*Environmental Research & Technology, Vol. 1 (2), pp. 3-12, 2018*

Turkish JournalPark ACADEMIC

Environmental Research & Technology

http://dergipark.gov.tr/ert

**RESEARCH ARTICLE**

# Effect of gas composition on the selective reduction of $NO_x$ with ammonia over Vanadia based catalysts

Souad Djerad[1,*], Marcus Crocoll[2], Lakhdar Tifouti[1], Werner Weisweiler[2]

[1] Laboratory of Environmental Engineering, Department of Process Engineering, University of Annaba, P.O. Box 12, Annaba, ALGERIA
[2]Institut für Chemische Technik und Polymer Chemie, Universität Karlsruhe (TH), GERMANY

## ABSTRACT

The catalytic reduction of $NO_x$ under different oxygen concentrations leading to different $NO/NO_2$ compositions has been studied in the presence of V3W9Ti and V8W9Ti catalysts in a tubular flow reactor. The results have shown that increasing $O_2$ concentration leads to increase the $NO_x$ reduction in low temperature range [150-275 °C]. Slight effect of $O_2$ concentration on $NO_x$ conversion was observed at higher temperatures. SCR reaction also occurred in the absence of gaseous oxygen but with low NO conversion indicating the strong redox properties of both catalysts. Aged catalysts exhibited relative good activities in $NO_x$ reduction. This is probably due to the sol gel method used for the preparation of the catalysts known to improve the catalysts properties.

***Keywords:*** SCR; Oxygen concentration; NO-$NO_2$ mixture; ammonia oxidation; TPD; aging

## 1. INTRODUCTION

Nitrogen oxides remain a major source in air pollution [1]. Nowadays, it is known that not only $NO_x$ but also $N_2O$ contributes to the greenhouse effect and to the depletion of the ozone layer. Both gases are emitted from many industrial processes and from all means of transport.

From a global warming perspective, diesel engines are presently preferred alternatives to conventional Otto engines in heavy-duty vehicles due to lower fuel consumption and hence lower emissions of $CO_2$.

An established technique for stationary units, which recently has gained increased attention for automotive applications, is selective catalytic reduction of $NO_x$ using ammonia-releasing compounds (e.g, urea) as the reducing agent ($NH_3$-SCR) [2]. Ammonia is added to the exhaust gas, where it reacts selectively with the $NO_x$ over a catalyst to form harmless nitrogen and water. Catalytic systems constituted by $V_2O_5$ dispersed over a $TiO_2$-anatase support are widely used in the selective catalytic reduction (SCR) of $NO_x$ with $NH_3$ [3]. Vanadia supported on the anatase type of titania is a commercial catalyst for the SCR process due to the high NO removal activity and its relatively strong resistance to the poisons including $SO_2$, which is commonly contained in the flue gas. $WO_3$ frequently used with vanadia presents a much lower activity in both denitrification and $SO_2$ oxidation reactions and is used to preserve the structural and morphological characteristics of $TiO_2$-anatase upon addition of vanadia [4].

It is known that the catalytic mechanism is divided into a reduction reaction where a vanadium atom is reduced due to an electron transfer from the adsorbate and a reoxidation reaction where +5 oxidation state of vanadium atom is restored by a reverse electron transfer involving gaseous oxygen [5]. Since $O_2$ is important for the reoxidation of vanadium atom and restore the initial sites, it is an interesting task to study the effect of its concentration but also its absence on the course of the $NO_x$ reduction. In this study, two catalysts with low (3%) and high (8%) vanadia contents were prepared and tested for the catalytic reduction of $NO_x$ in the absence and in the presence of gaseous $O_2$. Aging the catalysts may restrict their use, and therefore the activities of aged catalysts have been also studied.

Corresponding Author: s_djerad@hotmail.com (Souad Djerad)
Received 02 February 2018; Received in revised form 22 February 2018; Accepted 25 February 2018
Available Online 1 April 2018
***Doi:*** ISSN:
© Yildiz Technical University, Environmental Engineering Department. All rights reserved.

## 2. EXPERIMENTAL

### *2.1. Catalyst preparation*

Two catalysts: 3%$V_2O_5$-9%$WO_3$/$TiO_2$ (w/w) and 8%$V_2O_5$-9%$WO_3$/$TiO_2$ (w/w) were prepared by sol-gel method. The cordierite used as support has a cell density of 64 cells cm$^{-2}$ and a volume of 9.4 cm$^3$ and was coated with 200 mg of each catalyst labelled V3 and V8. Further details on the catalyst preparation are given in a previous publication [6].

BET measurements were performed with a Quantachrome Autosorb 1C using Nitrogen. X-ray diffraction patterns were obtained with a Siemens D-500 powder X-ray diffractometer using CuKα radiation (λ= 1,5406 Å) in step mode between 20° and 80°, using a step size of 0,02° s$^{-1}$. Mesopores distribution measurements have been obtained by mercury penetration method using a porosimeter Autopore III.

### *2.2. Activity measurements*

The catalytic activity measurements were carried out in a quartz tubular fixed bed reactor (i.d 30 mm). The composition of the feed was 500 ppm NO, 500 ppm $NH_3$ with varying the oxygen concentration (2, 4, 6, 8, 10 and 15 % vol $O_2$). The $N_2$ being a carrier gas (total flow rate = 2000 mL min$^{-1}$). K-type thermocouples provided the exhaust temperature before the catalyst. The temperature of all gas lines was kept at 150°C.

The activity data were collected at different temperatures in the range 150-500°C, each temperature was maintained until steady-state conditions were reached. The NO and $NO_2$ concentrations in the inlet and outlet gases were measured continuously by mean of a Chemiluminescence detector CLD 700 EL ht. $NH_3$ and $N_2O$ were analysed with non-dispersive IR spectrometry with a Siemens Ultramat 5E and Binos 4b.1 devices, respectively. The results of the catalytic tests performed over $V_3$ and $V_8$ catalysts are shown in terms of $NO_x$ conversion $XNO_x = 1-([NO_x]out/[NO_x]in)$ and $N_2$ selectivity $SN_2 = [N_2]/([N_2] + [N_2O])$, respectively. The moles of $N_2$ were determined from the following atomic nitrogen balance:

$N_{2out} = 1/2([NO_x]_{in}-[NO_x]_{out}) + 1/2([NH_3]_{in}-NH_3]_{out}) - N_2O_{out}$. All measurements were run in duplicates

## 3. RESULTS

### *3.1. Characteristics of the prepared catalysts*

Table 1 shows that BET surface areas of both catalysts $V_3$ and $V_8$ decreased with increasing the calcination temperature, while the mean pore radius increased. The effect of calcination temperature was more pronounced with $V_8$ due to the high vanadia content.

X-ray analyses show that up to 600°C, $V_3$ catalyst was monophasic and only anatase polymorph was formed (Fig. 1a). At 700°C the rutile form was detected and the transformation was complete at 800°C. No $V_2O_5$ crystallites were formed at high calcination temperatures, probably because vanadia was highly dispersed as isolated $VO_x$ species [7].

With the catalyst V8, rutile form of titania was detected at 600°C (58%) (Fig.1b) and weak peaks at 2θ = 20.3-26.3 and 31.2° appeared revealing the formation of crystalline $V_2O_5$ on the catalyst surface. Over this temperature, crystallites of vanadia disappeared again suggesting the formation of a solid solution between vanadia and titania support [8].

### *3.2. Catalytic activity measurements*

Activity measurements were carried out with the catalysts $V_3$ and $V_8$ calcined at 500°C for 2 hours. Their surface areas were respectively 77 and 22 m$^2$ g$^{-1}$ (Table 1). Preliminary reactions were carried out in the absence of oxygen over both catalysts (Fig. 2a-b). Low NO conversions were observed in temperature range [150-325°C]. Over 325°C, $NO_x$ conversions increased gradually with increasing temperature. The conversion of NO with $V_3$ was slightly higher than that with $V_8$ over the whole temperature range. Furthermore, differences were observed in the amounts of $N_2$ and $N_2O$ formed during the SCR reactions. In fact, higher amount of $N_2$ was produced in the presence of $V_3$ in temperature range [400-500°C] (not shown). In contrast, higher $N_2O$ amount was formed in the presence of $V_8$ in the whole temperature range (Fig. 3a-b). It was also observed that ammonia conversion was lower than that of NO in the whole temperature range in both cases (not shown).

The effect of oxygen concentration on the $NO_x$ conversion was also investigated in the temperature range [150-500°C] (Fig. 2 a - b).

$NO_x$ in diesel exhaust is usually composed of >90% NO. Therefore, the main reaction of SCR with ammonia will be:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

The reaction between NO and ammonia may also proceed in a different way, giving rise to the unwanted $N_2O$:

$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \qquad (2)$$

The presence of oxygen revealed in the interval of temperature [150-500°C] two quite distinct zones. In the first zone [150-250°C], the influence of the oxygen content was remarkable in the presence of both catalysts. Indeed, $NO_x$ conversion increased with the increase in the oxygen content and temperature. Catalyst V8 had the highest activity compared to $V_3$ in this temperature range.

In the second zone [250-500°C], the effect of $O_2$ was weak. We observed however, that with 2, 4 and 6 % $O_2$ in the presence of $V_3$, the $NO_x$ conversions were maintained at 100% in the temperature range [250-400°C] before decreasing. With 8, 10 and 15% $O_2$, $NO_x$ conversions were less than those observed at lower $O_2$ concentrations. At higher temperatures [400-500°C], the conversion of $NO_x$ in the presence of $V_3$ decreased slowly and reached 68% at 500°C regardless of the oxygen content.

**Table 1.** Morphological properties

| Catalyst | T (°C) | $S_g$ (m$^2$/g) | Phase | $D_c$ (Å) | $V_p$ (cm$^3$/g) | $rp_{exp}$ (Å) |
|---|---|---|---|---|---|---|
| V3W9Ti | 400 | 115 | A | 265 | 0.336 | 16.6 |
| | 500 | 77 | A | 319 | 0.289 | 20 |
| | 600 | 22 | A | 579 | 0.248 | 23.2 |
| | 800 | - | R | 783 | - | - |
| V8W9Ti | 400 | 154 | A | 265 | 0.31 | 30 |
| | 500 | 22 | A | 682 | 0.29 | 72 |
| | 600 | 14 | 43%A+57%R | 1068 | - | - |
| | 800 | - | - | - | - | - |

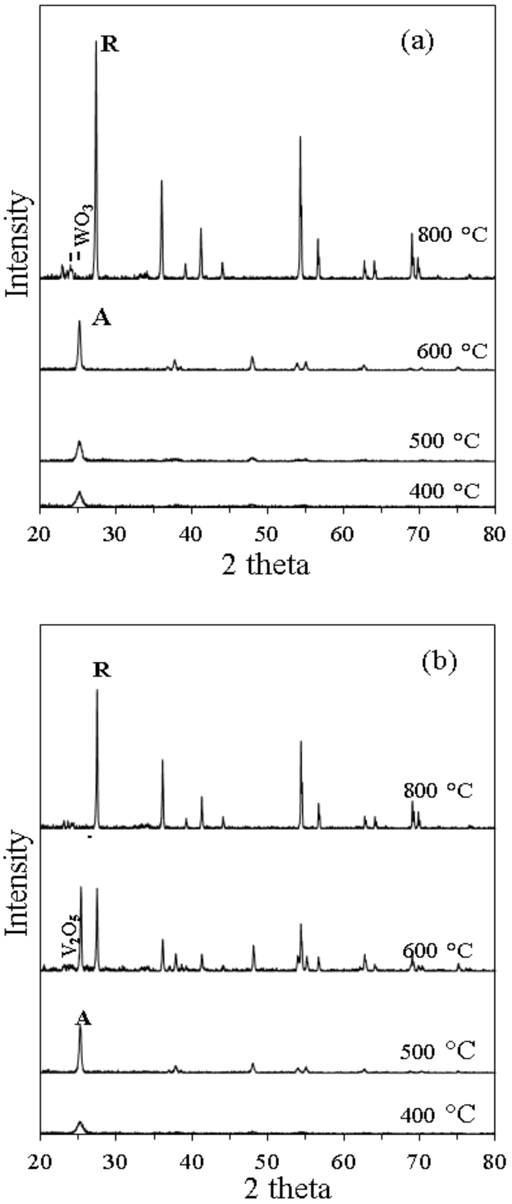

**Fig 1.** X-ray powder diffraction patterns of (a) V3W9Ti and (b) V8W9Ti calcined from 400 to 800°C

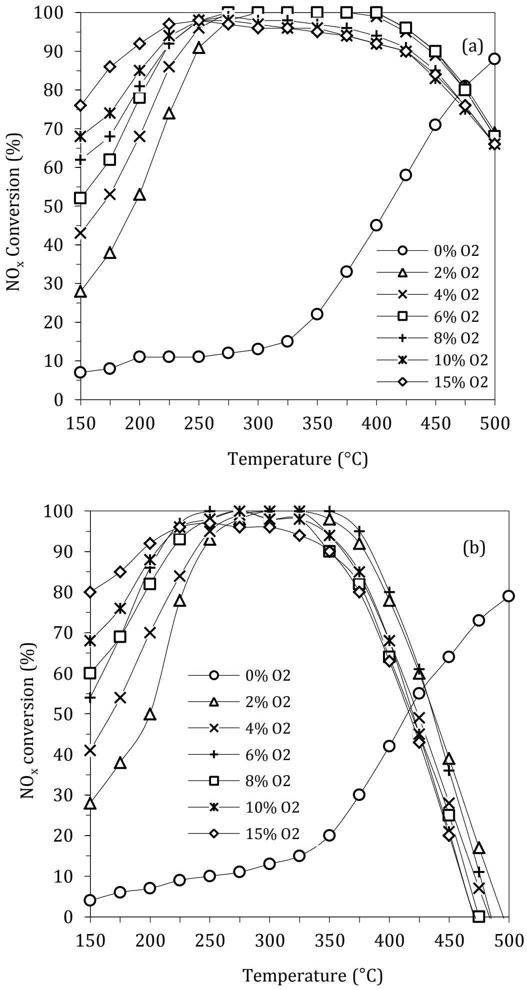

**Fig 2.** $NO_x$ conversion over $V_3W_9Ti$ (a) and $V_8W_9Ti$ (b) during the SCR reaction (Experimental conditions: catalyst weight: 200mg, flow rate: 2000 mL min$^{-1}$, feed: $N_2$ + 500 ppm $NH_3$ + 500 ppm NO, (2-4-6-8-10-15% vol$O_2$))

In the presence of $V_8$, the maximum of $NO_x$ conversion was obtained in temperature range [250-350°C] with 2-4-6% $O_2$. With 15% $O_2$, the $NO_x$ conversion had the lowest value in temperature range [250-500°C]. The $NO_x$ conversion decreased abruptly over 375°C with all $O_2$ concentrations and reached negative values over 475°C due probably to ammonia oxidation which produced $NO_x$. With both catalysts, 6% $O_2$ seems to be the best $O_2$ concentration since a better stability in the results was observed in the whole temperature range.

The $N_2O$ production in the presence of $V_3$ during the SCR reaction started at 300°C (Fig. 3a). Its amount increased quickly with increasing temperature and decreased however with the increase in oxygen content. A total selectivity to $N_2$ in the presence of $V_3$ was observed in a large temperature range [150-300°C] and it decreased slowly starting from 325°C to reach values ranging between 60 and 70% at 500°C (not shown).

In the presence of $V_8$, the $N_2O$ was produced during the SCR reaction starting from 250°C (Fig. 3b) and reached a maximum at 450°C over which it decreased. This behaviour was not observed in the presence of $V_3$. The selectivity to $N_2$ was total up to 250°C over which it decreased reaching values ranging between 20 and 30 % at 500°C (not shown).

According to our experiments, $NO_2$ concentration increased with increasing $O_2$ content upstream the catalysts as shown in Table 2, which caused the increase in the SCR rate reaction in low temperature range. We can conclude that the presence of $NO_2$ in the inlet flow increased the catalytic activity of V-W-Ti catalysts.

At 15% $O_2$ the gas composition did not reach the equimolar composition between NO and $NO_2$ to be referred as "Fast SCR reaction". In automotive application 90~95% of the $NO_x$ in Diesel exhaust is NO and the fast SCR is promoted by an oxidizing catalyst upstream to the SCR catalyst that forms $NO_2$ to yield a near optimum of $NO/NO_2=1$ [9].

In our experiments, no oxidation catalyst was used and $NO_2$ was formed through the thermodynamic equilibrium which depends on the $O_2$ concentration and temperature:

$$NO + \frac{1}{2} O_2 \leftrightarrow NO_2 \qquad (3)$$

### 3.3. Ammonia oxidation

For a better understanding of the side reactions, catalytic tests were also carried out in which the feed contained only $NH_3$ and $O_2$ under the same operation conditions as those conducted for the SCR reaction experiments.

The ammonia may be oxidized by oxygen instead of NO through one of the following ways:

$$2NH_3 + 3/2\, O_2 \rightarrow N_2 + 3H_2O \qquad (4)$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \qquad (5)$$

$$2NH_3 + 5/2\, O_2 \rightarrow 2NO + 3H_2O \qquad (6)$$

$$4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O \qquad (7)$$

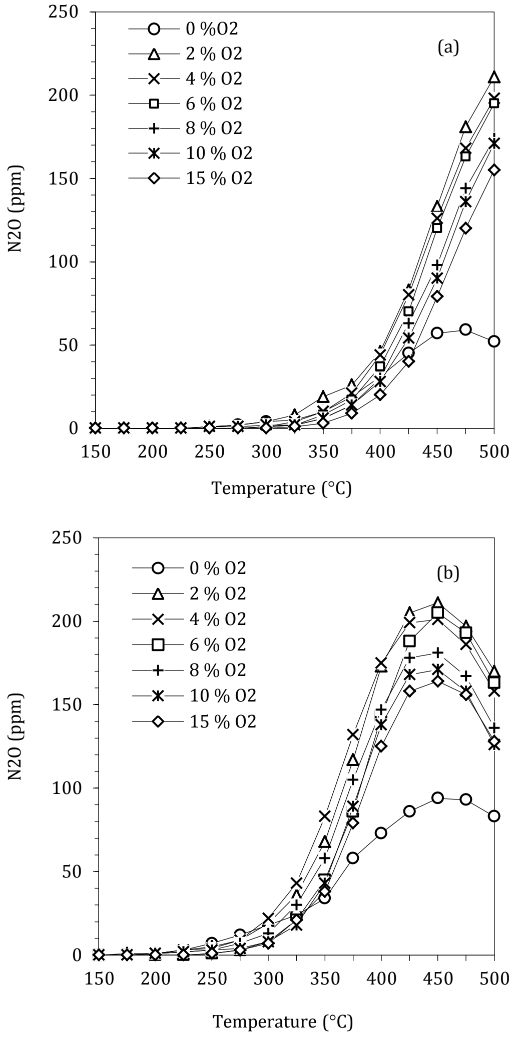

**Fig 3.** $N_2O$ formation during the SCR reaction over $V_3W_9Ti$ (a) and $V_8W_9Ti$ (b) (Experimental conditions: catalyst weight: 200mg, flow rate: 2000mL/min, feed: $N_2$ + 500 ppm $NH_3$ + 500 ppm NO, (2-4-6-8-10-15% vol $O_2$))

**Table 2.** Composition of $NO_x$ versus $O_2$ concentration

| Oxygen concentration | Composition of $NO_x$ (ppm) | Composition of $NO_x$ (%) |
|---|---|---|
| 0% vol | $500NO+0NO_2$ | $100\%NO+0\%NO_2$ |
| 2% vol | $460NO+40NO_2$ | $92\%NO+08\%NO_2$ |
| 4% vol | $420NO+80NO_2$ | $84\%NO+16\%NO_2$ |
| 6% vol | $400NO+100NO_2$ | $80\%NO+20\%NO_2$ |
| 8% vol | $375NO+125NO_2$ | $75\%NO+25\%NO_2$ |
| 10% vol | $360NO+140NO_2$ | $72\%NO+28\%NO_2$ |
| 15% vol | $310NO+190NO_2$ | $62\%NO+38\%NO_2$ |

In the presence of oxygen, the decrease in the ammonia concentration during its oxidation was observed over both catalysts. In the presence of $V_3$, ammonia oxidation started at 275°C producing only $N_2$ (Fig. 4a). The $N_2O$ was formed starting from 300°C (Fig. 4b) and increased gradually until 130 ppm at 500°C regardless of $O_2$ content. The production of NO was very weak and started at 450°C reaching a maximum of 18 ppm at 500°C with 2% vol $O_2$ (Fig. 4c). NO formation of $NO_2$ was observed under our experimental conditions.

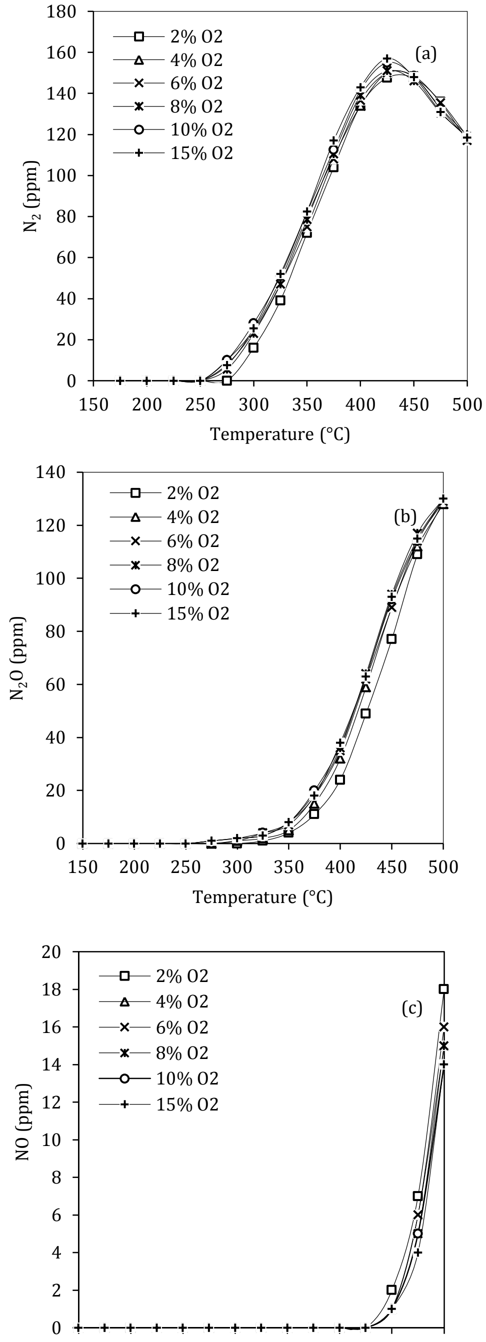

**Fig 4.** $N_2$ (a), $N_2O$ (b) and NO (c) formation during $NH_3$ oxidation over $V_3W_9Ti$ (Experimental conditions: catalyst weight: 200mg, flow rate: 2000mL/min, feed: $N_2$ + 500 ppm $NH_3$ + (2-4-6-8-10-15 % vol $O_2$))

Higher activity in $NH_3$ oxidation was achieved in the presence of $V_8$ with the formation of $N_2$, $N_2O$, NO and $NO_2$ (Fig. 5a-d). In fact, ammonia oxidation produced $N_2$ starting from 225°C (Fig. 5a) which quickly reached a first maximum at 350°C and decreased thereafter up to 425°C before increasing again. The formation of $N_2O$ started at 275°C and reached a maximum at 425°C coinciding with the minimum of $N_2$ produced (Fig. 5b). The formation of NO started at 375°C (Fig. 5c) and the amounts produced were more important than those of $N_2$ and $N_2O$ at higher temperatures. The formation of $NO_2$ was the last reaction to occur starting at 425°C (Fig. 5d). The oxidation of ammonia in the presence of $V_8$ gave all the products indicated by the thermodynamic namely $N_2$, $N_2O$, NO and $NO_2$ while $V_3$ produced only $N_2$, $N_2O$ and NO. This multitude of products formed with $V_8$ indicated a more active surface in the ammonia oxidation. It should be noticed that $O_2$ content affected slightly the amount of the products formed during ammonia oxidation in the presence of both catalysts on the contrary of its effect on the SCR reaction.

The amounts of $N_2O$ produced during the SCR reaction in the presence of both catalysts were slightly higher than those produced by the oxidation of ammonia. Comparing the $N_2O$ amounts formed during SCR reaction and ammonia oxidation with $V_3$ for example, shows that increasing $O_2$ content leads to increase the importance of ammonia oxidation in the $N_2O$ formation. In fact, with 2% $O_2$ at 450°C, 42% of the total $N_2O$ amount formed during the SCR reaction was due to the ammonia oxidation. This value increased with increasing oxygen concentration until reaching 100% with 8, 10 and 15% $O_2$ at the same temperature.

Thus, it can be concluded that the main $N_2O$ amount produced during the SCR reaction in the presence of both catalysts was due to ammonia oxidation (R5), the remainder $N_2O$ was produced by the secondary SCR reaction (R2).

### *3.4. TPD measurements*

It is usually agreed that SCR activity is positively related to the surface acidity of the vanadia-based catalysts [9-11]. The acidic properties of the catalysts were evaluated by temperature programmed desorption of ammonia. TPD experiments were performed in situ with V3 and V8 with the same reactor used for the catalytic tests. Before the experiments, the samples were pre-treated with $N_2$ at 500°C for 1h to remove adsorbed $H_2O$ and other gases. After that the samples were cooled down to 50°C, the $N_2$ flow was switched to a flow of 500 ppm $NH_3/N_2$. When NDIR analysis showed that the concentration of $NH_3$ has stabilized, the reactor was then purged with $N_2$ for 1 h. The temperature was raised at 10°C/min to 500°C. The TPD profiles of ammonia on V3 and V8 are shown in figures 6a and 6b. Ammonia desorption was observed over a wide temperature range for $V_3$. Two main peaks were found at 105 °C (203 ppm) and 210°C (142 ppm). Ammonia profile with $V_8$ showed a predominant feature in the low temperature region with two maxima at 118°C (137 ppm) and 215°C (68 ppm). $NH_3$ desorption signal drops down after a shoulder-like feature around 286°C (23 ppm) but continued to show small quantities of $NH_3$ desorption at higher temperatures.

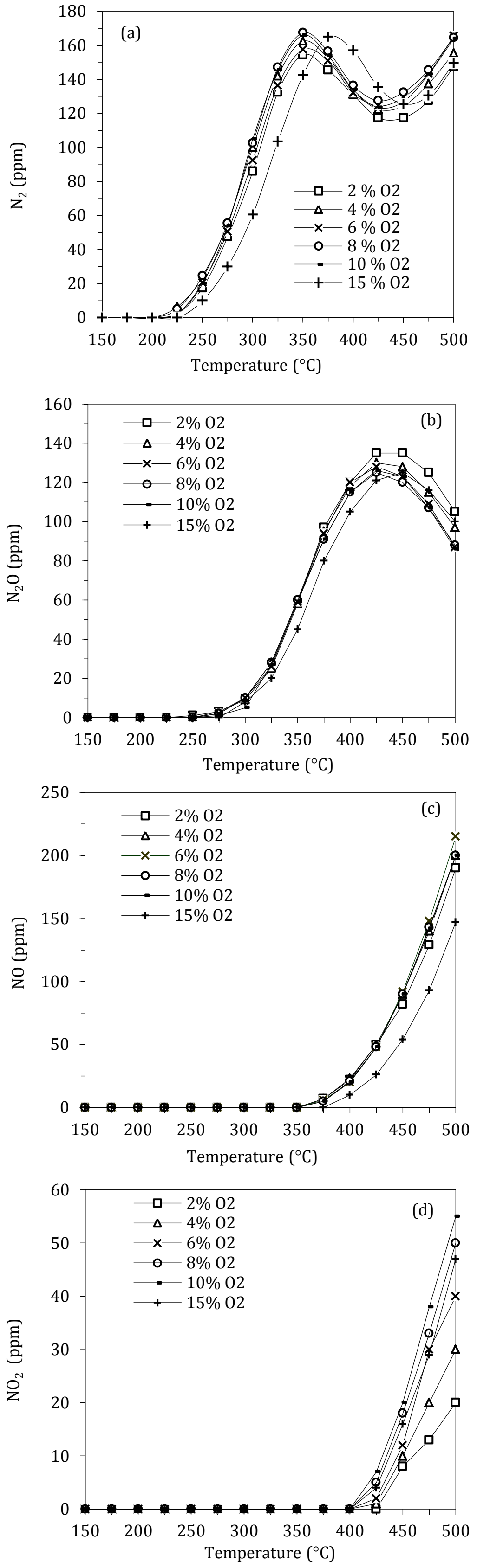

**Fig 5.** $N_2$ (a), $N_2O$ (b), NO (c) and $NO_2$ (d) formation during $NH_3$ oxidation over V8W9Ti (Experimental conditions: catalyst weight: 200mg, flow rate: 2000 mL min$^{-1}$, feed: $N_2$ + 500 ppm $NH_3$ + (2-4-6-8-10-15 % vol $O_2$))

The amount of $NH_3$ desorbed from V8 was lower than that desorbed from V3. For both catalysts, the features obtained from ammonia desorption indicated the presence of different types of adsorbed species.

The total amount of ammonia desorbed was calculated by integration of the areas under the curves in the temperature range between 50°C and 500°C. Higher amount of ammonia was desorbed from $V_3$ surface compared to that desorbed from $V_8$, but the amount of the desorbed ammonia per unit of surface area indicated that the density of acidic surface sites was significantly higher for V8 (8.43 µmole/m$^2$) compared to V3 (4.85 µmole/m$^2$).

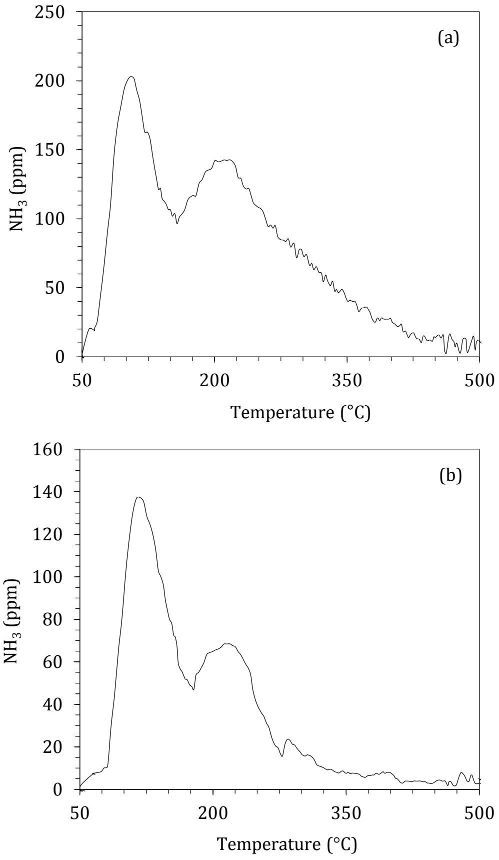

**Fig 6.** Temperature Program Desorption of ammonia for V3W9Ti (a) and V8W9Ti (b)

### 3.5. *Aged samples*

The catalysts V3 and V8 were calcined for 25 hours at 500°C to evaluate their durability. Activities (with 6% $O_2$ vol) in SCR reaction as well as the surface characteristics of these catalysts were evaluated after this treatment.

The specific surface area of aged V3 was 72 m$^2$/g with a multimodal pore distribution (rp=18-35-57-70Å) while that of fresh one was 77 m$^2$/g with a monomodal pore distribution (rp=20 Å) (not shown). The X-ray results did not show any rutile form of titania on the aged V3 (Fig. 7a), but an increase in the crystallinity was observed.

The aged V3 catalyst exhibited the same activity as that of the fresh one in temperature range [250-500°C] (Fig. 8a). In low temperature range, $NO_x$ conversion over the aged catalyst was slightly lower than that of the fresh one. Higher amount of $N_2O$ was produced in the presence of aged V3 (not shown) but the difference remained slight. Thus, we can assume that a prolonged exposure of V3 to 500°C did not affect greatly the physicochemical characteristics of the catalyst. Aged V8 catalyst showed a decrease in the activity at low and high temperatures ranges compared to the fresh one (Fig. 8b). The same $NO_x$ conversion as that of fresh V8 was obtained in a tighter temperature range [250-350°C]. Higher amount of $N_2O$ was also formed compared with the fresh V8 (not shown). The specific surface area of aged V8 was 15 $m^2/g$ with a multimodal pore distribution (rp = 49-63-257Å).

As for V3, the X-ray analysis of aged V8 did not reveal traces of rutile but an increase in the crystallinity of the sample was also observed (Fig. 7b). Thus, a long exposure to 500°C affected more V8 than V3. The presence of high vanadia loading on V8 has probably accelerated the sintering process even there was no rutile form detected on the catalyst surface.

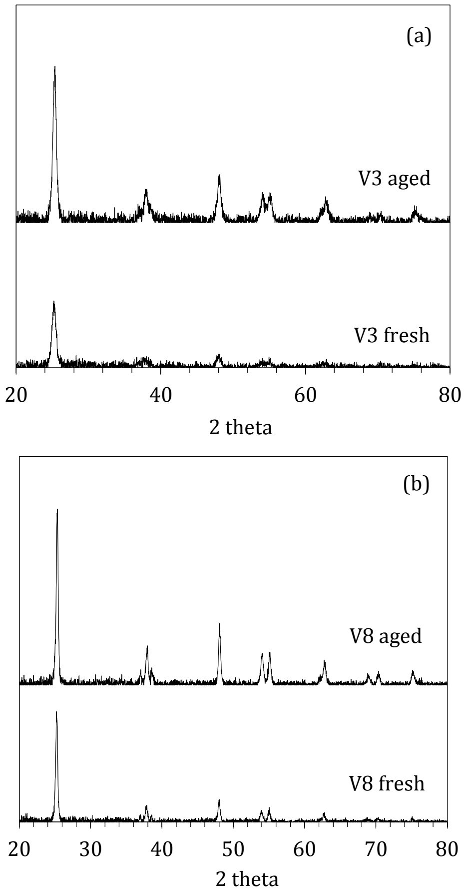

**Fig 7.** X-Ray analysis before and after aging the catalysts V3W9Ti (a) and V8W9Ti (b)at 500°C - 25 hours

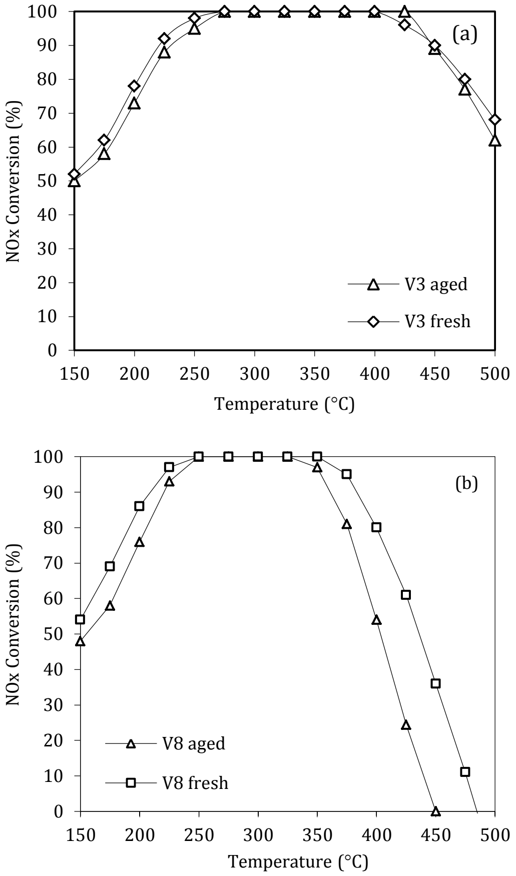

**Fig 8.** NOx conversion before and after aging the catalysts V3W9Ti (a) and V8W9Ti (b) at 500°C - 25 hours

## 4. DISCUSSION

The conditions used for the preparation of V3 and V8 catalysts allowed the occurrence of the SCR reaction in the absence of oxygen but with lower rates and efficiencies compared to the reactions in the presence of $O_2$. The SCR reaction of NO was rarely elucidated with the mobility of oxygen and even less in case of the absence of gaseous oxygen. There is a report published by Garcia el al. [12] where they attribute the increase in SCR activity in the absence of gaseous oxygen to the mobility of the lattice oxygen, which promoted the oxidation of the reduced vanadium. Thus, the fact that the SCR reactions did not stop in the absence of oxygen in our case suggested that the surface of catalysts contained enough oxygen surface available for incorporation into the reactions and that the bridging oxygen species that link the vanadia or tungsta species to the surface or the units of vanadyl species to each other provided a continuing source of unlabeled oxygen to the surface leading to the reaction:

$$2NH_3 + 2NO + O_l \rightarrow 2N_2 + 3H_2O \qquad (8)$$

The fact that the NO conversions remained low (<20%) in temperature range [150-325°C] indicated that there was another kind of oxygen (lattice oxygen) that was involved in the SCR mechanism. Over 325°C, the SCR reaction may proceed without the need of oxygen as reported by Lietti and Forzatti [13] to form $N_2$ and $N_2O$ as follows:

$$4NH_3 + 6NO \rightarrow 5\,N_2 + 6H_2O \qquad (9)$$

$$2NH_3 + 8NO \rightarrow 5N_2O + 3H_2O \qquad (10)$$

In fact, the authors reported that the SCR reaction in the absence of oxygen was observed above the temperature that roughly corresponded to the threshold of the reactions (9) and (10) at T≥300°C. Our results have shown differences between both catalysts in $N_2$ and $N_2O$ amounts formed during NO conversion in the absence of oxygen over 325°C. Furthermore, our TPD results showed strong acid strength of both catalysts favouring the adsorption of ammonia and its activation. This indicated that the surfaces participate to the reaction leading to different products as observed in our results.

Rosanska et al. [14] reported that $N_2O$ may reoxidize the reduced vanadyl groups and that it is a less effective oxidizing agent compared to gaseous oxygen. Thus, we can speculate that as the reaction (10) proceeded the produced $N_2O$ may reoxidize the reduced vanadium sites allowing the reaction (8) to occur in the same time of reactions (9) and (10). This can explain the increase in NO conversions observed over 325°C. In the presence of oxygen, the catalytic activity of V3 and V8 clearly increased with increasing $O_2$ concentration in temperature range [150-275°C]. Over 275°C the NOx conversion almost stabilized up to 425°C and decreased thereafter up to 500°C. The $O_2$ concentration of 6% registered higher $NO_x$ conversion with V3 and V8. The results indicated that the reaction mechanism included the oxidation of NO to $NO_2$ in gas phase. We have observed that the higher the $NO_2$ content in the feed gas, the faster was the SCR reaction. However, we do not know the mechanistic model of the primary reactions involved in the SCR reaction in our case. Despite its importance, there is no clear consensus in the literature on the details of the mechanism of $NO_x$ reduction with ammonia over vanadia based catalysts, nor other catalytic systems active in the SCR reaction. Many mechanistic studies have been proposed to explain the SCR model. All authors agree that oxygen is involved in the reoxidation of the catalyst, whereas different opinions are available concerning its interaction with the catalytic surface since the chemistry of the SCR reaction involving NO, $NH_3$ and $O_2$ at the interface of oxide materials is very complex [5].

Inomata et al. [15] and later agreed by most authors [16], concluded that on vanadia based catalysts, the ammonia reacts from a strongly adsorbed state while NO reacts from the gaseous or weakly adsorbed state. In our previous paper [6], we have studied the adsorption of NO over V3 catalyst. The exposed catalyst did not show DRIFT bands even after exposure to NO for 3 hours. The introduction of oxygen (6% vol) into the same flow gas caused the appearance of bands due to the adsorbed $NO_2$ [17-19]. Ammonia was also strongly adsorbed over V3 catalyst. Furthermore, TPD of NO conducted over V3 and V8 catalysts did not show any NO adsorption. These data allowed us to suggest that in our case, NO reacted in gaseous phase with adsorbed ammonia and that $NO_2$ when present was effective in the SCR mechanism.

Koebel et al. [20] proposed a mechanism for the SCR reaction where $NO_2$ was involved in the reoxidation of the reduced sites of vanadia. They suggested that the $V^{4+}$ species formed during the reduction of NO with ammonia are reoxidized faster by $NO_2$ than by $O_2$:

$$2V^{4+}\text{-}OH + NO_2 \rightarrow 2V^{5+}{=}O + NO + H_2O \qquad (11)$$

Resulting in an increased rate of the SCR reaction. NO formed from the reaction (11) reacted with $NH_3$ and $NO_2$ according to the following reaction:

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O \qquad (12)$$

On the other hand, Tagaki et al. [21] suggested that NO-$NH_3$ reaction in the presence of oxygen over vanadia based catalyst proceeded via the two adsorbates, $NO_2$(ad) and $NH_4^+$(ad), which reacted through a Langmuir-Hinshelwood mechanism. Many different ways and reaction schemes are possible, in theory, to perform the reduction of $NO_x$ by ammonia in the presence of oxygen. In our case, we can suppose that the SCR reaction involved the preliminary oxidation of NO to $NO_2$ in gas phase (according to our results), and since there is adsorption of $NO_2$ on the active surfaces as shown in our previous paper [6], we think that in low temperature range, several reactions may occur such as :

- Adsorption of ammonia and its reaction with gaseous NO,
- Adsorption of $NO_2$ and its reaction with adsorbed ammonia,
- Reoxidation of reduced sites with $NO_2$ (the reoxidizing role of oxygen was substituted by $NO_2$ in this case considered as more effective than $O_2$).

With increasing the temperature, the thermodynamic equilibrium: $NO + ½\ O_2 \leftrightarrow NO_2$ tends to left side. We can thus suppose that $NO_2/NO_x$ ratio decreased which implied that the SCR reaction evolved toward a limiting mechanism in which NO became a main reagent. The reoxidation of the active phase was then performed by gas phase oxygen instead of $NO_2$. Oxygen is known to be weaker oxidant than $NO_2$. Furthermore, there will be less adsorbed $NO_2$ reacting with the adsorbed ammonia. We do not know however, if this is the major reason for the decrease of the $NO_x$ conversion at higher temperature. A general relationship between the $NO_2$ content and the reaction rate was observed. Our point of view is that both mechanisms (Eley-Rideal and Langmuir-Hinshelwood) occurred under our reaction conditions, and that both mechanisms could be affected when the feed composition changed.

However, several details on the proposed reaction scheme are still to be better clarified. These aspects include the catalyst characterization, the nature of the active sites and of the active ammonia species.

It was shown by Myamoto et al. [22] that the V=O species of supported vanadia catalysts played an important role in the selective catalytic reduction of NO with ammonia. In the proposed mechanism, V=O is reduced to V-OH, which is then reoxidized by gaseous oxygen. The oxidation of V-OH may be more important with $NO_2$ in our case. Srnak et al. [23] proposed that both reaction mechanisms could be valid, depending on the reaction conditions. On the other hand, Tuenter et al. [24] have shown that above approximately 0.5% vol oxygen, the reaction rate was almost independent of the oxygen concentration. However, in the present study, we have observed that the higher the $O_2$ concentration, the faster the SCR reaction in temperature range [150-275°C]. It is interesting to note that despite of the relatively low surface area of V8 ($22m^2/g$) comparatively to that of V3 ($77m^2/g$), its activity in $NO_x$ conversion was higher in temperature range [150-275°C]. Thus, a simple relation does not apparently exist between the surface area and the SCR activity. This is certainly due to the complexity of the surface with the simultaneous presence of several species of vanadia in V-W-Ti mixed oxides [25]. One can speculate that the presence of high vanadia content may reduce the $TiO_2$ surface area so that the vanadium coverage is eventually increased. This will favour the formation of polyvanadate species which are associated with superior redox properties [12, 26]. This was observed in case of V8. In fact, over 450°C the $NO_x$ conversion was negative indicating that ammonia oxidation into nitrogen oxides occurred on a very active surface. Low vanadia loading leads to well dispersion of vanadia on Ti support improving the selectivity towards $N_2$. It was reported that specific activity on polymeric vanadate species was 10-30 times larger than on monomeric vanadyl, and 5 times larger than on crystalline $V_2O_5$ [26-28]. Moreover, these structural properties depended on several factors namely: the amount of vanadia phase on the support, the surface area and nature of the support, the method adopted for the preparation of the catalyst, the nature of chemicals and thermal treatments of the catalyst.

The role of vanadia with different forms in the reaction, if actually existing, is still far from being completely clarified. Our results have also shown that increasing oxygen concentration did not affect the temperature at which the maximum of $NO_x$ conversion was attained in the presence of V3 and V8. In fact, lower than 275°C with V3 and 250°C with V8, $NO_x$ conversion was less than 100% even with high $O_2$ concentration (15%). This indicated that the effect of temperature on the $NO_x$ conversion was more important than $O_2$ content, since we could use 2% vol $O_2$ with V3 for example at 275°C to reach the same $NO_x$ conversion as with 15% $O_2$ at the same temperature. This effectively determines the maximum catalyst operating temperature and $O_2$ concentration.

Aging both catalysts did not have a great effect on their physico-chemical characteristics. This may be due to the sol-gel method used for the preparation of both catalysts which is known to improve the V-Ti interactions resulting in a general good behaviour of the catalysts in the NOx reduction.

## 5. CONCLUSION

The SCR reaction was influenced by vanadia content and gas composition. In our case, SCR reaction occurred in the absence of oxygen due to the superior redox properties of the catalysts that allow the reoxidation of the reduced sites of vanadium.

In the presence of oxygen, V8 was more active than V3 at temperatures lower than 250°C, whereas V3 had lower ammonia oxidation during SCR reaction and better $N_2$ selectivity.

The results have shown that NO was partially oxidized in feed gas by $O_2$ into $NO_2$. Increasing $O_2$ concentration led to increase the $NO_2$ content which enhanced the low temperature $NO_x$ reduction on V3 and V8 catalysts. However, once the maximum of $NO_x$ conversion was attained the effect of $O_2$ concentration was less effective. On the other hand, the sol gel method used for the preparation of both samples led to good stabilities for the aged catalysts.

## ACKNOWLEDGEMENT

Souad DJERAD thanks the German Academic Exchange Service (DAAD) for the scholarship received during her stay in Germany.

## REFERENCES

[1]. J. Jiang and D. Li, "Theoretical analysis and experimental confirmation of exhaust temperature control for diesel vehicle $NO_x$ emissions reduction," *Applied Energy*, Vol. 174, pp. 232-244, 2016.

[2]. I. Nova and E. Tronconi (Eds.), "*Urea-SCR Technology for deNO$_x$ after treatment of diesel exhausts*," Springer, 2014.

[3]. A. Marberger, M. Elsener, D. Ferri and O. Kröcher, "$VO_x$ surface coverage optimization of $V_2O_5/WO_3$-$TiO_2$ SCR catalysts by variation of the V loading and by aging," *Catalysts,* Vol. 5, pp. 1704-1720, 2015.

[4]. C. Wang, S. Yang, H. Chang, Y. Peng, J. Li, "Dispersion of tungsten oxide on SCR performance of $V_2O_5WO_3/TiO_2$: Acidity, surface species and catalytic activity," *Chemical Engineering Journal,* Vol. 225, pp. 520-527, 2013.

[5]. L. Arnarson, H. Falsig, S. B. Rasmussen, J.V. Lauritsen and P.G. Moses, "The reaction mechanism for the SCR process on monomer $V^{5+}$ sites and the effect of modified Brønsted acidity," *Physical Chemistry Chemical Physics,* Vol. 18, pp. 17071-17080, 2016.

[6]. S. Djerad, M. Crocoll, S. Kureti, L. Tifouti and W. Weisweiler, "Effect of oxygen concentration on the NOx reduction with ammonia over $V_2O_5$–$WO_3/TiO_2$ catalyst," *Catalysis Today,* Vol. 113, pp. 208-214, 2006.

[7]. A. Marberger, D. Ferri, M. Elsener, A. Sagar, C. Artner, K. Schermanz and O. Kröcher, "Relationship between structures and activities of supported metal vanadates for the selective

catalytic reduction of NO by $NH_3$," *Applied Catalysis B: Environmental,* Vol. 218, pp. 731-742, 2017.

[8]. M.A. Banares, L. J. Alemany and M. Carmen Jimenez, "The role of vanadium oxide on the titania transformation under thermal treatments and surface vanadium states," *Journal of Solid State Chemistry,* Vol. 124, pp. 69-76, 1996.

[9]. L. Arnarson, H. Falsig, S.B. Rasmussen, J.V. Lauritsen, P.G. Moses, "A complete reaction mechanism for standard and fast selective catalytic reduction of nitrogen oxides on low coverage $VO_x/TiO_2(001)$ catalysts," *Journal of Catalysis,* Vol. 346, pp. 188–197, 2017.

[10]. H. Schneider, S. Tsuchudin, M. Schneider, A. Wokaun, A. Baiker, "In situ diffuse reflectance FTIR study of the selective catalytic reduction of NO by $NH_3$ over vanadia-titania aerogels," *Journal of Catalysis,* Vol. 147, pp. 5-14, 1994.

[11]. M.A. Centeno, I. Carrizosa, J. A. Odriozola, "In situ DRIFTS study of the SCR reaction of NO with $NH_3$ in the presence of $O_2$ over lanthanide doped $V_2O_5/Al_2O_3$ catalysts," *Applied Catalysis B*, Vol. 19, pp. 67-73, 1998.

[12]. E. Garcia-Bordejé, J. L. Pinilla, M. J. Làzaro, R. Moliner, J. L. G. Fierro, "Role of sulphates on the mechanism of $NH_3$-SCR of NO at low temperatures over presulphated vanadium supported on carbon-coated monoliths," *Journal of Catalysis*, Vol. 233, pp. 166-175, 2005.

[13]. L. Lietti, P. Forzatti, "Temperature programmed desorption/reaction of ammonia over $V_2O_5/TiO_2$ De-NOxing catalysts," *Journal of Catalysis,* Vol. 147, pp. 241-249, 1994.

[14]. X. Rosanska, E. V. Kondratenko, J. Sauer, "Oxidative dehydrogenation of propane: Differences between $N_2O$ and $O_2$ in the reoxidation of reduced vanadia sites and consequences for selectivity," *Journal of Catalysis,* Vol. 256, pp. 84-94, 2008.

[15]. M. Inomata, A. Miyamoto, Y. Murakami, "Mechanism of the reaction of NO and $NH_3$ on vanadium oxide catalyst in the presence of oxygen under the dilute gas condition," *Journal of Catalysis*, Vol. 62, pp. 140-148, 1980.

[16]. G. Busca, L. Lietti, G. Ramis and F. Berti, "Chemical and mechanistic aspects of the selective catalytic reduction of $NO_x$ by ammonia over oxide catalysts: A review," *Applied Catalysis,* Vol. 18, pp. 1-36, 1998.

[17]. G. Ramis, G. Busca, V. Lorenzelli, 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," *Applied Catalysis,* Vol. 64, pp. 259-278, 1990.

[18]. T. J. Dines, C. H. Rochester, A. M. Ward, "Infrared study of the reaction between nitrogen oxides and ammonia on titania-supported vanadia catalysts," *Journal of the Chemical Society, Faraday Transactions,* Vol. 87, pp. 1473-1477, 1991.

[19]. M. Hesse, H. Meier, B. Zeeh, "*Spektroskopische methoden in den organischen chemie*," Georg Thieme Verlag, Stuttgart, New York, 1995.

[20]. M. Koebel, G. Madia, F. Raimondi, A. Wokaun, "Enhanced Reoxidation of Vanadia by $NO_2$ in the Fast SCR Reaction," *Journal of Catalysis*, Vol. 209, pp. 159-165, 2002.

[21]. M. Tagaki, T. Kowai, M. Soma, T. Onishi, K. Tamaru, "The mechanism of the reaction between $NO_x$ and $NH_3$ on $V_2O_5$ in the presence of oxygen," *Journal of Catalysis*, Vol. 50, pp. 441-446, 1977.

[22]. [22] A. Miyamoto, K. Kobayashi, M. Inomata, Y. Murakami, "Nitrogen-15 tracer investigation of the mechanism of the reaction of nitric oxide with ammonia on vanadium oxide catalysts," *The Journal of Physical Chemistry*, Vol. 86, pp. 2945-2950, 1982.

[23]. T. Z. Srnak, J. A. Dumesic, B. S. Clausen, E. Tornquist, N. Y. Topsoe, "Temperature-programmed desorption/reaction and in situ spectroscopic studies of vanadia/titania for catalytic reduction of nitric oxide," *Journal of Catalysis,* Vol. 135, pp. 246-262, 1992.

[24]. G. Tuenter, W. F. Van Leewen, L. J. M. Snepvangers, "Kinetics and mechanism of the $NO_x$ reduction with $NH_3$ on $V_2O_5$- $WO_3$-$TiO_2$ Catalyst," *Industrial & Engineering Chemistry Product Reseacrh and Development,* Vol. 25, pp. 633-636, 1986.

[25]. L. Arnarson, S. B. Rasmussen, H. Falsig, J. V Lauritsen and P. G. Moses, "Coexistence of square pyramidal structures of oxo vanadium (+5) and (+4) species over low-coverage $VOX/TiO_2$ (101) and (001) anatase catalysts," *Journal of Physical Chemistry C.,* Vol. 119, pp. 23445–23452, 2015.

[26]. G. T. Went, L. J. Rosin, R. R, A. T. Bell, "The effects of structure on the catalytic activity and selectivity of $V_2O_5/TiO_2$ for the reduction of NO by NH3," *Journal of Catalysis,* 134, 492-505, 1992.

[27]. A. Baiker, P. Dollenmeier, M. Glinski, A. Reller, "Selective catalytic reduction of nitric oxide with ammonia: I. monolayer and multilayers of vanadia supported on titania," *Applied Catalysis,* Vol. 35, pp. 351-364, 1987.

[28]. W. J. Stark, K. Wegner, S. E. Pratsinis, A. Baiker, "Flame aerosol synthesis of vanadia–titania nanoparticles: structural and catalytic properties in the selective catalytic reduction of NO by $NH_3$," *Journal of Catalysis,* Vol. 197, pp. 182-191, 2001.