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Vanadium as a catalyst for NO, N_2O and CO_2 reaction with activated carbon

Sónia A. Carabineiro [a,*], F. Brás Fernandes [b], Ana M. Ramos [a], Joaquim Vital [a], Isabel F. Silva [a]

[a] *Departamento de Química, C.Q.F.B., Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologia, 2825–114 Caparica, Portugal*

[b] *Departamento de Ciência dos Materiais, CENIMAT, Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologia, 2825–114 Caparica, Portugal*

Abstract

The kinetics of the reaction of NO, N_2O and CO_2 with activated carbon without catalyst and impregnated with a precursor salt of vanadium (ammonium monovanadate) was investigated. The conversion of NO, N_2O and CO_2 was studied (450–900°C) using a TGA apparatus and a fixed bed reactor. The reactor effluents were analysed using a GC/MS on line. The addition of vanadium increased carbon reactivity and adsorption at lower temperatures. For NO and N_2O conversion the main products obtained were N_2, N_2O, CO and CO_2 but for CO_2 conversion only CO was detected. In situ XRD was a useful tool for interpreting catalyst behaviour and identifying phases present during reaction conditions. The catalytic effect of vanadium can be explained by the occurrence of redox processes in which the catalyst is reduced to lower oxidation states such as V_2O_5/V_6O_{13}. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

NO removal from exhaust streams of various combustion sources has become increasingly important in the past few years [1–14].

Recently catalytic reduction of NO with carbons as reducing reagents has been intensively investigated [1–3,5–8,10,12–14]. The reaction depends significantly on the composition of the catalyst and nature of the reacting carbon [3].

According to earlier studies of Suuberg et al. at low temperatures, dissociative NO chemisorption results in the formation of a carbon oxygen complex and the decomposition of these complexes (at higher temperatures) leads to production of CO_2 and CO [11].

In recent studies Illan-Gomez et al. reported that the analysis of the reaction products reveals a mechanism for catalytic NO reduction with three stages [1,3,7,8,10]:

1. At low temperatures, N_2 and or N_2O are the only products. Oxygen is retained on the catalyst/carbon surface.
2. Above 300°C, N_2 continues to evolve but CO_2 evolution occurs and the rate of NO reduction increases.
3. Above 500°C, N_2 evolution becomes constant and CO becomes dominant.

The active sites that retain and transfer the oxygen to carbon are different, depending on the nature of the

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[*] Corresponding author.

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chemical species involved in each case [1,3,8,10]. CO_2 is a major source for the so called greenhouse effect, leading possibly to changes in climate.

To reduce the emission of CO_2 carbon gasification can be used as an important process in producing clean fuels and chemical feed stocks [15–21].

All carbonaceous materials can be gasified in CO_2 to produce CO, which is a useful product. If carbon is reacted with CO_2, CO is obtained in the reverse Boudouard reaction:

$$CO_2(g) + C(s) \rightarrow 2CO(g)$$

The use of catalysts was proposed for low temperature gasification to overcome slow reaction with CO_2 [16–19,21].

Group VIII metals as well as alkali and alkaline-earth catalysts are effective catalysts [16–19,21].

A generally postulated mechanism for catalytic CO_2 gasification consists of an oxidation–reduction cycle in which oxygen is transferred to the carbon matrix through the catalyst active phase, followed by decomposition of the oxidised carbon site, producing CO [17,19,21]. Several studies have shown that active alkaly species are able to chemisorb CO_2 and are capable of catalysing oxygen exchange reactions [16–18].

The aim of the present work is to study the behaviour of vanadium as a catalyst for C/NO, C/N_2O and C/CO_2 reaction.

In situ XRD is used to identify the phases present under reaction conditions. This technique combined with kinetic measurements is a useful tool for interpreting catalyst behaviour.

2. Experimental

Charcoal activated GR MERCK (powder) was used to carry out isothermal kinetic studies and adsorption of NO, N_2O and CO_2. This activated charcoal had a surface area of 1011 m^2/g and a pore total volume of 0.54 cm^2/g. The charcoal was impregnated with diluted solutions of ammonium monovanadate by the Incipient Wetness Method. The metal loading was 4 wt.%.

In order to prevent diffusional limitations, thermogravimetric sample weight was around 2–3 mg. Isothermal kinetic studies were carried out using a thermobalance system (CI electronics MK II microbalance) with continuous recording of change in weight between 300 and 900°C, with CO_2 and mixtures of Ar+0.5% N_2O and Ar+0.5% NO, with flow rates of 3.3 cm^3/s.

For the adsorption studies 10 mg of sample were weighted using the same apparatus, using CO_2, 0.5% N_2O in Ar and 0.5% NO in Ar, with a flow rate of 3.3 cm^3/s.

For comparison purposes, initial rates obtained at initial burn-off were used. The gasification rates at each temperature were derived from the relation

$$\text{rate } (s^{-1}) = (-\Delta w/\Delta t)/w_0$$

where w_0 is the initial weight of the sample.

Before each experiment, Ar was introduced with a flow rate of 3.3 cm^3/s, for 30 min, in order to eliminate traces of air. The samples were heated in flowing Ar to 500°C to decompose the precursor salt and eliminate volatiles adsorbed in carbon, until baseline sample weight was constant. The temperature was then adjusted to the desired value (20–900°C) and Ar was switched to CO_2, NO or N_2O mixture.

In situ XRD studies were conducted in a Rigaku D/max III C diffractometer with a Cu Kα radiation source (50 kV, 30 mA), equipped with a high temperature special chamber. All the experiments were carried out at exactly the same experimental conditions as in the thermogravimetric studies.

NO, N_2O and CO_2 conversion was studied using a fixed bed reactor. The reactor effluents were analysed using a GC/MS (Fisons MD800) apparatus, equipped with a column of GS-Molesieve (30 m×0.541 mm) type. These essays included heating of sample at 2°C/min (TPR) to 950°C in a mixture of 0.5% NO or 0.5% N_2O in He or CO_2. The flow rate was 3.3 cm^3/s. All samples were pre-treated in He at 500°C for 30 min.

3. Results and discussion

Fig. 1a and c show clearly that NO and CO_2 adsorption capacity is increased by adding vanadium, when compared with the samples without catalyst. In what concerns to N_2O (Fig. 1b) an even more pronounced

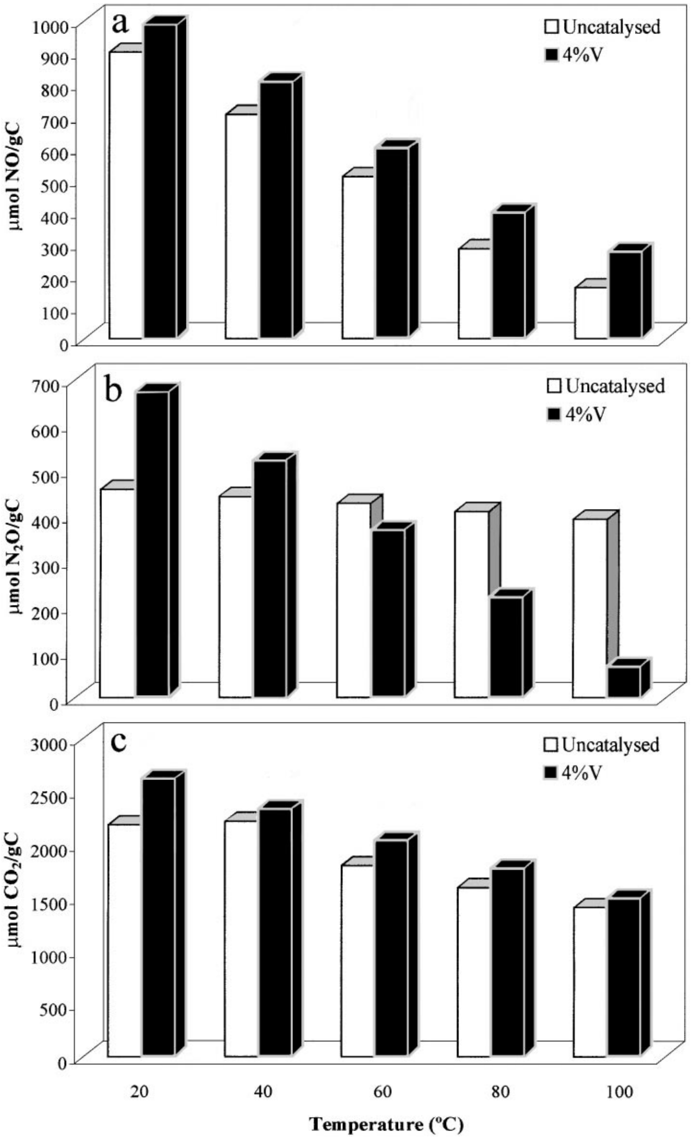

Fig. 1. NO (a), N_2O (b) and CO_2 (c) adsorption for carbon parent sample and sample doped with vanadium, at different temperatures.

effect is observed at lower temperatures. However at higher temperatures a decrease in adsorption capacity is observed.

Fig. 2a–c show the Arrhenius plots for NO, N_2O and CO_2 reaction. The values obtained for the apparent activation energies range from 43–200 kJ mol^{-1} in the presence of vanadium but from 127–289 kJ mol^{-1} for the uncatalysed reaction and lie relatively well within those reported in the literature [2,11].

A substantial decrease in activation energy for the vanadium catalysed reaction compared to the uncatalysed is observed with all gases (139–43 kJ mol^{-1} in NO, 127–97 kJ mol^{-1} in N_2O and 290–200 kJ mol^{-1} in CO_2).

Though N_2O is less adsorbed by carbon, it is more reactive than NO. External diffusional limitations to mass transfer seem to take place in the reaction with N_2O above 600°C.

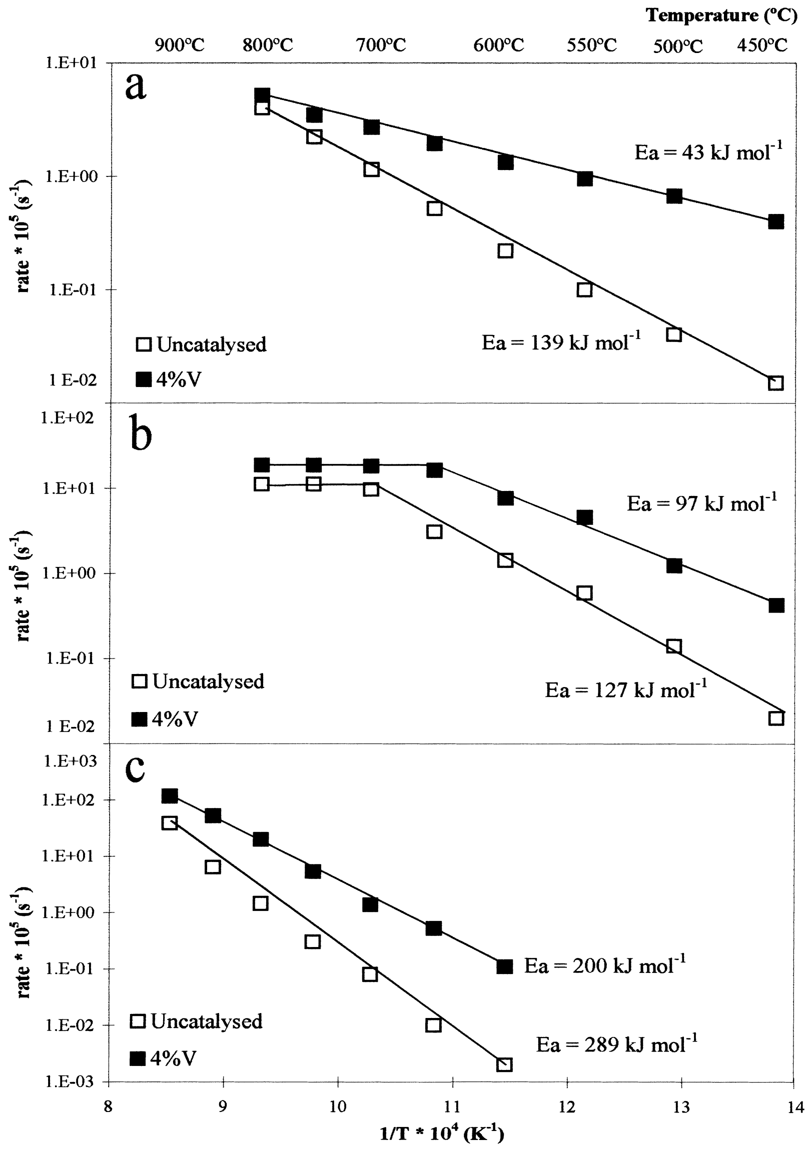

Fig. 2. Arrhenius plots for carbon gasification in NO (a), N_2O (b) and CO_2 (c) for carbon parent sample and sample doped with vanadium.

Fig. 3a shows the catalysed program temperature reaction profile for NO conversion. The analysis of the reaction products for the reaction with NO (Fig. 3b) using a GC/MS on line show the presence of N_2O, N_2, CO_2 and CO together with some unreacted NO. Between 400 and 500°C only CO_2, N_2O and N_2 were detected. CO was observed in minor quantities above 500°C. The greater the rate of CO_2 evolution the greater the NO conversion.

The analysis of the reaction produts for the uncatalysed reaction (Fig. 3c) showed a similar trend, but in this case CO_2 evolution was observed at higher temperatures (above 500°C) and much higher amounts of CO were detected above 550°C.

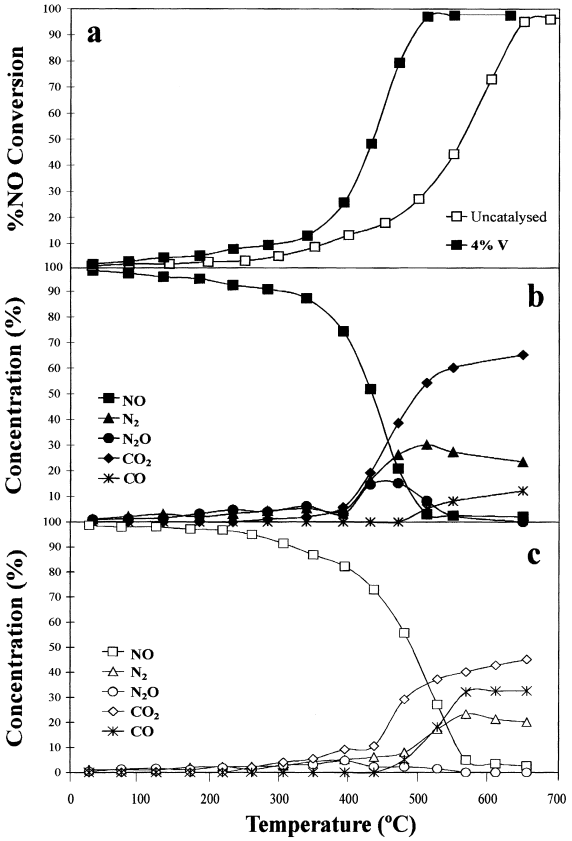

Fig. 3. NO conversion as a function of temperature (a) and reaction products for sample doped with vanadium (b) and carbon parent sample (c) in TPR.

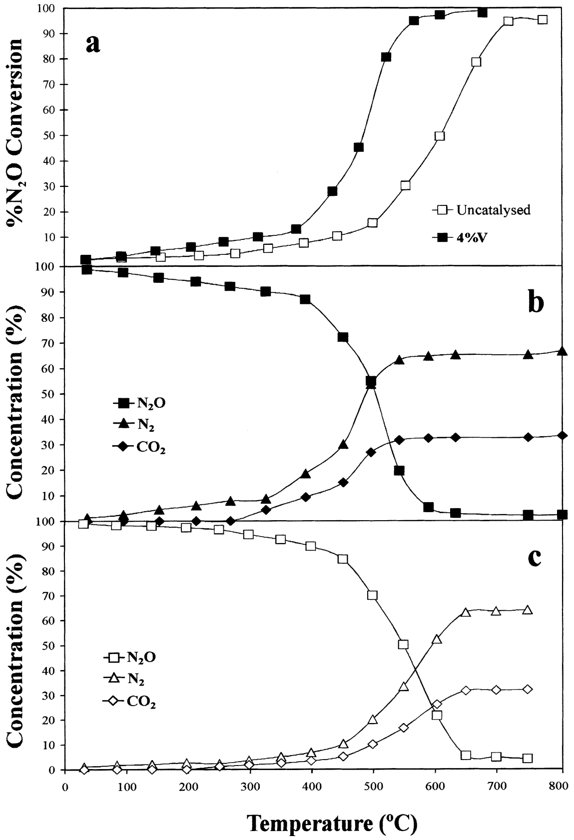

Fig. 4. N_2O conversion as a function of temperature (a) and reaction products for sample doped with vanadium (b) and carbon parent sample (c) in TPR.

The results obtained suggest that dissociative NO chemisorption occurs and the catalyst enhances the formation of a carbon oxygen complex. Decomposition of these complexes leads to production of CO_2 and CO.

In contrast to the mechanism proposed by Illán-Gomez et al. [1,3,7,8,10] neither N_2 nor N_2O were observed at low temperatures.. To observe N_2 formation is necessary to adsorbe and dissociate NO, i.e., to have sites to retain the oxygen atoms. Thus NO reduction can go further if oxygen atoms are removed by carbon otherwise that reduction is inhibited by the oxygen atoms produced. So at low temperatures, for this catalyst, either NO is not dissociated or oxygen is not removed.

Fig. 4a shows the temperature program (TPR) reaction profile for N_2O conversion for the uncatalysed and vanadium catalysed reaction. The products detected were N_2 and CO_2as shown in Fig. 4b (vanadium catalysed reaction) and 4c (uncatalysed reaction). It was reported by Rodriguez-Mirasol et al. [2,4] that the only products observed for the uncatalysed N_2O decomposition were N_2 and CO_2 according to the following mechanism:

$$N_2O + C \rightarrow N_2 + C(O)$$

$$N_2O + C(O) \rightarrow N_2 + CO_2$$

The stoichiometry for products is thus $2N_2{:}1CO_2$ and that is confirmed by the experimental results (Fig. 4b and c).

The results obtained for the vanadium catalysed reaction, suggest that the role of the catalysts is to decrease decomposition temperature without chang-

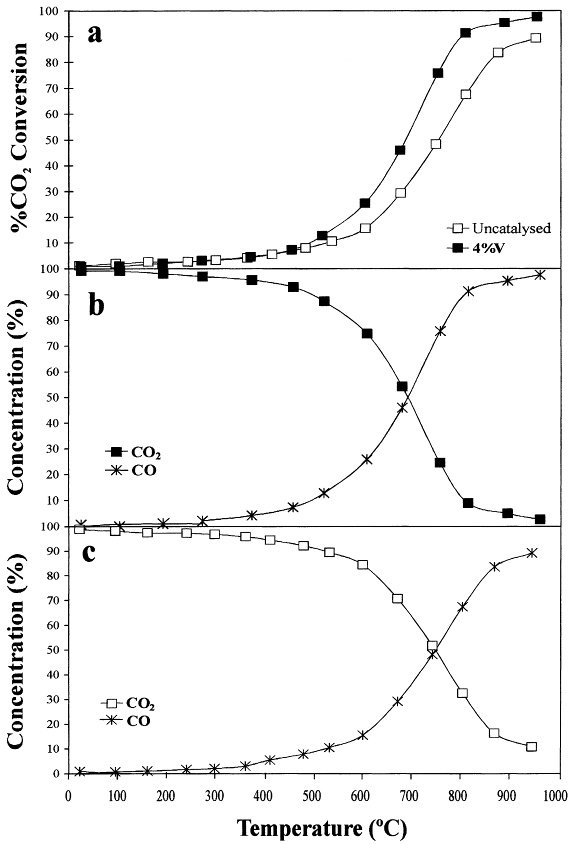

Fig. 5. CO_2 conversion as a function of temperature (a) and reaction products for sample doped with vanadium (b) and carbon parent sample (c) in TPR.

ing the gas products distribution as also referred by Rodriguez-Mirasol et al. using Ca and K as catalysts supported on carbon [4,22]. The reaction of N_2O with the catalysts active centers is generally envisaged as a charge donation from the catalyst into the antibonding of N_2O, destabilising the N–O bond and leading to scission [22].For the catalysed and uncatalysed CO_2 reaction, CO was the main product detected (Fig. 5).

Active phases play also an important role on the catalytic conversion of NO, N_2O and CO_2.

Fig. 6a–d show in situ XRD patterns obtained in N_2, NO, N_2O and CO_2 at several temperatures for carbon doped with vanadium. V_2O_5 is reduced by carbon to V_6O_{13} in all atmospheres.

The peaks show shifts to 2θ with increasing temperature, which reflects expansion of the crystal lattices. Pt peaks appear in the spectra resulting from exposure of the sample holder to the X-ray beam as carbon burned away.

It is known that V_2O_5 is good catalyst for carbon oxidation because of its low Tamman temperature. Various authors reported that V_2O_5 has the ability to spread and wet carbon surface [21,22]. The reduction of V_2O_5 to V_6O_{13} further reduces the melting point of the catalyst and could lead to more extensive spreading on carbon surface [21,22].

Fig. 4a–c show that both V_2O_5 and V_6O_{13} are present under reaction conditions. With increasing temperature, the peaks become less intense for both oxides, suggesting that the catalyst is spreading to form an amorphous film on the carbon surfaces improving catalyst/carbon contact.

The catalytic system is more or less active depending on the ability of the oxide to be reduced by carbon and undergo redox reactions on the carbon surface [1,3,7,8,10].

The same mechanism has been proposed to explain carbon catalysed reactions in other gaseous atmospheres such as CO_2 reaction [19–25].

In situ XRD shows clearly that catalyst is reduced to lower oxidation states such as V_2O_5/V_6O_{13}. The catalytic effect observed for the NO, N_2O and CO_2 conversion can be explained by the occurrence of redox processes in which the oxides particles are reduced by reaction with the carbon at points of contact with the carbon substrate to form lower oxides according to a redox mechanism such as:

$$3V_2O_5 + C(s) \rightarrow V_6O_{13}(s) + CO_2(g)$$

$$V_6O_{13}(s) + 2NO(g) \rightarrow 3V_2O_5(s) + N_2(g)$$

and in the case of CO_2 reaction:

$$3V_2O_5(s) + 2C(s) \rightarrow V_6O_{13}(s) + 2CO(g)$$

$$V_6O_{13}(s) + CO_2(g) \rightarrow 3V_2O_5 + C(s)$$

Vanadium seems to act as an oxygen acceptor from NO, N_2O and CO_2, transferring it to the carbon surface and recovering reduced state. Similar behaviour has been reported by several authors [1,3,7,8,10,12,13,19,21].

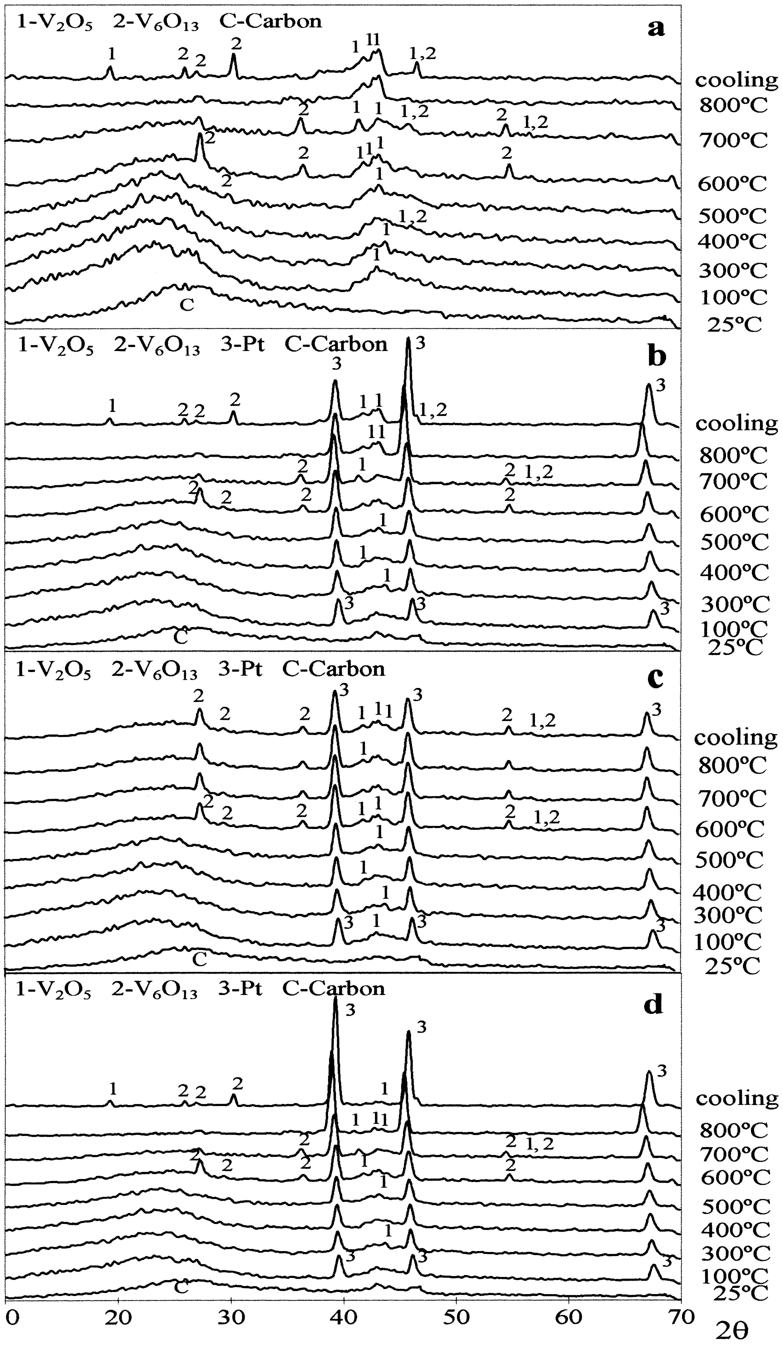

Fig. 6. In situ XRD data obtained in N_2 (a), NO (b), N_2O (c) and CO_2 (d) on heating sample doped with vanadium at several temperatures.

4. Conclusions

This study has indicated that kinetic measurements combined with in situ XRD are useful tool for interpreting catalyst behaviour. In the C–NO and C–N_2O and C–CO_2 reaction a reduced catalyst surface is required to NO, N_2O and CO_2 conversion.

The ability of the catalyst to be spread on the carbon surface and chemisorb the gases going through redox transference of oxygen to the carbon reactive sites seems to explain catalytic activity.

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