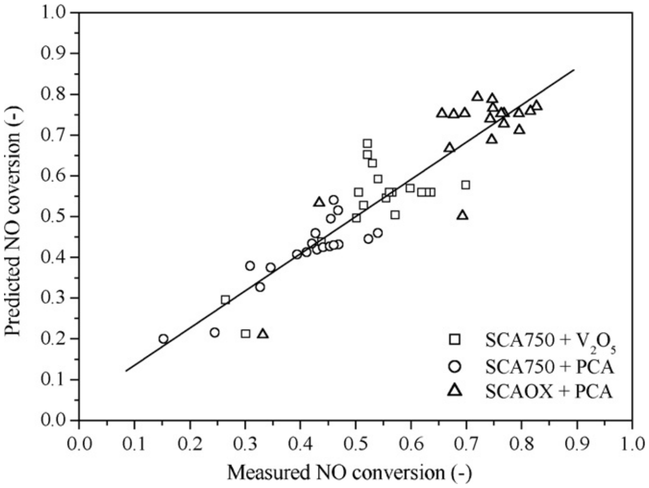

Fig. 8. Comparison between the experimentally measured NO conversion and the one predicted by the model.

$$r_{\mathrm{MvK}} = \frac{k_o C_{\mathrm{NO}}^{a} k_r C_{\mathrm{NH_3}}^{b} C_{\mathrm{O_2}}^{c}}{k_o C_{\mathrm{NO}}^{a} + k_r C_{\mathrm{NH_3}}^{b}} \qquad (3)$$

This equation contains a term that accounts for the influence of the presence of O_2 in the reaction mixture. The parameters, k_o and k_r, are kinetic constants of reactions (2) and (1), respectively, and a, b and c represent the reaction orders with respect to NO, NH_3 and O_2.

Table 3 presents the values of the parameters obtained in the fitting of the experimental data of activity, and the root mean square error, RMS, defined as: $\mathrm{RMS} = \sqrt{\frac{\sum_{i=1}^{n}(Y_i - \bar{Y}_i)^2}{n}}$, where Y_i are the experimental values of conversion and $\bar{Y}_i$ the ones predicted by the model.

The values of the parameters are quite similar for the three different catalysts. According to the results obtained, the value of k_r is much larger than that of k_o, suggesting a stronger dependence of the reaction rate on the concentration of NO than of NH_3, as can be observed in Fig. 7a–c for $C_{\mathrm{NH_3}}^{\mathrm{b}}$ >500 ppm. Fig. 7a–c, show how also the model adequately represents the trend marked by the experimental data of activity. Fig. 8 compares the values of NO conversion predicted by the model with the ones obtained experimentally. Good correspondence of the experimental data with the model is in general observed, as can be also concluded at the sight of the low RMS values presented in Table 3. The satisfactory fit to a Marx van Krevelen model implies that the reaction's rate limiting step is the reduction–oxidation process itself. NH_3 is adsorbed quickly on the catalyst surface occupying its active sites, subsequently interacting with the oxygen transferred from the metal oxide and leaving the active site in a

Table 3
Values of the parameters K_1, K_2, a, b and c obtained in the fitting of experimental data to Eq. (3)

Catalysts	k_o	k_r	a	b	c	RMS
SCA750 + V_2O_5	1.04	$4.18 \times 10^{+2}$	1.49	1.21	0.1	0.004
SCA750 + PCA	1.04	$3.88 \times 10^{+2}$	1.53	1.21	0.1	0.003
SCAOX + PCA	1.04	$3.88 \times 10^{+2}$	1.43	1.21	0.1	0.005

reduced state, ready to react with NO. As stated before, in this oxygen transfer, the H_2O produced in the reaction leaves the catalyst surface containing oxygen atoms from the active sites.

4. Conclusions

The mechanism of the reduction of NO in the presence of NH_3 and O_2 was investigated for a sort of carbon-based catalysts prepared with vanadium compounds, including the ashes of a petroleum coke.

Different characterization techniques were employed. Transient response analysis as well as NH_3 chemisorption followed by temperature programmed desorption showed that the reaction takes place between adsorbed species of ammonia and the NO in the gaseous phase. Ammonia can be adsorbed in two different active sites, metallic centres as well as oxygen surface groups. Oxygen surface groups can possibly favour ammonia adsorption as a reservoir, which would then migrate to metallic sites where reaction takes place. Gaseous O_2 most probably plays the role of regenerating the active sites spent during reaction. The results of the *in situ* DRIFTS confirmed what was observed in the transient response analysis.

At the sight of these experimental facts a mechanism was proposed for the SCR of NO over these catalysts. Best fit of the experimental data was obtained using a *Mars van Krevelen*-type kinetic model, which considers electronic and atom transfer between the reactants and the surface of the catalysts, involving several reaction sites at the same time.

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References

[1] H. Bosch, F. Janssen, Catalytic reduction of nitrogen oxides—a review on the fundamentals and technology, Catal. Today 2 (1988) 369–529.

[2] V.I. Pârvulescu, P. Grange, B. Delmon, Catalytic removal of NO, Catal. Today 46 (1998) 233–316.

[3] 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.

[4] Z. Zhu, Z. Liu, S. Liu, H. Niu, Catalytic NO reduction with ammonia at low temperatures on V_2O_5/AC catalysts: effect of metal oxides addition and SO_2, Appl. Catal. B: Environ. 30 (2001) 267–276.

[5] G. Busca, L. Lietti, G. Ramis, F. Berti, Chemical and mechanistic aspects of the selective catalytic reduction of NO_x by ammonia over oxide catalysts: a review, Appl. Catal. B: Environ. 18 (1998) 1–36.

[6] N.Y. Topsøe, H. Topsøe, J.A. Dumesic, Vanadia/titania catalysts for selective catalytic reduction (SCR) of nitric oxide by ammonia, J. Catal. 151 (1995) 226–240.

[7] I.E. Wachs, G. Deo, B.M. Weckhuysen, A. Andreini, M.A. Vuurman, M. de Boer, M.D. Amidiris, Selective catalytic reduction of NO with NH_3 over supported vanadia catalysts, J. Catal. 161 (1996) 211–221.

[8] G. Ramis, Y. Li, G. Busca, M. Turco, E. Kotur, R.J. Willey, Adsorption, activation, and oxidation of ammonia over SCR catalysts, J. Catal. 157 (1995) 523–535.

[9] W.S. Kijlstra, D.S. Brands, E.K. Poels, A. Bliek, Mechanism of the selective catalytic reduction of NO by NH_3 over MnO_x/Al_2O_3. I. Adsorption and desorption of the single reaction components, J. Catal. 171 (1997) 208–218.

[10] S. Soyer, A. Uzun, S. Senkan, I. Onal, A quantum chemical study of nitric oxide reduction by ammonia (SCR reaction) on V_2O_5 catalyst surface, Catal. Today 118 (2006) 268–278.

[11] F. Janssen, R. Meijer, Quality-control of deNO$_x$ catalysts—performance testing surface analysis and characterization of deNO$_x$ catalysts, Catal. Today 16 (1993) 157–185.

[12] 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.

[13] R. Willi, M. Maciejewski, U. Göbel, R.A. Köppel, A. Baiker, Selective reduction of NO by NH_3 over chromia on titania catalyst: investigation and modelling of the kinetic behaviour, J. Catal. 166 (1997) 356–367.

[14] F. Kapteijn, A.D. Vanlangeveld, J.A. Moulijn, A. Andreini, M.A. Vuurman, A.M. Turek, J.M. Jehng, I.E. Wachs, Alumina-supported manganese oxide catalysts. 1. Characterization-influence of precursor and loading, J. Catal. 150 (1994) 94–104.

[15] M. Koebel, M. Elsener, Selective catalytic reduction of NO over commercial DeNO$_x$-catalysts: experimental determination of kinetic and thermodynamic parameters, Chem. Eng. Sci. 53 (1998) 657–669.

[16] G. Ramis, G. Busca, F. Bregani, P. Forzatti, Fourier transform-infrared study of the adsorption and coadsorption of nitric oxide, nitrogen dioxide and ammonia on vanadia-titania and mechanism of selective catalytic reduction, Appl. Catal. 64 (1990) 259–278.

[17] V. Tufano, M. Turco, Kinetic modelling of nitric oxide reduction over a high-surface area V_2O_5-TiO_2 catalyst, Appl. Catal. B: Environ. 2 (1993) 9–26.

[18] E. Richter, H.Y. Schmidt, H.G. Schecker, Adsorption and catalytic reactions of NO and NH_3 on activated carbon, Chem. Eng. Tech. 13 (1990) 332–340.

[19] L. Singoredjo, F. Kapteijn, J.A. Moulijn, J.M. Martín-Martínez, H.P. Boehm, Modified activated carbons for the selective catalytic reduction of NO with NH_3, Carbon 31 (1993) 213–222.

[20] S. Teng, Y.T. Tu, Y.C. Lai, C.C. Li, Reduction of NO with NH_3 over carbon catalysts. The effect of treating carbon with H_2SO_4 and HNO_3, Carbon 39 (2001) 575–582.

[21] G. Marbán, T. Valdés-Solís, A.B. Fuertes, Mechanism of low temperature selective catalytic reduction of NO with NH_3 over carbon-supported Mn_3O_4—active phase and role of surface NO species, Phys. Chem. Chem. Phys. 6 (2004) 453–464.

[22] W.S. Kijlstra, D.S. Brands, H.I. Smit, E.K. Poels, A. Bliek, Mechanism of the selective catalytic reduction of NO by NH_3 over MnO_x/Al_2O_3. II. Reactivity of adsorbed NH_3 and NO complexes, J. Catal. 171 (1997) 219–230.

[23] M.J. Lázaro, M.E. Gálvez, I. Suelves, R. Moliner, S.V. Vassilev, C. Braekman-Danheux, Low cost catalytic sorbents for NO_x reduction. 3. NO reduction tests using NH_3 as reducing agent, Fuel 83 (2004) 875–884.

[24] M.E. Gálvez, M.J. Lázaro, R. Moliner, Novel activated carbon-based catalyst for the selective catalytic reduction of nitrogen oxide, Catal. Today 102 (2005) 142–147.

[25] S.V. Vassilev, C. Braekman-Danheux, R. Moliner, I. Suelves, M.J. Lazaro, T. Thieman, Low cost catalytic sorbents for NO_x reduction. 1 Preparation and characterization of coal char impregnated with model vanadium components and petroleum coke ash, Fuel 81 (2002) 1281–1296.

[26] M.J. Lázaro, M.E. Gálvez, S. Artal, J.M. Palacios, R. Moliner, Preparation of steam-activated carbons as catalyst supports, J. Anal. Appl. Pyrol. 78 (2007) 301–315.

[27] M.J. Lázaro, M.E. Gálvez, C. Ruiz, R. Juan, R. Moliner, Vanadium loaded carbon-based catalysts for the reductionof nitric oxide, Appl. Catal. B 68 (2006) 130–138.

[28] Z. Zhu, Z. Liu, S. Liu, H. Niu, Adsorption and reduction of NO over activated coke at low temperature, Fuel 79 (2000) 651–658.

[29] G. Marbán, T. Valdés-Solís, A.B. Fuertes, Mechanism of low-temperature selective catalytic reduction of NO with NH_3 over carbon-supported Mn_3O_4—role of NH_3 surface species: SCR mechanism, J. Catal. 226 (2004) 138–155.

[30] 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.

[31] A. Rajeev Rajadhyaksha, H. Knözinger, Ammonia adsorption on vanadia supported on titania-silica catalyst: an infrared spectroscopic investigation, Appl. Catal. 51 (1989) 81–92.

[32] N.Y. Topsøe, Mechanism of the selective catalytic reduction of nitric oxide by ammonia elucidated by in situ on-line fourier transform infrared spectroscopy, Science 265 (1994) 1217–1219.

[33] M.A. Centeno, I. Carrizosa, J.A. Odriozola, In situ DRIFTS study of the SCR reaction of NO with ammonia over a high loading (15% weight) vanadia-titania catalyst, Phys. Chem. Chem. Phys. 1 (1999) 349–354.

[34] S.M. Jung, P. Grange, The investigation of mechanism of SCR reaction on a TiO_2-SO_4^{2-} catalyst by DRIFTS, Appl. Catal. B: Environ. 27 (2000) L11–L16.

[35] S.M. Jung, P. Grange, DRIFTS investigation of V=O behavior and its relations with the reactivity of ammonia oxidation and selective catalytic reduction of NO over V_2O_5 catalyst, Appl. Catal. B: Environ. 36 (2002) 325–332.

[36] H. Kamata, K. Takahashi, C.U.I. Odenbrand, Kinetics of the selective reduction of NO with NH_3 over a $V_2O_5(WO_3)/TiO_2$ commercial catalyst, J. Catal. 185 (1999) 106–113.

[37] H. Schneider, S. Tschudin, M. Schneider, A. Wokaum, A. Baiker, In situ diffuse reflectance FTIR study of the selective caalytic reduction of NO by NH_3 over vanadia-titania aerogels, J. Catal. 147 (1994) 5–14.

[38] H. Schneider, M. Maciejewski, K. Köhler, A. Wokaum, A. Baiker, Chromia supported on Titania. VI. Properties of different chromium oxide phases in the catalytic reduction of NO by NH_3 studied by in situ diffuse reflectance FTIR spectroscopy, J. Catal. 157 (1995) 312–320.

[39] J.J. Venter, M.A. Vanice, Applicability of "DRIFTS" for the characterization of carbon-supported metal catalysts and carbon surfaces, Carbon 26 (1988) 889–902.

[40] A. Dandekar, M.A. Vannice, Carbon-supported copper catalysts: I. Characterization, J. Catal. 183 (1999) 131–154.

[41] A. Askoylu, J.L. Faria, M.F.R. Pereira, J.L. Figueiredo, P. Serp, J.-C. Hierso, R. Feurer, Y. Kihn, P. Kalck, Appl. Catal. A 243 (2003) 357–365.

[42] J.J. Venter, M.A. Vannice, Olefin selective carbon-supported k-fe-mn co hydrogenation catalysts—a kinetic, calorimetric, chemisorption, infrared and mossbauer spectroscopic investigation, Catal. Lett. 7 (1991) 219–240.

[43] C. Doornkamp, V. Ponec, The universal character of the Mars van Krevelen mechanism, J. Mol. Catal. A: Chem. 162 (2000) 19–32.

[44] B. Coq, M. Mauvenzin, G. Delahay, S. Kieger, Kinetics and mechanism of the N_2O reduction by NH_3 on a Fe-zeolite-beta catalytst, J. Catal. 195 (2000) 298–303.

[45] G. Delahay, S. Kieger, N. Tanchoux, P. Trens, B. Coq, Kinetics of the selective catalytic reduction of NO by NH_3 on a Cu-faujasite catalysts, Appl. Catal. B: Environ. 52 (2004) 251–257.

[46] L.Y. Hsu, H. Teng, Catalytic NO reduction with NH_3 over carbons modified by acid oxidation and by metal impregnation and its kinetic studies, Appl. Catal. B: Environ. 35 (2001) 21–30.

[47] C.C. Liu, H. Teng, Cu/MCM-41 for selective catalytic NO reduction with NH_3-comparison of different Cu-loading methods, Appl. Catal. B: Environ. 58 (2005) 69–77.