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Effect of oxygen concentration on the NO_x reduction with ammonia over V_2O_5–WO_3/TiO_2 catalyst

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Abstract

The catalytic reduction of NO_x in the typical operation temperatures and oxygen concentrations of diesel engines has been studied in the presence of V3W9Ti in a tubular flow reactor. The results have shown that the selective catalytic reduction is strongly affected by the oxygen concentration in low temperature range (150–275 °C). At higher temperatures, the reaction becomes independent of the O_2 concentration. The rate of the selective catalytic reduction of NO with ammonia may be considerably enhanced by converting part of the NO into NO_2. DRIFT measurements have shown that NH_3 and NO_2 are adsorbed on the catalyst surface on the contrary of NO. The experiments have shown that the decrease in N_2 selectivity of the SCR reaction is mainly due to the SCO of ammonia and to the formation of nitrous oxide.

Keywords: SCR; Oxygen concentration; Ammonia oxidation; N_2O; Side reactions; DRIFT

1. Introduction

The new generation of diesel engines (common-rail with direct injection) allows one to achieve very high energetic efficiency and quite limited pollutant emissions: both carbon monoxide and unburned hydrocarbons outlet concentrations are in fact lower than those produced in spark ignition engines. However, diesel engines produce specific pollutants that are hazardous for human health: primarily particulate, dangerous due to its potential mutagenic and carcinogenic activity, and nitrogen oxides, which are well-known promoters of acid rain phenomenon and of the so-called photochemical smog. For these vehicles, three-way catalysts are useless due to net-oxidizing conditions of their exhaust streams. NO_x is a by-product of high temperature and high pressure combustion of fuel in air. Its primary component in internal combustion engine exhaust is NO.

The exhaust temperature of a diesel engine is lower, and there are more little HCs remaining in the exhaust compared with a gasoline engine.

On the other hand, diesel engine exhaust contains heavy HCs which are harder to use as a NO_x reducing agent, along with SO_2 that causes catalytic deactivation. These conditions have thwarted practical application of HC–SCR technology to diesel engines.

The selective catalytic reduction (SCR) of nitrogen oxides with N-containing reducing agents is presently considered as the most promising technique for the removal of NO_x from lean exhaust gases of automotive engines. Urea is the preferred reducing agent for toxicological and safety reasons. It can be considered as a solid storage compound for ammonia [1].

Vanadium oxide catalysts are currently used because of their resistance to poisoning by SO_2 and their high activity at low temperatures. Nevertheless, there is still an open area for investigation concerning the use of these catalysts in high oxygen concentration because of the side reactions where N_2O may be formed. Selectivity to N_2O is particularly undesirable because N_2O is approximately 200 times worse than CO_2 as a green house gas and in the upper atmosphere it interferes with ozone.

Specific aims of this study were: for the prepared V_2O_5–WO_3/TiO_2 catalyst, to evaluate the relative contributions of the selective reduction of NO_x and the ammonia oxidation reaction to product formation under different oxygen concentrations (2–6–10–15 vol.%).

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2. Experimental

2.1. Catalyst preparation

The V_2O_5–WO_3/TiO_2 has been prepared by the sol–gel method using titania(IV)-bis ethylacetoacetato-isopropylat ($C_{18}H_{32}O_8Ti$, Fluka Chemicals Inc., ≥95%) as precursor for TiO_2, vanadyl(IV) acetylacetonat ($VC_{10}H_{14}O_5$, Fluka Chemicals Inc., ≥97%) as precursor for V_2O_5 and NH_4 metatungstate hydrate ($H_{26}N_6O_{41}W_{12}$ aq) as precursor for WO_3. Acetyl acetone (0.7 g), ethylene glycol (5 g) and water (0.72 g) were added to the ternary mixture. After stirring the mixture for ca. 15 min at ambient temperature, the excess solvent was removed by a first drying on an evaporator at 70 °C followed by an overnight drying at 120 °C. The catalysts were subsequently calcined in air at 400–800 °C for 2 h.

The ternary catalyst contains 3 wt.% V_2O_5 and 9 wt.% WO_3. WO_3 is employed in larger amount (9 wt.%), it acts both as chemical and structural promoter by enlarging the temperature window of the SCR reaction and by improving the mechanical, structural and morphological properties of the catalyst [2].

BET measurements were performed with a quantochrome autosorb 1C using nitrogen.

X-ray diffraction patterns were obtained with a siemens D-500 powder X-ray diffractometer using Cu Kα radiation (λ = 1.5406 Å) in step mode between 20° and 80°, using a step size of 0.02 step/s.

Mesopores distribution measurements have been obtained by mercury penetration method using a porosimeter Autopore III.

DRIFT measurements were performed with an ATi Mattson Galaxy 5020 FTIR spectrometer.

2.2. Activity measurements

Catalytic activity measurements have been carried out in a quartz tubular fixed bed reactor (i.d. 30 mm). The catalyst V3W9Ti was a coated type (200 mg) supported on a cordierite monolith having a cell density of 64 cells/cm^2 and a volume of 9.4 cm^3. The composition of the feed was 500 ppm NO, 500 ppm NH_3, with varying the oxygen concentration (2, 6, 10 and 15 vol.% O_2). The N_2 being a carrier gas (total flow rate = 2000 ml/min). K-type thermocouples provided the exhaust temperature before the catalyst. The temperature of all gas lines was kept at 150 °C.

Activity data have been collected at different temperatures in the range 150–500 °C, each temperature was maintained until steady-state conditions were reached. The NO_x content have been determined with a CLD 700 EL ht Chemiluminescence detector. 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 V3W9Ti catalyst are shown in terms of NO_x conversion $X_{NO_x} = 1 - ([NO_x]_{out}/[NO_x]_{in})$ and N_2 selectivity $S_{N_2} = [N_2]/([N_2] + [N_2O])$, respectively.

Table 1
Morphological properties

Catalyst	T_{calc} (°C)	S_g (m^2/g)	Phase	D_c (Å)	V_p (cm^3/g)	$r_{p_{exp}}$ (Å)
V3W9Ti	400	115	A	265	0.036	16.6
	500	77	A	319	0.289	20
	600	22	A	579	0.248	23.2
	800	–	R	783	–	–

The moles of N_2 can be determined from the following atomic nitrogen balance:

$$N_{2out} = (1/2)([NO_x]_{in} - [NO_x]_{out}) + (1/2) \times ([NH_3]_{in} - [NH_3]_{out}) - N_2O_{out}.$$

3. Results and discussion

3.1. Characteristics of the prepared catalyst

Table 1 shows the surface area (S_a), the phase composition, the mean crystallite dimensions (D_c) (calculated from XRD measurements), the pore volume (V_p) and the mean pore radius (r_p) obtained from the experimental pore size distribution.

Up to the calcination temperature of 600 °C, the samples of V3W9Ti are monophasic and only anatase polymorph of TiO_2 ($2\theta = 25.3$–38–48°) is detected. The surface area decreases as the calcination temperature increases. The mean pore radius increases and the pore volume decreases. The anatase to rutile phase transformation ($2\theta = 27.5$–36–54.5°) is detected starting from 700 °C and is complete at 800 °C (Fig. 1).

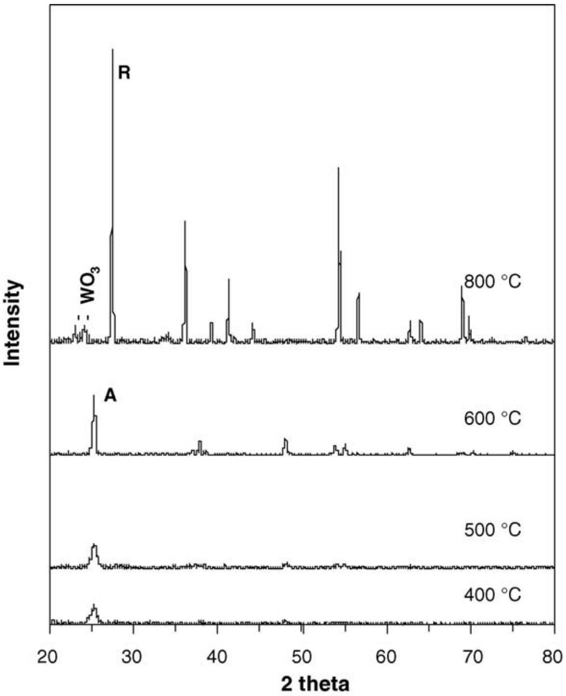

Fig. 1. X-ray powder diffraction patterns of V3W9Ti calcined from 400 to 800 °C.

No V_2O_5 crystallites have been detected even at high temperatures, probably because vanadia was highly dispersed as isolated VO_x species [3]. However WO_3 crystallites have been detected at 800 °C.

The presence of WO_3 without V_2O_5 crystallites on Ti support at high calcination temperatures suggests that titania interacts more strongly with vanadia than with tungsten [4].

The catalyst V3W9Ti calcined at 500 °C has been used for further investigations.

3.2. Catalytic activity measurements

The study of the effect of O_2 on the NO_x conversion was investigated.

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

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O. \quad \text{(R1)}$$

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

$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O. \quad \text{(R2)}$$

Fig. 2a shows the effect of the concentration of O_2 on the NO_x conversion over V3W9Ti calcined at 500 °C in temperature range (150–500 °C). The results show that the effect of oxygen concentration is more pronounced at low temperatures (150–275 °C) where an increase in the reaction rate is most essential. Over 275 °C, two different features in NO_x conversion are observed. In fact, reactions with 2 and 6 vol.% O_2 exhibit a total NO_x conversion in temperature range (275–400 °C). In case of 10 and 15 vol.% O_2, the maximum of NO_x conversion obtained is 99% at 250 °C. Over 250 °C, NO_x conversions gradually decrease and attained 68% at 500 °C due to the competitive reactions. At 500 °C, NO_x conversions in all cases are almost the same.

It is shown in Fig. 2c that the amount of N_2O formed depends on the gaseous oxygen concentration; as the oxygen concentration increases, the nitrous oxide concentration decreases. In all cases, N_2O is formed starting from 325 °C. The N_2O production was generally weak up to 350 °C resulting in a high N_2 selectivities (Fig. 2d). At temperatures above 350 °C, the N_2O amounts significantly increase and reach 210 ppm with 2 vol.% O_2 and 160 ppm with 15 vol.% O_2 at 500 °C, which leads to a decline in the N_2 selectivities. Hence, the NO conversion and N_2 selectivity are greatly amplified on

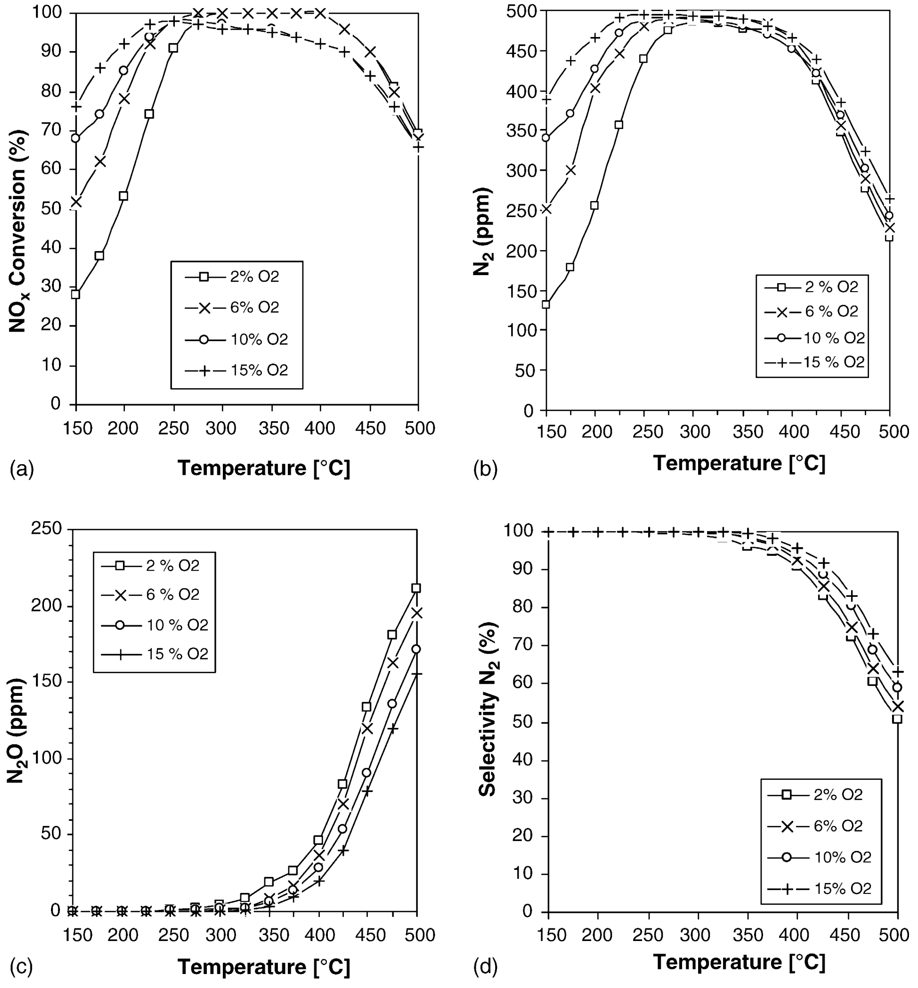

Fig. 2. NO_x conversion (a), N_2 formation (b), N_2O formation (c) and N_2 selectivity (d) during SCR reaction, over V3W9Ti under different O_2 concentrations. Experimental conditions: catalyst weight; 200 mg, flow rate; 2000 ml/min, feed: N_2 + 500 ppm NH_3 + 500 ppm NO + (2–6–10–15 vol.% O_2).

increasing O_2 concentration at temperatures below 350 °C. Over 350 °C, unstable behaviour in NO_x conversion was observed with high oxygen concentrations (10 and 15 vol.% O_2), on the contrary of cases 2 and 6 vol.% O_2 where the total conversions of NO_x were maintained in a large temperature range.

N_2O may be formed from reaction (R2) or by ammonia oxidation (R4). The question is which reaction is prevailing in this case.

In order to obtain a better understanding of the relative importance of the side reactions of ammonia oxidation, catalytic tests were also carried out in which the feed contained only $NH_3 + O_2$ with the same O_2 concentration and temperature range as those of SCR reaction experiments.

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

$$2NH_3 + (3/2)O_2 \rightarrow N_2 + 3H_2O \tag{R3}$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \tag{R4}$$

$$2NH_3 + (5/2)O_2 \rightarrow 2NO + 3H_2O \tag{R5}$$

$$4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O \tag{R6}$$

N_2, N_2O and NO were the three nitrogen containing products of ammonia oxidation. NO_2 formation was not observed under the experimental conditions used in these runs. The formation of NO was detectable only in temperature range (450–500 °C) (Fig. 3c) and the amount was not significant comparing to that of N_2O (Fig. 3b).

The increase in the O_2 concentration has no effect on the amount of the products formed. However, the formation of NO seems to be slightly dependent on the O_2 concentration.

During ammonia oxidation, N_2O is formed starting from 325 °C and increase gradually until 130 ppm at 500 °C regardless of the O_2 content.

Comparing the N_2O amounts formed during SCR reaction and ammonia oxidation have shown 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, 58% of the total N_2O amount formed during the SCR reaction is due to the ammonia oxidation. This value increases with increasing the oxygen concentration until reaching 100% with 10 and 15% O_2 at the same temperature.

Thus, we can conclude that ammonia oxidation into N_2O is the major reason for the decrease in the selectivity to N_2 during SCR reaction in temperature range (450–500 °C).

As shown in Fig. 2a, the NO_x conversion over V3W9Ti catalyst is markedly accelerated by O_2 in low temperature range. According to our experiments, the oxidation of NO by O_2 upstream the catalyst in the gas phase takes place readily under our experimental conditions (Table 2).

It is clear from our data that an improved SCR process relies on the fact that the SCR reaction is much faster with increasing the NO_2 fraction in NO_x mixture. In fact, according to the thermodynamic, at low temperatures the equilibrium:

$$NO + (1/2)O_2 \leftrightarrow NO_2 \tag{R7}$$

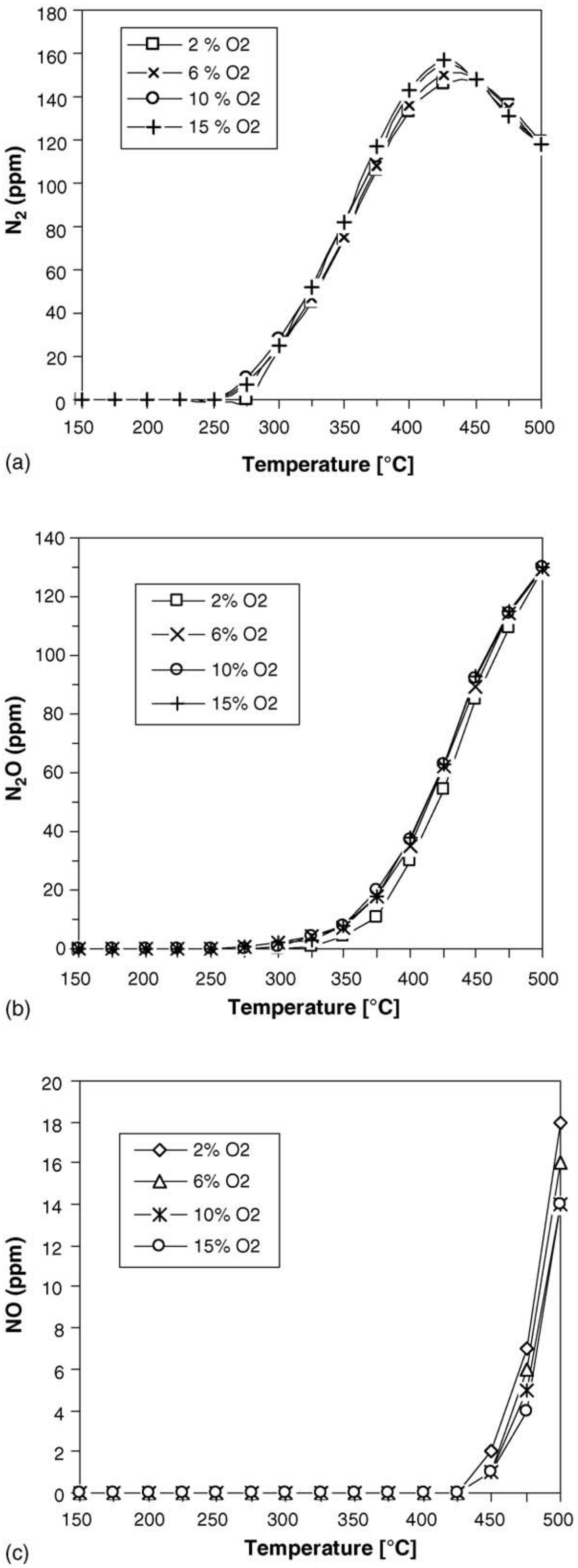

Fig. 3. N_2 (a), N_2O (b) and NO (c) formations during NH_3 oxidation over V3W9Ti catalyst. Experimental conditions: catalyst weight; 200 mg, flow rate; 2000 ml/min, feed: N_2 + 500 NH_3 + (2–6–10–15 vol.%) O_2.

Table 2
Composition of NO_x vs. O_2 concentration

Oxygen concentration (vol.%)	Composition of NO_x (ppm)	Composition of NO_x (%)
2	$460NO + 40NO_2$	$92\%\ NO + 8\%\ NO_2$
6	$400NO + 100NO_2$	$80\%\ NO + 20\%\ NO_2$
10	$360NO + 140NO_2$	$72\%\ NO + 28\%\ NO_2$
15	$310NO + 190NO_2$	$62\%\ NO + 38\%\ NO_2$

tends to form an increased fraction of NO_2 promoted by increasing O_2 concentration [5]. With 15% O_2, the NO_x mixture is not far from the equimolar composition of $NO + NO_2$ which is known to be the most effective composition in $DeNO_x$ [5].

Thus, NO_2 fraction strongly influences the reaction rate on V3W9Ti catalyst.

3.3. DRIFT measurements

Before the spectra are collected, the catalyst is charged in the sample holder of the cell, heated for 60 min at 400 °C in nitrogen (500 ml/min) and cooled down to 150 °C in the N_2 flow. The catalyst is than exposed to 500 ppm NH_3 in N_2 (500 ml/min). After 15 min, the cell is purged with N_2 and the spectra are recorded. Furthermore, a new charge of catalyst treated as before is used for the adsorption of NO in N_2 and NO + 6% O_2 in N_2.

DRIFT spectrum of the adsorbed ammonia shows different bands at 1405, 3040 and 2810 cm^{-1} referred to ammonium species (Fig. 4a) that might be originated from the reaction of NH_3 with Bronsted acid OH groups [6,7]. The bands observed at 3150 and 1610 cm^{-1} are due to ammonia molecularly adsorbed on Lewis acid sites [6].

A fresh V3W9Ti amount has been used to study NO adsorption. The exposed catalyst does not show any DRIFT bands even after exposition to NO for 3 h. The introduction of oxygen into the same flow gas (6% O_2) have shown the appearance of a bands due to distinct adsorbed species, probably assigned to molecularly adsorbed NO_2 and/or to NO_3^-. In fact, Fig. 4b shows a large and intense doublet with bands observed at 1380, 1415 cm^{-1} and another weaker band at 1768 cm^{-1} due to nitrate ion [8,9]. A weak band detected as a shoulder at 1680 cm^{-1} may be due to nitrite species [10]. A weak band observed in region 2090 cm^{-1} might correspond to the adsorbed NO^+ [11–13].

These results shows the high adsorption capacity for ammonia and NO_2 on V3W9Ti surface.

Thus, we can conclude that during the SCR reaction, the NO_2 formed from NO oxidation may be adsorbed on the surface of the catalyst. As a result, the rate of NO_x conversion is enhanced.

However, we do not know if this acceleration is due to the reaction between NO_2(ad) and NH_3(ad), as it was proposed by Tagaki et al. [14]. In fact, Tagaki et al. proposed that NO–NH_3 reaction in the presence of oxygen over vanadia based catalyst proceeds via the two adsorbates, NO_2(ad) and NH_4^+(ad), which react on the catalyst surface through a Langmuir–Hinshelwood mechanism to form nitrogen and water. Inomata et al. [15] argued that the oxidation of NO to NO_2 before adsorption can easily take place at the experimental condition employed by Tagaki et al. (i.e. room temperature, high NO and oxygen partial pressures) but it can hardly occur under the dilute gas conditions that are characteristics of the SCR process. However, in our case, we have observed that NO is easily oxidized into NO_2 under our experimental conditions which are also a dilute gas conditions.

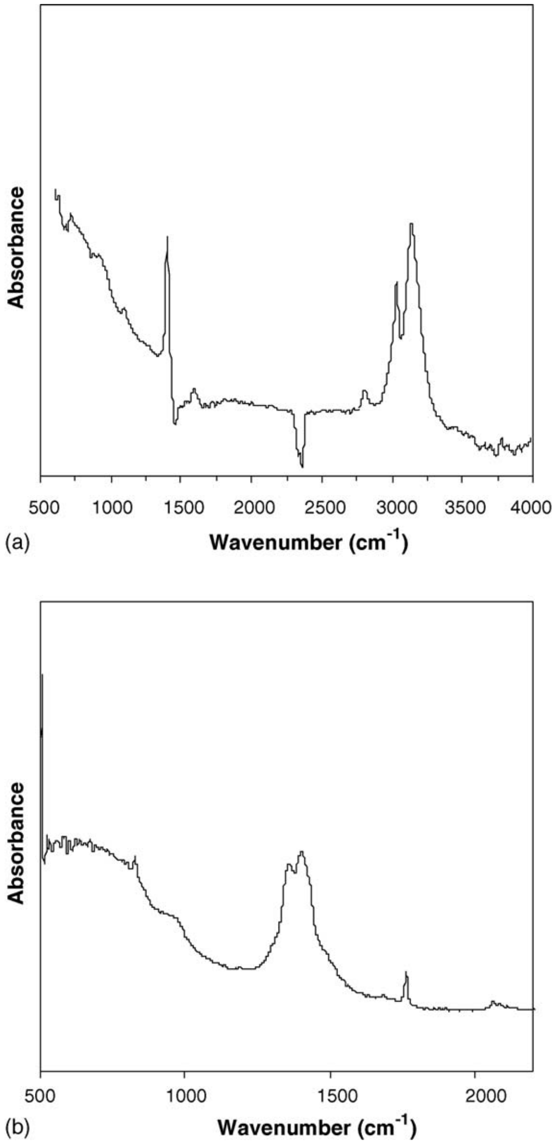

Fig. 4. DRIFT spectra of NH_3 (a) and NO + 6% O_2 (b) on V3W9Ti after heating at 400 °C in N_2 and cooling at 150 °C.

In order to provide a better understanding of the effect of NO_2, we have investigated the SCR reaction under high NO_2 content (400 ppm NO_2 + 100 ppm NO) i.e (80% NO_2 + 20% NO). The results have shown that in this case, the reaction rate is low and the maximum of NO_x conversion obtained was 88% attained at 300 °C (Fig. 5). Thus, NO_2 is not directly involved in SCR reaction.

Koebel et al. [5] proposed a mechanism to explain the acceleration of reaction rate in the presence of oxygen. They

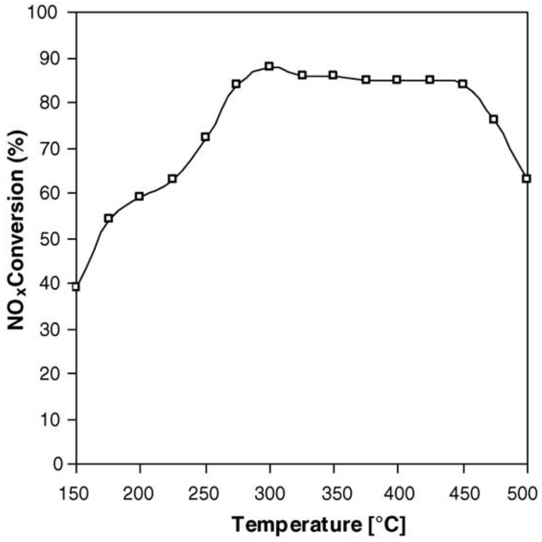

Fig. 5. NO_x conversion vs. temperature over V3W9Ti. Experimental conditions: catalyst weight; 200 mg, flow rate; 2000 ml/min, feed: N_2 + 400 ppm NO_2 + 100 ppm NO + 500 ppm NH_3.

suggest that the V^{4+} species formed during the reduction of NO with ammonia are reoxidized faster by NO_2 than by oxygen:

$$2V^{4+}{-}OH + NO_2 \rightarrow 2V^{5+}{=}O + NO + H_2O$$

resulting in an increased rate of the SCR reaction. Thus, NO_2 not only reacts with ammonia but also reoxidizes the V^{4+} sites, thereby forming NO. This NO reacts with NH_3 and NO_2 according to following reaction:

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O.$$

This explanation seems to be more in agreement with our results.

A number of suggestions have been made to account for the decrease in NO conversion over vanadia-based catalysts at temperatures above 400 °C. The reaction of ammonia with oxygen to produce N_2 was invoked by Miyamoto et al. [16] as the major reason for decreases in the NO conversion.

However, the results of the present study show that the amount of N_2O arising from ammonia oxidation is also important.

There is still a lack of the detailed knowledge about the reaction mechanisms such as the interaction between oxygen and the active surface. It should be kept in mind that the products formed during NO_x reduction and ammonia oxidation depend on several factors, such as the amount of the vanadia phase on the support and the surface area of the support, the method adopted for the preparation of the catalyst and thermal treatment.

The mechanism of N_2O formation has not been fully explained. Indeed, in spite of their obvious importance and the large number of studies conducted over these catalysts, questions still remain about the mechanisms that lead to selective reduction of NO or formation of N_2O. According to Odenbrand et al. [17], the three parameters that influence N_2O formation on vanadium based catalysts are temperature, active phase content and the presence of H_2O in the stream. An exponential relationship between temperature and N_2O formation on vanadium based catalysts, reaching a selectivity for N_2O around 40% at 450 °C, was shown by Turco et al. [18]. Delahay et al. [19] observed a linear relationship between N_2O formation and O_2 concentration in the feed. According to Koebel et al. [20], the adsorption of NO_2 may lead to nitrous and nitric acid formation which may react with ammonia forming ammonium nitrite and nitrate:

$$2NO_2 \leftrightarrow N_2O_4 \tag{1}$$

$$N_2O_4 + H_2O \leftrightarrow HNO_3 + HNO_2 \tag{2}$$

$$HNO_3 + NH_3 \leftrightarrow NH_4NO_3 \tag{3}$$

$$HNO_2 + NH_3 \leftrightarrow NH_4NO_2 \tag{4}$$

Ammonium nitrite is known to be unstable compound and may lead to nitrogen and water formation:

$$NH_4NO_2 \rightarrow NH_2{-}NO + H_2O \tag{5}$$

$$NH_2{-}NO \rightarrow N_2 + H_2O \tag{6}$$

The sum of the reactions (1)–(6) will yield Eq. (7):

$$2NH_3 + 2NO_2 \rightarrow NH_4NO_3 + N_2 + H_2O \tag{7}$$

The ammonium nitrate formed may deposit as a solid on the catalyst surface.

In the present work, we have exposed the catalyst to NH_3 and the cell was flushed with N_2. After that, gas flow was switched to (NO + 6 vol.% O_2) in N_2 (500 ml/min) for 10 min at 150 °C. Fig. 6 shows that all bands due to ammonia adsorption disappeared and a new band appear at 1380 cm^{-1} corresponding to nitrate ion. Which confirms the results obtained by Koebel et al.

NH_4NO_3 may be decomposed into N_2O and water [21]:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \tag{8}$$

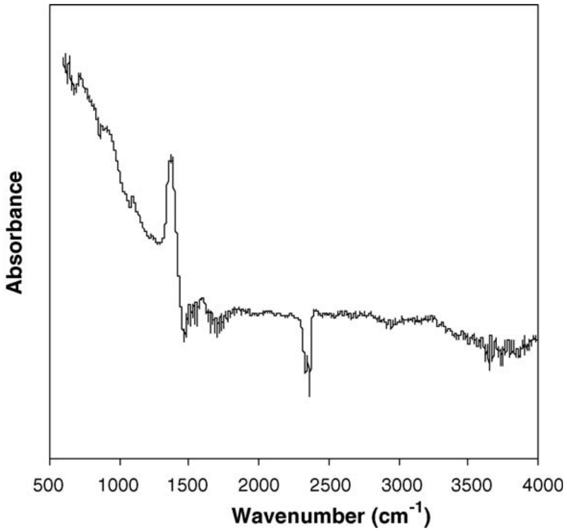

Fig. 6. DRIFT spectrum after SCR reaction; adsorbed ammonia followed by NO + 6% O_2 in gas stream at 150 °C.

However, this latest reaction has not been evidenced in the present study.

It is not always possible to explain the results obtained from the experiments. We have to take into consideration the complex network of reactions occurring during the SCR reaction in the presence of active phase.

Our experiments have also shown that at temperatures above 350 °C, SCR reaction seems to be independent of the oxygen concentration. This feature of the behaviour of V3W9Ti catalyst, effectively determines the maximum catalyst operating temperature and oxygen concentration.

4. Conclusion

The rate of NO_x conversion of the SCR reaction is influenced by the presence of oxygen at temperatures below 350 °C. In fact, increasing O_2 concentration leads to increase the rate of SCR reaction. For temperatures below 350 °C, complete N_2 selectivities have been measured for all cases. At higher temperatures, NO conversion decreases and ammonia oxidation becomes increasingly important. The production of N_2O during SCR reaction decreased with increasing O_2 content, while that formed during ammonia oxidation did not vary. The results have shown that oxygen is involved in the rate determining step of the SCR reaction. Thus, oxygen is essential for the reoxidation of the vanadium sites of the catalyst. However, the effect of oxygen seems to be effective through the NO_2 formation. Indeed, increasing NO_2 fraction leads to improve the NO_x reduction. However, questions still remain about the mechanism of the SCR reaction in the presence of NO_2 and also the nature of active sites that lead to N_2 and N_2O formation.

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