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Temperature Programmed Desorption/Reaction of Ammonia over V_2O_5/TiO_2 De-NO_xing Catalysts

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Temperature programmed desorption (TPD) of ammonia, temperature programmed surface reaction (TPSR) of adsorbed ammonia with gas phase NO, temperature programmed reaction (TPR), and steady state reaction (SSR) experiments of NH_3 + NO under diluted gas conditions in the presence and in the absence of oxygen are performed on a series of V_2O_5/TiO_2 (anatase) catalysts with V_2O_5 loadings ≤3.56% w/w that are comparable to those of commercial De-NO_xing catalysts. Both isolated vanadyls and polymeric metavanadate species are observed on the surface of submonolayer vanadia/titania samples, the relative concentration of the latter species increasing with the vanadia content. TPR, TPSR, and SSR experiments performed in the presence and in the absence of oxygen provide new and more direct evidence than previously reported in the literature for a greater reactivity of polymeric metavanadate species as compared to isolated vanadyls and for a faster reduction by NH_3 and a faster reoxidation by gaseous oxygen of the polymeric metavanadate groups. This has been related to the presence of more labile oxygen atoms, that is beneficial for the activity but is also detrimental for the selectivity of the SCR reaction. The turnover frequency measured at 500 K under steady state conditions over high-vanadia loading catalysts is six times larger than that of low-vanadia loading catalysts, due to the higher amounts of polyvanadate species. The temperature window of the SCR reaction, corresponding to high NO conversion and complete selectivity to nitrogen, is shifted towards lower temperatures on increasing the vanadia loading and extends towards higher temperatures under steady state conditions and in the presence of oxygen due to a proper oxidation level of the catalyst.

INTRODUCTION

V_2O_5/TiO_2 catalysts are known as highly active systems for the selective catalytic reduction (SCR) of nitrogen oxides by NH_3 (1, 2). It has been reported that the activity of V_2O_5/TiO_2 catalysts depends on the vanadia loading (2–8) and that vanadia dispersed on TiO_2 anatase is present in the form of both monomeric vanadyl and polymeric vanadate species in submonolayer samples (9–14). Monomeric vanadyls predominate at low V_2O_5 loadings; crystallites of V_2O_5 are also observed when the vanadia content is raised above the dispersing capacity of the support (5, 6, 12–15). Based on the analysis of the turnover frequency for NO conversion data collected in a recycle reactor operated with a feed consisting of He + 5000 ppm NH_3 + 5000 ppm NO and 0–5000 ppm O_2, it has been reported by Bell and co-workers (6) that polymeric species are about 10 times more active than the monomeric species and that they are less selective particularly in the presence of oxygen.

The present work has been undertaken with the aim to provide new insights on the reactivity, acid–base and redox properties of the surface vanadium species present in vanadia/titania de-NO_xing catalysts as a function of the V_2O_5 loading. This has been addressed by the use of temperature programmed desorption/reaction techniques, which due to their transient nature provide a powerful tool for evaluating the sequence of steps in a catalytic process and the order of reactivity of the different surface active species. Temperature programmed desorption (TPD) experiments of ammonia were performed to obtain information on the acid/base and redox properties of the V_2O_5/TiO_2 catalysts; temperature programmed surface reaction (TPSR) runs of preadsorbed ammonia with gas phase NO have been undertaken to investigate the reactivity of adsorbed NH_3 with gaseous NO; temperature programmed reaction (TPR) experiments of NH_3 + NO were performed to study the reactivity of the catalysts at high temperatures, that could not be investigated during TPSR experiments due to the depletion of adsorbed ammonia species. TPSR and TPR experiments were accomplished both in the absence and in the presence of gaseous oxygen to establish the role of catalyst lattice oxygen and the effect of gas-phase O_2.

Finally, steady state reaction (SSR) experiments with feed consisting of NH_3 + NO and of NH_3 + NO + O_2 were also performed for comparison to collect additional information on the reactivity and selectivity of the different vanadia surface species. Transient and steady-state experiments have been performed under diluted gas conditions ($NH_3 \approx 800$ ppm, NO ≈ 800 ppm) and with excess oxygen (≈1% v/v), that are representative of SCR commercial operation.

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METHODS

Catalyst preparation. The TiO_2 support consisting of pure anatase was prepared by neutralization at constant pH (pH = 6) of an acid solution of high purity grade $TiCl_4$ (Aldrich). The white precipitate was filtered and washed with hot water, dried at 385 K overnight and then calcined at 873 K for 4 h. The V_2O_5/TiO_2 samples were prepared by dry impregnation of the TiO_2 support with a water solution of ammonium metavanadate (Carlo Erba) followed by calcination at 873 K for 2 h. Catalysts with V_2O_5 content of 0.8, 1.47, and 3.56% w/w have been prepared, in line with typical compositions of commercial SCR catalysts. In the following, V_2O_5/TiO_2 catalysts will be reported as V*x*/Ti, where *x* is the weight percentage of V_2O_5.

Physicochemical characterization. Surface area data, XRD analysis and FTIR spectra have been collected as described in (16).

Activity measurement. TPD, TPSR, and TPR experiments were performed in a quartz tubular fixed bed microreactor (i.d. 7 mm). In a typical TPD experiment, the catalysts (160 mg, 60–100 mesh) was oxidized in He + 5% O_2 at 773 K for 30 min, and subsequently heated at 773 K in pure He for 10 min. Then the catalyst was cooled down to 313 K and saturated with a stream of He + 5000 ppm NH_3 for 30 min. After 1 h of purge in He at 313 K, the catalyst was heated at 15 K/min in He up to 773 K. In the case of TPSR experiments, the catalyst was heated under He + ≈800 ppm NO instead of pure He; likewise during TPR experiments a reacting mixture consisting of He + ≈800 ppm NH_3 + ≈800 ppm NO was used. TPSR and TPR experiments were also performed in the presence of oxygen in the carrier gas stream (≈1% v/v). The total flow rate was always set at 60 N cm^3/min. The gases exiting the reactor were continuously analyzed by a quadrupole mass detector (UTI model 100 C) coupled with an IBM AT Personal Computer for data acquisition and processing.

SSR measurements were performed with the same feed used for TPR experiments but by operating the microreactor under stationary conditions. In these experiments the analysis of N_2O and N_2 has been carried out by on-line GC using a Poraplot Q capillary column and a 5 Å molecular sieve column in a parallel arrangement. Helium, oxygen, ammonia, and nitric oxide were taken from commercial cylinders from SAPIO.

RESULTS AND DISCUSSION

1. Catalyst Characterization

Table 1 shows the specific surface area (S_a) and the vanadia surface coverage of V_2O_5/TiO_2 catalysts as a function of the vanadia content. Assuming a monolayer capacity of 0.145% w/w of V_2O_5/m^2 (17), it follows that the vanadia coverage of the catalysts is always lower than that corresponding to the formation of the monolayer.

TABLE 1

BET Surface Area and V_2O_5 Surface Coverages of the Vanadia/Titania Catalysts

V_2O_5 (% w/w)	BET surface area (m^2/g)	Surface coverage
0	72	0
0.8	62	0.09
1.47	46	0.21
3.56	48	0.51

As discussed in details in (16), the FTIR and Laser Raman spectra of V_2O_5/TiO_2 catalysts indicate that: (i) both isolated vanadyls and polymeric metavanadate type species are present over submonolayer vanadia/titania catalysts. The presence of isolated vanadyls is argued from the detection of the υ(V=O) stretching mode, that is both IR and Raman active, at 980 cm^{-1} in wet conditions (KBr pressed disks) and at 1030 cm^{-1} in dry conditions (pure powder pressed disks), and of the first overtone 2υ(V=O) at 2045 cm^{-1} in dry conditions. The presence of polymeric species of the metavanadate type is revealed by the detection of the stretching mode at 870 cm^{-1} in the FTIR spectra of KBr pressed disks; (ii) the components associated with metavanadate type species markedly grow on increasing the V_2O_5 content, in good agreement with the results of Went *et al.* (14, 18); (iii) a different type of isolated vanadyls characterized by slightly higher V=O stretching frequencies (υ(V=O) at 1037 cm^{-1} and 2υ(V=O) at 2055 cm^{-1} in dry conditions) appears to form on increasing the vanadia loading.

2. Temperature Programmed Desorption (TPD) of Ammonia

Figure 1 shows the results of ammonia TPD obtained over titania and vanadia/titania catalysts.

In the case of TiO_2 (Fig. 1A), only ammonia and to a lower extent water are detected among the desorption products. The evolution of ammonia occurs in a wide *T* range (310–700 K), due to the presence of different types of adsorbed species, as indicated by previous FTIR studies (19–21). Water desorbs in the low temperature region with maximum at ≈430 K. The desorption of water is likely due to the presence of water impurities in the ammonia cylinder since products of ammonia oxidation, such as N_2, NO, or N_2O, are not detected. Our data compare well with those of Srnak *et al.* (7) but not with those of Bell *et al.* (6) who observed significant amounts of N_2, NO and N_2O during TPD of ammonia from TiO_2 possibly due to the different pretreatment of the samples.

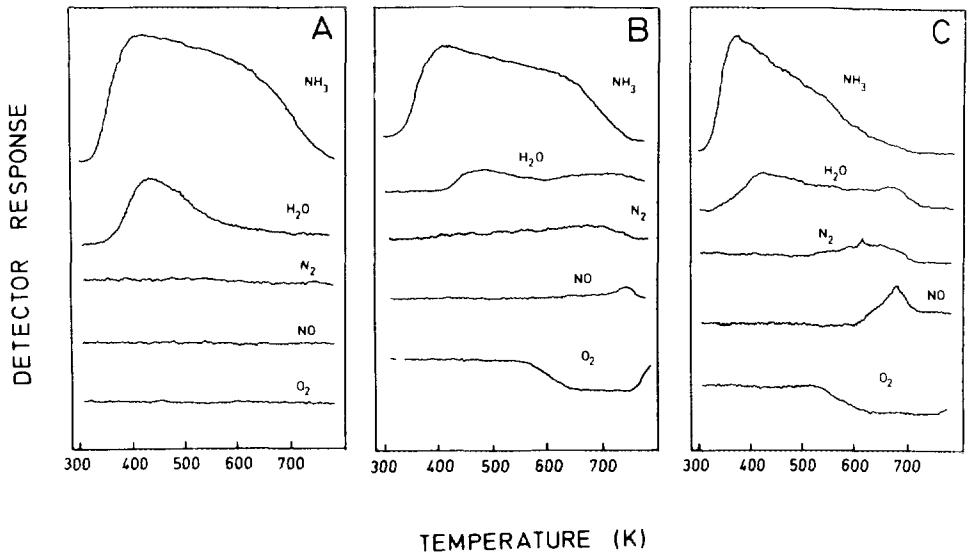

FIG. 1. TPD profiles following exposure of pure titania and vanadia/titania samples to He + ≈4000 ppm of ammonia at 313 K for 30 min. (A) TiO_2, (B) V0.8/Ti, (C) V3.56/Ti.

The TPD spectra of ammonia over vanadia/titania catalysts with V_2O_5 loadings ranging from 0.8 and 3.56% w/w (Figs. 1B, C) present similar features. They show a composite ammonia desorption peak which extends in a wide temperature range (310–720 K), again due to the presence of several ammonia species with different thermal stability (22). Small amounts of water with two distinct desorption maxima at low and high temperatures are also observed. As already discussed in the case of TiO_2, the evolution of water below 500 K is due to the presence of water impurities in the ammonia cylinder. The desorption of water in the high temperature region is due to the oxidation of ammonia and is accompanied by the evolution of N_2 and NO. No formation of N_2O is observed to a significant extent.

Figure 1 also shows that O_2 present in the feed as impurity (40–50 ppm) is consumed over V_2O_5/TiO_2 and not over TiO_2. Besides the temperature threshold of the consumption of oxygen is observed above 500 K where the desorption of N_2 and NO is also detected. This eventually indicates that the oxidation of ammonia is associated with the presence of vanadia, and besides that gaseous oxygen is likely involved in the reoxidation of the reduced catalyst (see below).

3. TEMPERATURE PROGRAMMED SURFACE REACTION (TPSR) OF AMMONIA

3.1. *TPSR of Ammonia in He + NO*

Figures 2–4 show the results of TPSR experiments of ammonia in He + NO (solid lines, traces a) over TiO_2 and V_2O_5/TiO_2 catalysts. For the purpose of comparison, the figures also report the TPD desorption traces of ammonia (traces c) and the results of TPSR experiments performed in the presence of oxygen (dotted lines, traces b).

In the case of TiO_2, the desorption of ammonia is monitored up to 770 K and only a small NO conversion is observed at high temperature (above 620 K) with correspondent evolution of nitrogen and of water. The desorption of water is also observed in the low temperature region for reasons already discussed.

A completely different picture is apparent over vanadia/titania catalysts. In the case of the low vanadia content catalyst (V_2O_5 = 0.8% w/w, Fig. 3), the reaction between adsorbed NH_3 and gaseous NO is detected at $T > 460$ K through the conversion of NO and the correspondent evolution of N_2 and H_2O. A maximum in NO conversion

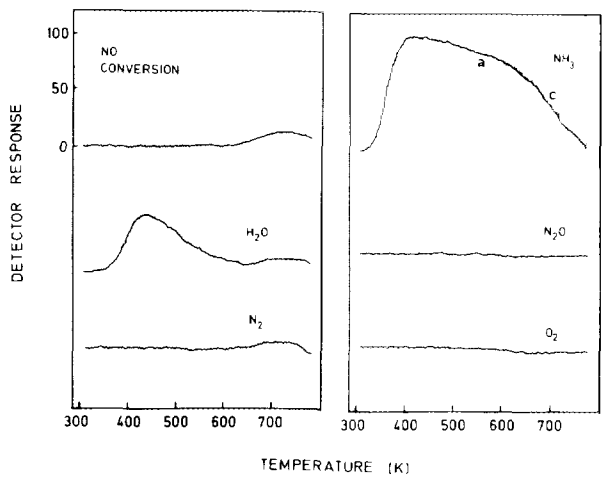

FIG. 2. TPSR profiles in He + 800 ppm NO following exposure of pure titania to He + 5000 ppm of ammonia at 313 K for 30 min. Trace c represents the results of the correspondent TPD experiments.

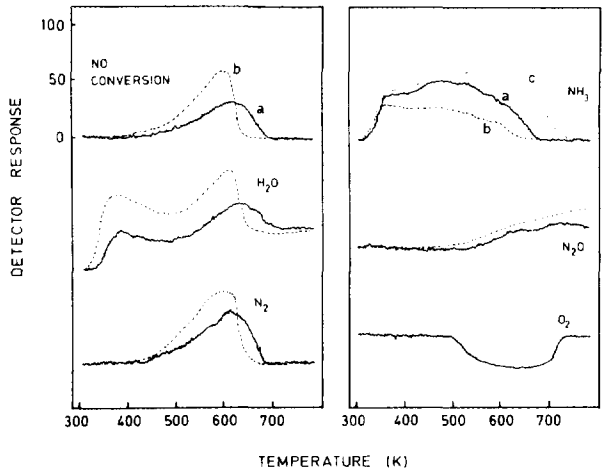

FIG. 3. TPSR profiles in He + 800 ppm NO (traces a, solid lines) and He + 800 ppm NO + ≈1% O_2 (traces b, dotted lines) following exposure of V0.8/Ti to He + 5000 ppm of ammonia at 313 K for 30 min. Traces c represents the results of the correspondent TPD experiments.

is monitored at $T \approx 650$ K due to the depletion of adsorbed ammonia. By comparing the TPSR and TPD desorption traces of ammonia it appears that a small fraction of the initially adsorbed ammonia has reacted with NO. Small amounts of N_2O are also observed at high temperature (above 550 K). Oxygen, present as impurity, is consumed starting from almost the same temperature where NO is converted; the initial oxygen concentration level is restored after the reaction between NH_3 and NO has been completed but at slightly higher temperatures.

On increasing the V_2O_5 content NO is progressively converted also in the low temperature region so that in the case of V3.56/Ti (Fig. 4) two distinct maxima for NO consumption centered at 470 and 600 K are evident. In this case the consumption of NO in the low temperature region is more relevant than that measured at high temperatures. A correspondent evolution of nitrogen and water is also observed.

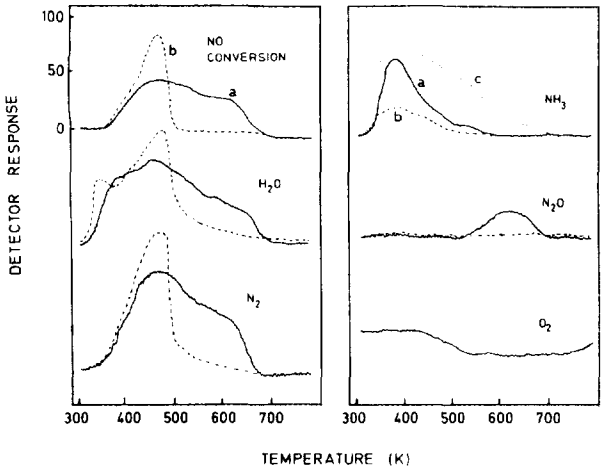

FIG. 4. TPSR profiles in He + 800 ppm NO (traces a, solid lines) and He + 800 ppm NO + ≈1% O_2 (traces b, dotted lines) following exposure of V3.56/Ti to He + 5000 ppm of ammonia at 313 K for 30 min. Traces c represents results of the correspondent TPD experiments.

The comparison of the area of the ammonia TPSR trace (trace a) with that of the TPD trace (trace c) further indicates that the fraction of adsorbed ammonia consumed by the reaction with NO is significantly higher in V3.56/Ti than in V0.8/Ti. The temperature threshold of O_2 consumption decreases on increasing the vanadia content from ≈500 K for V_2O_5 = 0.8% w/w down to ≈420 K for V_2O_5 = 3.56% W/W. In this case the consumption of oxygen has been observed well above the temperature threshold of NO consumption (420 K vs 350 K). Again the original oxygen concentration level is restored after the reaction between NH_3 and NO has been completed but at higher temperatures.

As previously discussed, FTIR and Laser–Raman spectra have shown that isolated vanadyls and polymeric metavanadate type species are present over the investigated submonolayer vanadia/titania catalysts and that the amount of metavanadate species markedly grows on increasing the V_2O_5 content. Accordingly, the low-temperature NO consumption peak which has been observed over V3.56/Ti but not over V0.8/Ti can be associated with the highly reactive polymeric metavanadate species, whereas the high temperature peak, which is evident for all samples, can be associated with poorly reactive isolated vanadyls. The behaviour of the V1.47/Ti catalyst (not reported) can be considered intermediate between those of high and low vanadia content catalysts.

A possible explanation of the consumption of impurity oxygen and the restoration of the original oxygen concentration level in TPSR experiments is attempted in the following. First we note that the occurrence of the SCR reaction below the temperature threshold of oxygen consumption implies reduction of the catalyst since it is unlike that the catalyst can be reoxidized by NO at these temperatures because the SCR reaction is known to be faster in the presence than in the absence of oxygen (23). Only at higher temperatures oxygen becomes involved in the reoxidation of the reduced sites. However, the observation that the original oxygen concentration level is restored after the reaction has been completed and at slightly higher temperatures suggests that the catalyst operates in a reduced state and that oxygen takes part in the reoxidation of the reduced catalyst. It has also been observed that the temperature threshold of oxygen consumption decreases on increasing the vanadium loading. This eventually indicates that the greater reactivity of polyvanadate species as compared to isolated vanadyls can be attributed to the greater lability of oxygen atoms, that is, to their greater reducibility.

The results of catalyst characterisation indicated that a

second type of vanadyl species characterized by a slightly higher V=O stretching frequency is possibly formed at high vanadia loading. Accordingly this new type of vanadyl may be in principle more reactive in the SCR reaction, eventually accounting for the greater reactivity of vanadia/titania catalysts with high vanadia content. This explanation, however, can hardly account for faster reduction by NH_3 and faster reoxidation by gaseous oxygen of the active sites in the catalyst with high vanadia content.

3.2. TPSR of Ammonia in He + NO + O_2

The results of TPSR of ammonia in He + NO + O_2 (traces b of Figs. 3 and 4) show that NO is always consumed starting from the same temperature observed in the absence of oxygen; however, the SCR reaction is completed at progressively lower temperatures on increasing the vanadia content. This results in a single NO consumption peak and in a completely symmetrical evolution of nitrogen and of water. In these experiments the temperature threshold of oxygen consumption could hardly be determined due to the high oxygen concentration level.

These results indicate that the presence of gaseous oxygen enhances the rate of NO removal and confirm that polyvanadate species are more reactive than isolated vanadyls in the presence of oxygen as well. In line with the role of oxygen in a redox mechanism, gaseous oxygen does not affect significantly the temperature threshold of the SCR reaction, that is associated with catalyst reduction, whereas it does accelerate the rate of reaction above the temperature corresponding to O_2 consumption during TPSR experiments in He + NO, that is limited by catalyst reoxidation.

4. Temperature Programmed Reaction (TPR) of Ammonia

4.1. TPR of Ammonia in He + NO

The results of TPR experiments of ammonia in He + NO over low and high vanadia loading catalysts are shown in Figs. 5 and 6 respectively (solid lines, traces a). The NO conversions compare well with those observed during the correspondent TPSR experiments (traces c) for low conversion levels where the rate of reaction is controlled by the reactivity of the catalysts and not by the ammonia surface coverage. At higher temperatures the NO conversion is larger than that measured during TPSR experiments due to the availability of ammonia in the gaseous phase.

For all the catalysts the NH_3 concentration profile is complex, showing a maximum at $T \approx 350$ K originating from the desorption of ammonia at low temperatures and

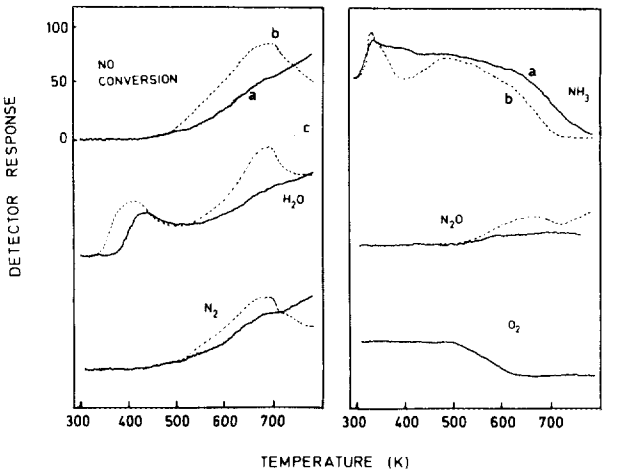

FIG. 5. TPR profiles in He + 800 ppm NO + 800 ppm NH_3 (traces a, solid lines) and He + 800 ppm NO + 800 ppm NH_3 + ≈1% O_2 (traces b, dotted lines) following exposure of V0.8/Ti to He + 5000 ppm of ammonia at 313 K for 30 min. Trace c represents the results of the correspondent TPSR experiments in He + NO.

from its consumption due to the reaction with NO at higher temperatures. The consumption of oxygen is monitored at the same temperatures as in the case of the correspondent TPSR experiments, whereas N_2O is produced at high temperatures. The production of N_2O increases on increasing the vanadium content.

In the case of V3.56/Ti (Fig. 6, trace a) the NO conversion profile shows three distinct temperature regions:

(i) below 430 K NO is converted to the expense of the catalyst lattice oxygen (O_l) according to the stoichiometry

$$2NH_3 + 2NO + O_l \rightarrow 2N_2 + 3H_2O + cat_{red}. \quad [1]$$

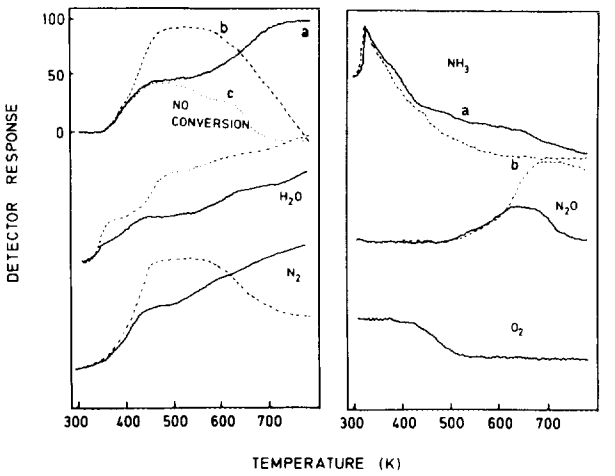

FIG. 6. TPR profiles in He + 800 ppm NO + 800 ppm NH_3 (traces a, solid lines) and He + 800 ppm NO + 800 ppm NH_3 + ≈1% O_2 (traces b, dotted lines) following exposure of V3.56/Ti to He + 5000 ppm of ammonia at 313 K for 30 min. Trace c represents the results of the correspondent TPSR experiments in He + NO.

This has already been discussed in the case of TPSR experiments and is confirmed by steady state measurements in the absence of oxygen (see below). In Eq. [1] cat_{red} stands for the reduced catalyst;

(ii) at 430 K $< T <$ 560 K, in correspondence to the consumption of gaseous oxygen, the reaction is also expected to take place

$$2NH_3 + 2NO + \tfrac{1}{2}O_2 \rightarrow 2N_2 + 3H_2O. \qquad [2]$$

The extent of reaction [2] is limited by the availability of gaseous oxygen;

(iii) at $T >$ 560 K, in spite of the fact that gaseous oxygen is fully consumed, the conversion of NO increases further due to the occurrence of the reaction

$$2NH_3 + 3NO \rightarrow \tfrac{5}{2}N_2 + 3H_2O. \qquad [3]$$

At high temperatures, the oxidation of ammonia leading to N_2O also occurs.

Reactions [1] and [2], that imply the reduction of the catalyst and the participation of gaseous oxygen, respectively, were evidenced during the corresponding TPSR experiments. On the other hand, reaction [3] could not be evidenced in TPSR runs due to the limited residual amount of adsorbed ammonia at high temperature.

The three temperature regions are less evident in the catalyst with lower vanadia content since they are apparently shifted towards higher temperatures and are somehow superimposed to each other.

4.2. TRP of Ammonia in He + NO + O_2

The results of TPR experiments performed in the presence of oxygen (≈1% v/v) in the feed (traces b of Figs. 5 and 6) show that (i) NO is consumed starting roughly from the same temperatures observed in the absence of oxygen (470 K for V0.8/Ti, 450 K for V1.47/Ti, and 340 K for V3.56/Ti; (ii) a greater increase in NO conversion is observed in the presence of oxygen above a temperature that corresponds to the temperature threshold of oxygen consumption monitored during TPR (and TPSR) experiments in He + NO (traces a); (iii) a maximum in NO conversion is detected at progressively lower temperatures on increasing the vanadia loading; (iv) at high temperatures a decrease in NO conversion is observed which is accompanied by a correspondent evolution of N_2O. This indicates that ammonia is directly oxidised to NO and N_2O. The oxidation of ammonia to N_2O is more evident at high vanadia content and is favored by the presence of gaseous oxygen.

The results of TPR experiments performed in the presence of oxygen confirm that gaseous oxygen greatly enhances the rate of NO removal. The data also confirm that in the presence of oxygen polyvanadate species are more reactive than isolated vanadyls. However, they also present a lower selectivity, as proved by the formation of N_2O as a by-product. The lower amounts of N_2O during the correspondent TPSR experiments performed in the presence of oxygen are due to the lack of adsorbed NH_3 species at high temperature (Figs. 3 and 4).

5. Steady State Reaction (SSR) of NH_3 + NO in the Presence and in the Absence of Oxygen

The results of steady state reaction of NH_3 + NO in the presence and in the absence of oxygen are presented in Figs. 7A and B, respectively, together with those of the correspondent TPR experiments for comparison.

In the presence of oxygen the reactivity of the catalysts increases significantly on increasing the vanadia loading: the temperature required to achieve 50% conversion is lowered from 580 K in the case of V0.8/Ti to 450 K in the case of V3.56/Ti. A similar order of reactivity has been observed during TPR experiments. Accordingly it is confirmed that polymeric metavanadate species are more reactive than monomeric vanadyls under steady state conditions as well.

Inspection of Fig. 7 also indicates that the NO conversion measured under steady-state conditions is lower than that observed during TPR experiments in the low temperature region. Besides the N_2 selectivity (defined as $[N_2]/[[N_2] + [N_2O]]$) under steady state conditions is nearly complete over V0.8/Ti, and it shows a small decline above 670 K over V1.47/Ti and above 600 K over V3.56/Ti. On the contrary the NO conversion (and correspondingly the N_2 selectivity) declines markedly with temperature during the corresponding TPR experiments.

The greater reactivity and the lower N_2 selectivity exhibited during TPR experiments as compared to steady-state measurements can be related to the different oxidation levels of the catalysts. Indeed at the beginning of TPR runs it is expected that vanadium species are more oxidised than during steady-state reaction, due to the pretreatment in He + 5% O_2 at 773 K. On the other hand the catalytic activity is comparable at high temperatures where the catalyst reoxidation is fast, so that the NO conversion measured during TPR experiments becomes nearly equal to that observed under steady-state conditions. In this respect it is worth noting that the temperature thresholds where the same NO conversion under transient and steady state conditions have been measured compare well with those corresponding to the complete consumption of impurity oxygen during TPR or TPSR experiments in He + NO + NH_3 (620 K vs 600 K over V0.8/Ti, 600 K vs 570 K over V1.47/Ti, and 520 K vs 500 K over V3.56/

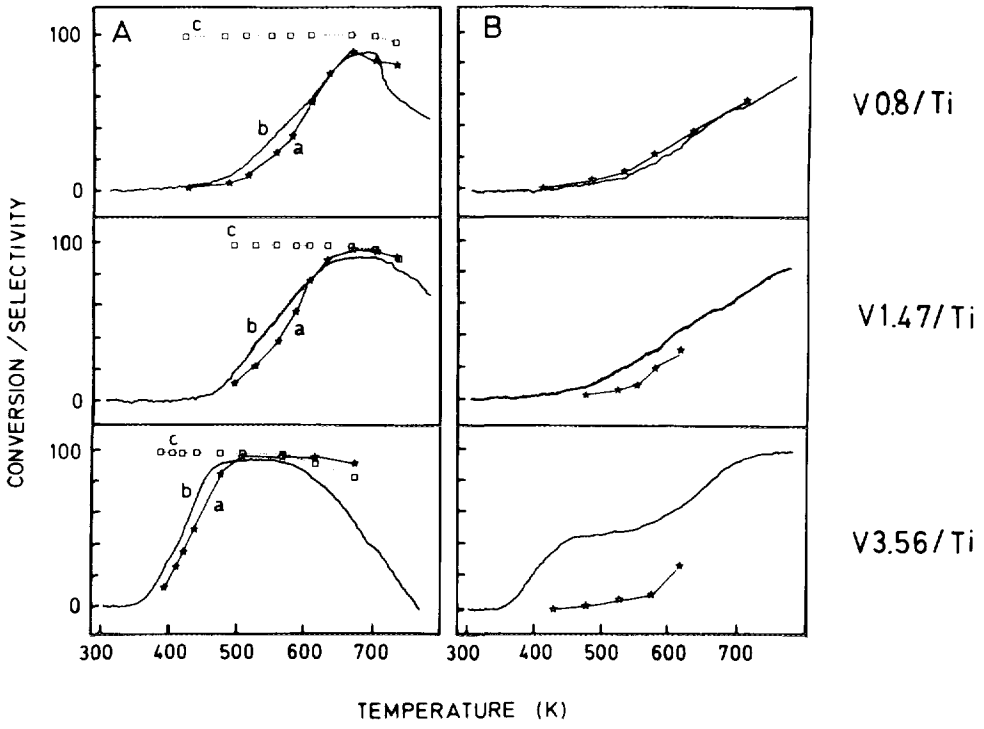

FIG. 7. NO conversion (traces a) and N_2 selectivity (traces c) versus temperature in the presence (A) and in the absence (B) of oxygen (≈1%) during SSR experiments over V0.8/Ti, V1.47/Ti, and V3.56/Ti. The results of the correspondent TPR experiments are also reported (traces b).

Ti). At high temperatures the catalysts are expected to preserve a different and more appropriate oxidation level under steady state conditions than under transient conditions, which eventually accounts for the lower oxidation of ammonia to N_2, NO and N_2O observed in the former case. Accordingly, the temperature window of the catalysts, corresponding to high NO conversion and complete selectivity to nitrogen, is preserved up to higher temperatures under steady state conditions. Notice that the temperature window is shifted towards lower temperatures on increasing the vanadia content, due to the higher reactivity of polyvanadate species as compared to isolated vanadyls. However, because of the lower selectivity of polyvanadate species the upper limit of the temperature window is also slightly shifted towards lower temperatures on increasing the vanadia loading.

The conclusions concerning the role of lattice oxygen during transient experiments are further supported by the results of steady-state measurements performed in the absence of oxygen (Fig. 7B). In the case of V3.56/Ti the NO conversion measured under steady state conditions is lower than that observed under transient conditions (trace b), particularly below 550–600 K where it is almost negligible. Actually, reaction [1], that has been associated to NO consumption at low temperature under unsteady-state conditions, implies the participation of lattice oxygen and, accordingly, it cannot provide a significant reaction rate under steady-state conditions. The SCR reaction in the absence of oxygen is observed above a temperature that roughly corresponds to the temperature threshold of reaction [3] and is characterised by a lower rate than in the presence of oxygen in line with previous literature reports.

A similar picture is evident over V1.47/Ti. However, in this case the consumption of NO measured under steady-state conditions is only slightly lower than under transient conditions, because of the lower amount of polyvanadates species. This confirms that the SCR reaction involves the direct participation of catalyst lattice oxygen, and that the oxygen atoms of the monomeric species are less reactive than those of the polymeric species. Among similar lines the reactivity of V0.8/Ti at low temperatures is even lower than that measured over V1.47/Ti, and no significant differences have been observed between NO conversion under transient or steady-state conditions in the absence of oxygen.

The steady-state reaction data obtained in the presence of oxygen have been analysed assuming an isothermal plug flow reactor model and a first order rate equation ($r = k^\circ \exp(-E_{act}/RT)P_{NO}$) (8), after verifying the absence of interphase and intraparticle diffusional limitations. The kinetic parameters (k°, preexponential factor and E_{act}, activation energy) were estimated by linear regression in a

TABLE 2

Calculated Kinetic Parameters of the Vanadia/Titania Catalysts from SSR Experiments in the Presence of Oxygen

V_2O_5 (% w/w)	E_{act} (kcal mol^{-1})	$k°$ (mol s^{-1} atm^{-1} g_{cat}^{-1})
0.8	13.4	16.7
1.47	13.4	29.2
3.56	11.2	50.9

temperature range where the formation of N_2O was found negligible; their values are given in Table 2. The activation energies are in the range of 11.2–13.4 kcal/mol, in line with previous reports (24), and are slightly lower than those measured in dry (19 kcal/mol) and wet (22.4 kcal/mol) conditions over WO_3–V_2O_5/TiO_2 commercial SCR catalysts (25, 26).

The values of $k°$ and E_{act} reported in Table 2 have been used to estimate the turnover frequency (mol of NO converted s^{-1} atm^{-1} mol of vanadium^{-1}) of the catalysts at 500, 600, and 650 K as function of the vanadium surface coverage. The results are reported in Table 3. It appears that the turnover frequency of V3.56/Ti is significantly higher than that of the low-vanadia loading catalysts. Considering that the relative amounts of polyvanadate species is much higher over V3.56/Ti, it is concluded that polymeric species are more active per vanadium atom than isolated vanadyls. In particular the turnover frequency of V3.56/Ti at 500 K is roughly six times greater than that of V0.8/Ti. This is in good agreement with the results of Bell and co-workers (6) that have been obtained under slightly different experimental conditions. This conclusion is also in line with the results of TPSR and TPR experiments discussed in the previous sections and with the results of Szakacs *et al.* (27) showing a second order dependence in the vanadium surface coverage of the activity of V_2O_5/ZrO_2 catalysts.

TABLE 3

Calculated Turnover Frequency (TOF, mol NO Converted s^{-1} atm^{-1} mol V^{-1}) for the Vanadia/Titania Catalysts

Catalyst	Surface coverage	Turnover frequency (TOF) 500 K	600 K	650 K
V0.8/Ti	0.09	$0.26\ 10^{-3}$	$2.5\ 10^{-3}$	$5.9\ 10^{-3}$
V1.47/Ti	0.21	$0.25\ 10^{-3}$	$2.4\ 10^{-3}$	$5.6\ 10^{-3}$
V3.56/Ti	0.51	$1.66\ 10^{-3}$	$10.8\ 10^{-3}$	$22.3\ 10^{-3}$

Note. Assumed NO concentration = 1000 ppm.

SUMMARY

The results obtained during transient (TPD, TPSR, TPR) and steady-state (SSR) measurements in the presence and absence of oxygen over vanadia/titania catalysts provide new insights on the reactivity, acid–base and redox properties of the vanadium species in the selective catalytic reduction of NO by NH_3.

Isolated vanadyls and polymeric metavanadate species are present on the surface of vanadia/titania samples with V_2O_5 contents <3.56% w/w, that are comparable to those of commercial SCR de-NO_xing catalysts; on increasing the vanadia coverage the relative amount of metavanadate species markedly grows and different types of isolated vanadyls appears to form.

New and more direct evidence than previously reported in the literature for the greater reactivity of polyvanadate species as compared to isolated vanadyls is obtained by means of transient TPSR experiments of NH_3 in He + NO. These experiments allowed to separate the contribution of the reaction over polymeric metavanadate and isolated vanadyls that are observed in the temperature ranges 350–500 K and 550–650 K, respectively.

The greater reactivity of polyvanadate species is related to the greater lability of lattice oxygen atoms, which results in faster reduction by NH_3 and faster reoxidation by gaseous oxygen. This has been proved by the higher NO consumptions measured during transient experiments (TPSR and TPR of ammonia in He + NO) as compared to the corresponding steady state experiments (SSR in He + NH_3 + NO) and by the observed shifts towards lower temperatures of the consumption of impurity oxygen during TPSR and TPR experiments in He + NO on increasing the vanadia loading.

Transient and steady state experiments confirm that polyvanadate species are more reactive than isolated vanadyls in the presence of oxygen as well. However, over the high vanadia loading catalyst the formation of N_2O is significantly higher in the presence of oxygen and under transient conditions. Accordingly, it appears that the superior redox properties of polyvanadate species, although beneficial for the activity of the SCR reaction, may be detrimental for selectivity, and that a more appropriate oxidation level of the catalyst is guaranteed under steady state conditions. This proves how critical the actual oxidation level of the catalyst is for the selectivity of the SCR reaction.

The turnover frequency measured over the high vanadia loading catalyst at 500 K under representative SCR conditions has been found to be about six times larger than that of the vanadia–titania samples with lower vanadia content, in good agreement with previous results obtained under slightly different experimental conditions.

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