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Catalysis Today 56 (2000) 389–401

CATALYSIS TODAY

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Electrical properties of V_2O_5–WO_3/TiO_2 EUROCAT catalysts evidence for redox process in selective catalytic reduction (SCR) deNO$_x$ reaction

Jean-Marie Herrmann (F-4) *, Jean Disdier (F-4)

Lab. de Photocatal. Catalyse et Envir, Ecole Centrale de Lyon, IFOS (UMR CNRS No. 5621), BP 163, 69131 Ecully Cedex, France

Abstract

Electrical conductivity measurements on EUROCAT V_2O_5–WO_3/TiO_2 catalyst and on its precursor without vanadia were performed at 300°C under pure oxygen to characterize the samples, under NO and under NH_3 to determine the mode of reactivity of these reactants and under two reaction mixtures ((i) 2000 ppm NO + 2000 ppm NH_3 without O_2, and (ii) 2000 ppm NO + 2000 ppm NH_3 + 500 ppm O_2) to put in evidence redox processes in SCR deNO$_x$ reaction.

It was first demonstrated that titania support contains certain amounts of dissolved W^{6+} and V^{5+} ions, whose dissolution in the lattice of titania creates an n-type doping effect. Electrical conductivity revealed that the so-called reference pure titania monolith was highly doped by heterovalent cations whose valency was higher than +4. Subsequent chemical analyses revealed that so-called pure titania reference catalyst was actually the WO_3/TiO_2 precursor of V_2O_5–WO_3/TiO_2 EUROCAT catalyst. It contained an average amount of 0.37 at.% W^{6+}dissolved in titania, i.e. 1.07×10^{20} W^{6+} cations dissolved/cm^3 of titania. For the *fresh* catalyst, the mean amounts of W^{6+} and V^{5+} ions dissolved in titania were found to be equal to 1.07×10^{20} and 4.47×10^{20} cm^{-3}, respectively. For the *used* catalyst, the mean amounts of W^{6+} and V^{5+} ions dissolved were found to be equal to 1.07×10^{20} and 7.42×10^{20} cm^{-3}, respectively. Since fresh and used catalysts have similar compositions and similar catalytic behaviours, the only manifestation of ageing was a supplementary progressive dissolution of 2.9×10^{20} additional V^{5+} cations in titania.

After a prompt removal of oxygen, it appeared that NO *alone* has an electron acceptor character, linked to its possible ionosorption as NO^- and to the filling of anionic vacancies, mostly present on vanadia. Ammonia had a strong reducing behaviour with the formation of singly ionized vacancies. A subsequent introduction of NO indicated a donor character of this molecule, in opposition to its first adsorption. This was ascribed to its reaction with previously adsorbed ammonia strongly bound to acidic sites. Under NO + NH_3 reaction mixture *in the absence of oxygen*, the increase of electrical conductivity was ascribed to the formation of anionic vacancies, mainly on vanadia, created by dehydroxylation and dehydration of the surface. These anionic vacancies were initially subsequently filled by the oxygen atom of NO. N^o atoms, resulting from the dissociation of NO and from ammonia dehydrogenation, recombined into dinitrogen molecules. The reaction corresponded to $3NO + 2NH_3 \rightarrow \frac{5}{2}N_2 + 3H_2O$. *In the presence of oxygen*, NO did not exhibit anymore its electron acceptor character, since the filling of anionic vacancies was performed by oxygen from the gas phase. NO reacted directly with ammonia strongly bound on acidic sites. A tentative redox mechanism was proposed for both cases. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: EUROCAT catalyst; SCR; DeNO$_x$ reaction; Vanadia-tungsten/titania; V_2O_5–NO_3/TiO_2 redox processes; Electron processes; Electrical conductivity; Doping effects

1. Introduction

Electrical conductivity measurements carried out on oxide catalysts can provide information about the

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* Tel.: +33-4-7218-6493; fax: +33-4-7833-0337.
E-mail address: jean-marie.herrmann@ec-lyon.fr (J.-M. Herrmann (F-4)).

PII: S0920-5861(99)00299-0

nature of surface structure defects, the existence of oxidizing species (ionosorbed oxygen species, active surface anions, ...), the nature of the oxidic phase involved in catalytic reactions, the solubility limits of heterocations in solid solutions, etc. A general description of the method has been presented [1,38].

In the case of a supported catalyst, the measured conductivity is essentially that of the support. This remains true if the percentage of the supported phase is below a certain level called the percolation threshold [2]. It corresponds to a minimum relative amount above which the electrical conductivity can be established through preferential paths along the sample constituted exclusively by the more conductive minority phase. This percolation threshold is close to ca. 40% in the case of two oxide phases [3].

By comparison with the pure oxide support, electrical conductivity measurements enable one to detect electronic interaction between the active phase and its support. This has been established for deposited metals [4,39] and for deposited oxides [5–8].

EUROCAT V_2O_5–WO_3/TiO_2 catalysts have been characterized by several techniques and tested in the different European laboratories associated in the EUROCAT Oxide Group project and whose contributions constitute the other chapters of this special issue [9].

In the present work, one has to consider that all three oxide phases, V_2O_5, WO_3 and TiO_2, are semiconductors, i.e. that they have an electrical conductivity, which varies exponentially with temperature according to an Arrhenius type law. On a powder catalyst, it was shown [1,38] that electrical conductivity variations are directly proportional to the variations of the concentration in the main charge carriers. In the case of n-type semiconductors such as TiO_2, WO_3, and V_2O_5, the main charge carriers are electrons.

The concentration in quasi-free electrons of conduction depends on several factors such as (i) the presence of ionizable defects of structure, (ii) the existence of ionosorbed species at the surface (mainly oxygen species), (iii) the presence of a reducing gaseous phase such as hydrocarbons, CO and ammonia and (iv) electronic interactions between the supported active phase and its support.

Since (mild) oxidation reactions are based on redox processes between the reactants and the catalyst, it is important to know the electrical behaviour of the solid. This behaviour is generally a function (i) of temperature T, whose influence can be followed in the same range as that of catalysts, (ii) of the oxygen pressure and (iii) of the weight percentage of the supported active phase. DC electrical conductivity measurements constitute a useful tool to investigate such gas–solid and solid–solid electronic interactions.

Several reviews outline the importance of supported vanadium oxide catalysts in various oxidation reactions concerning mostly the mild oxidation of hydrocarbons and the selective catalytic reduction (SCR) of nitrogen oxides by ammonia in flue gases from stationary sources [10–12]. In these oxidation reactions, it is revealed that vanadium oxide supported on titania is a superior catalyst compared to vanadia supported on alumina or silica. In addition to the role of the support, the vanadium oxide loading is also crucial in determining an active and selective catalyst. The active catalyst possesses a well dispersed vanadium oxide phase, which is usually more active and selective than bulk V_2O_5. The behaviour of certain catalysts have been attributed to various factors: (i) the stability of surface vanadium oxide phase on titania; (ii) the structure of the deposited vanadium oxide phase; (iii) the strength and the number of $V=O$ bonds; (iv) the acidity of the surface vanadium oxide and (v) the ease of reduction of the supported vanadium oxide catalyst. Electrical conductivity measurements appear as a choice method to better characterize titania-deposited vanadia, especially with regard to points (i), (iii) and (v).Very few electrical studies have been devoted to titania–vanadia systems. Some of them concerned either Ti–V–P–O glasses [13] or Ti–V–O gel coatings [14], whereas only six references were found to be directly related to titania–vanadia catalysts [6–8,15–17]. In Ref. [15], the authors studied the electrical conductivity of vanadium oxide–titanium oxide mixtures heated at 1023 K and concluded that there was dissolution of some V^{4+} ions in the rutile structure. In Refs. [16,17], the authors followed the variations of the conductivity of V_2O_5/SiO_2–TiO_2 catalysts used in $(NO + NH_3)$ deNO_x reaction. NH_3 was found to be a reducing agent with respect to supported vanadia. Similarly, NO alone behaved as a reducing agent, probably because of the formation of NO_2. In the presence of oxygen (or air), it was proposed that NO reacted directly from the gas phase with chemisorbed NH_3 following an Eley–Rideal mechanism.

The semiconductive properties of V_2O_5/TiO_2 catalysts were studied in the case of EUROCAT catalysts with nominal contents of 1 and 8 wt.% V_2O_5 [6]. It has been found that some pentavalent vanadium ions were able to dissolve in the lattice of titania during the preparation — more precisely during the final calcination — and that the dissolved amount of V^{5+} increased with the nominal content of deposited vanadia. This was subsequently confirmed by chemical analysis. Semiquantitative estimations concerning the amount of dissolved V^{5+} ions could be done with the same samples etched in isobutanol. For these samples, the results of conductivity were in favour of the simultaneous presence of a monolayer of V_2O_5, of V_2O_5 particles but also of dissolved V^{5+} ions in the periphery of the support particles [6]. Additionally, it was demonstrated that titania was not an inert support by contrast to alumina or silica since, under varying the partial pressure of oxygen, the formation of anionic vacancies could be observed. Similar results were obtained on vanadia/titania deNO$_x$ catalysts prepared by the equilibrium adsorption method [18].

In the present article, electrical conductivity was studied to detect possible electronic interactions between vanadia and associated tungsten and titania. Therefore, the electrical conductivity of the industrial $V_2O_5/WO_3/TiO_2$ catalysts was followed in situ during successive sequences under NO, NH_3 and $(NO+NH_3)$ atmospheres, at the same pressures and temperature as those used in catalysis, in order to detect any electronic effect occurring at the surface or at the V_2O_5–WO_3/TiO_2 interface under working conditions.

2. Experimental

2.1. Electrical conductivity measurements

A sample of V_2O_5–WO_3/TiO_2 catalyst (230 mg) was placed between two platinum electrodes where it was slightly compressed (ca. 10^5 Pa) to ensure good electrical contacts between the grains without modifying the texture or preventing gas–solid interactions on all the surface of the solid. To control the temperature, both electrodes were soldered to thermocouples whose wires were also used, when short-circuited, to determine the electrical conductivity σ of the given powder sample by the formula

$$\sigma = \frac{1}{R}\frac{t}{S}$$

where R is the electrical resistance measured with an ohmmeter (Kontron, Model DMM 4021) for $1 \leq R \leq 2\times10^6\,\Omega$ and with a teraohmmeter (Guildline Instruments Model 9520) for $10^6 \leq R \leq 10^{14}\,\Omega$ and t/S is the geometrical factor including the thickness t (ca. 2.5 mm) and the cross sectional area S of the circular electrodes whose diameter is equal to 1.00 cm. A general description of this static cell has been given in Ref. [1,38].

2.2. Procedure

Parts of the three catalysts ($V_2O_5/WO_3/TiO_2$, fresh, used and WO_3/TiO_2 intermediate support) were previously crushed in a mortar and then submitted to the following procedure which enables one to obtain information which are not perturbed by the preceding steps.

- Introduction of 230 mg of catalyst in the cell;
- evacuation at room temperature;
- introduction of 400 Torr (1 Torr = 133.3 Pa) of oxygen (L'Air Liquide, 99.9995% pure);
- heating at 5°C/min up to 300°C and attaining of the steady-state conductivity;
- evacuation of oxygen and introduction of 1.52 Torr NO which corresponds to the partial pressure of 2000 ppm NO (2000 ppm = 0.2%·760 Torr = 1.52 Torr NO);
- evacuation of NO and introduction of 2000 ppm NH_3 (1.52 Torr NH_3, temporal variations of σ);
- evacuation of NH_3 and re-admission of NO to check the reversibility of the electrical conductivity under NO atmosphere;
- evacuation of NO and admission of the reaction mixture $(NO+NH_3)$ 2000 ppm each to follow in situ the redox processes during reaction;
- evacuation of the reaction mixture and introduction of 400 Torr O_2 to follow the reoxidation of the catalyst;
- evacuation of O_2 and introduction of a second reaction mixture $(NO+NH_3)$ to follow σ variations under reaction mixture.

3. Results and discussion

3.1. Preliminary remarks

3.1.1. Definition of a reference state

For (semi)quantitative comparisons of the electrical conductivities of the various supported vanadia samples, it is required that solids have similar textures and identical surface states. This requirement is easily fulfilled since all the samples have the same support. Indeed, the electrical conductivity of a n-type semiconductor powder can be written as

$$\sigma = A[e^-] \tag{1}$$

where $[e^-]$ is the concentration of quasi-free electrons and A the textural parameter which depends on the compression of the powder and on the number and quality of contact points between particles (1). Because of the identity of the procedure for electrical measurements and of the use of the same titania support, A can be considered as identical for all the samples under identical conditions.

The common reference state for σ determination has been chosen with the following conditions: 400 Torr oxygen at 300°C (1 Torr = 133.3 Pa). It has the advantages of (i) eliminating most of ionically adsorbed species such as H_3O^+, OH^-, which would produce an additional surface conductivity and (ii) avoiding the formation of surface structure defects, such as anionic vacancies, whose ionization produce additional free electrons which could mask or perturb the possible electronic interaction between vanadia and titania under neutral conditions (6). In addition, these conditions are identical to those used in the catalytic deNO$_x$ reaction.

3.1.2. Origin of the semiconductivity of pure titania

All the samples behave as semiconductors according to Eq. (1). Moreover, they are all of the n-type since $\partial\sigma/\partial P_{O_2} < 0$, in agreement with the nature of pure and doped titania. σ varies with T and P_{O_2} according to the general equation

$$\sigma = \sigma_0 \exp(-E_c/RT) P_{O_2}^{-1/n} \tag{2}$$

If n is equal to special integer values, the mode of conduction will be related to a special type of structure defects acting as electron sources. It has been shown that a conduction model, with $n = 4$ corresponds to singly ionized anionic vacancies, whose formation involves the following equations:

$$O_s^{2-} - \Leftrightarrow O_2(g) + V_O \tag{3}$$

$$V_O \Leftrightarrow V_O^+ + e^- \tag{4}$$

with

$$K_3 = P_{O_2}^{-1/2}[V_O] \tag{5}$$

$$K_4 = \frac{[V_O^+][e^-]}{[V_O]} \tag{6}$$

V_O represents an anionic vacancy with two electrons trapped (neutral entity with respect to the lattice). V_O^+ is a singly ionic vacancy with only one electron trapped (positive entity with respect to the solid). The electroneutrality condition ($[e^-] = [V_O^+]$) combined with the mass action law applied to Eqs. (3) and (4) yields

$$[e^-] = [(K_3)_o(K_4)_o]^{1/2} \exp\left[-\frac{\Delta H_3 + \Delta H_4}{2RT}\right] P_{O_2}^{-1/4} \tag{7}$$

where ΔH_3 and ΔH_4 are the enthalpies of reactions 3 and 4. Generally, the ionization energy of the first electron can be neglected with respect to the enthalpy of formation of anionic vacancies ($\Delta H_3 \gg \Delta H_4$) (1). Consequently, the heat of formation of an anionic vacancy according to Eqs. (3) and (4) is equal to $\Delta H_3 = 2E_c = 2 \times 41$ kcal/mol $= 82$ kcal/mol (343 kJ mol^{-1}).

At higher temperatures ($T > 800$°C), the second electron can be ionized (1):

$$V_O^+ \Leftrightarrow V_O^{2+} + e^- \tag{8}$$

and σ becomes equal to

$$\sigma = \sigma_0 \exp(-E_c/RT) P_{O_2}^{-1/6} \tag{9}$$

with $E_c = \frac{1}{3}(\Delta H_3 + \Delta H_4 + \Delta H_8)$. In the present case, at $T = 300$°C, only singly ionized vacancies can be encountered. There are several notations for anionic vacancies in the literature. They are listed in Table 1. The notation with squares will be sometimes used further to avoid confusion with symbol V of vanadium.

Table 1
Different notation systems for anionic vacancies[a]

Entity	Electrical charge	Notation chosen	Notation with squares	Rees notation (41)	Kröger and Vink notation (42)
Neutral	0	V_o	$\boxed{=}$	$(e_2/\square)$	V_O
Singly ionized Anionic vacancy	+1	V_o^+	$\boxed{-}$	$(e\ /\square)$	$V_o^{\bullet}$
Doubly ionized Anionic vacancy	+2	V_o^{2+}	$\square$	$(\square)$	$V_o^{\bullet\bullet}$

[a] From [41,42].

3.1.3. Conductivity of supported phases

In a mixture of two conducting oxides, the overall conductivity of the sample becomes governed by the more conducting component above a certain percentage, called the percolation threshold [19]. It corresponds to a minimum relative amount above which the electrical conductivity can be established through preferential paths along the sample constituted exclusively by the more conductive minority phase. It has been estimated to be close to 40% for a mixture of oxides of similar texture (particle size and shape) [20,21]. It can also be suggested in the case of a deposited oxide that the conductivity data might be explained by a percolation threshold when the surface coverage of the titania particles reaches a point where there is a connected path from particle to particle that runs through a more conducting V_2O_5 surface. Such a "surface percolation threshold" problem has been previously analyzed for SnO_2-deposited Sb_2O_4 [22] and for titania-deposited Pt [4,23,24,39]. For Sb_2O_4/SnO_2, it was expected that the conductivity of SnO_2 would decrease abruptly when the increasing Sb content would correspond to a monolayer of poorly conductive Sb_2O_4. By contrast, the deposition of Sb_2O_4 gave a strong increase of conductivity because of the n-type doping of SnO_2 by Sb^{5+} ions [5,22,25]. For Pt/TiO_2 catalysts with metal loadings as high as 10 wt.%, one could have expected an increase of conductivity because of a possible improvement of the surface conductivity and of the quality of the intergranular contact points. Actually, the reverse was observed with a decrease in conductivity [4,23,39] or in photoconductivity [24] when Pt.% was increased from 0 to 10%. This was explained by an electron transfer from titania to Pt. These two examples illustrate the fact that in a supported catalyst the electrical conductivity is mainly that of the support (in electronic interaction with the supported phase).

In the present case, the above considerations strongly suggest that the overall conductivity measured is essentially that of the support, i.e. of titania, which is an n-type semiconductor (1).

3.2. Evidence for a partial dissolution of V^{5+} and W^{6+} ions in titania's sublattice

The electrical conductivities of the three catalysts have been measured at steady state at 300°C under 400 Torr O_2 (1 Torr = 133.3 kPa). They are given in Table 2. For comparison, the values of the electrical conductivities of various titania samples are given in Table 3.

In Refs. [1,2,5–8,38], it has been shown that depositing a divided oxide on top on an oxide support

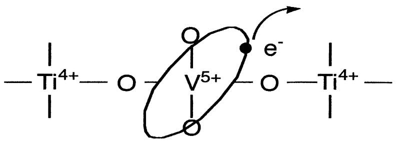
Table 2
Electrical conductivities of crushed EUROCAT samples (400 Torr O_2, 300°C)

Catalyst	σ (Ω^{-1} cm^{-1})
$V_2O_5/WO_3/TiO_2$ (fresh)	2.16×10^{-8}
$V_2O_5/WO_3/TiO_2$ (used)	3.105×10^{-8}
WO_3/TiO_2 (monolith without vanadia)	7.39×10^{-9}

Table 3
Electrical conductivity of other titania supports under identical conditions (400 Torr O_2, 300°C)

Catalysts	σ ($1\,\Omega^{-1}$ cm^{-1})	References
TiO_2 (EUROCAT1) 10 m^2/g	2.38×10^{-10}	[6]
TiO_2 (Tioxide) 125 m^2/g	4.59×10^{-10}	[18]
EL10V1–D[a] 10 m^2/g	2.39×10^{-9}	[6]
EL 10 V8–D[a] 10 m^2/g	5.41×10^{-9}	[6]

[a] Samples etched in boiling isobutanol for 16 h (Ref. [6]).



Scheme 1. Doping of titania by V^{5+} dissolved ions.

caused a limited partial dissolution of the cation of the deposited oxide. This is a quite general phenomenon observed on V_2O_5/TiO_2 catalysts [1,6–8,38] as well as on Sb_2O_4/SnO_2 ones [5,25]. The dissolution of V^{5+} in the lattice of titania occurs via the substitution of V^{5+} ions to Ti^{4+} ions in the lattice positions of titania. This causes a doping effect according to the valence induction law of Verwey [26]. Each dissolved V^{5+} cations shares four electrons with four O^{2-} neighbour anions, whereas the fifth electron is delocalized around the positive V^{5+} impurity (see Scheme 1).

A small thermal energy ε is sufficient to ionize this fifth electron and to enable it to reach the conduction band.

This ionization can be written as

$$[(-\overset{|}{\underset{|}{V}}{}^{5+}-)e^-] \Leftrightarrow (-V^{5+}-) + e^- \tag{10}$$

or

$$D \Leftrightarrow D^+ + e^- \tag{11}$$

with D and D^+=neutral and ionized donor centers.

Generally equilibrium (10) or (11) are totally shifted to the right. The law of mass conservation gives

$$[D_O] = [D] + [D^+] \approx [D^+] \tag{12}$$

The electroneutrality of the solid gives $[D^+] = [e^-]$. Thence

$$[D_O] \approx [D^+] = [e^-] \tag{13}$$

For a doped sample, the electron concentration becomes equal to that of $[D_O]$, i.e. to the total concentration of donor centres introduced.

In the case of the EUROCAT I V_2O_5/TiO_2 systems, it has been shown that σ increased linearly with the amount of dissolved vanadia [6]. If the amount of dissolved titania is converted into the atomic fraction of V^{5+} cations dissolved in titania according to the formula

$$V^{5+}\ \text{at.\%} = \frac{80\,(V_2O_5\ \text{wt.\%})}{91 - 11\,(V_2O_5\ \text{wt.\%})/100} \tag{14}$$

one gets the linear calibration curve of Fig. 1 with a coefficient of linear regression equal to $r = 0.99985$.

The slope $\partial\sigma/\partial(V^{5+}$ at.%) gives the increase in electrical conductivity as a function of the amount of dissolved vanadium 5+ions.

In the present study, the conductivity of neat titania is much higher than that of other supports (Table 2). This could be due to the initial presence of heterovalent impurities with a valence higher than +4 (such as Nb^{5+}, Ta^{5+}, V^{5+}, Sb^{5+}, Mo^{6+}, W^{6+}, etc.).

Using the calibration curve of Fig. 1, the electrical conductivity σ of V_2O_5–WO_3/TiO_2 could be expressed as

$$\sigma = \sigma(TiO_2) + k[V^{5+}\ \text{at.\%}_{\text{dissolved}}]$$

with k being the slope of the straight line of Fig. 1.

$$k = \partial\sigma/\partial[V^{5+}\ \text{at.\%}_{\text{dissolved}}]$$

Actually, the chemical analysis revealed that the so-called pure titania monolith was in reality the WO_3/TiO_2 precursor monolith (Table 4). The atomic percentage of pentavalent-equivalent impurities was found equal to 0.746 M^{5+} at.%. Half of this value

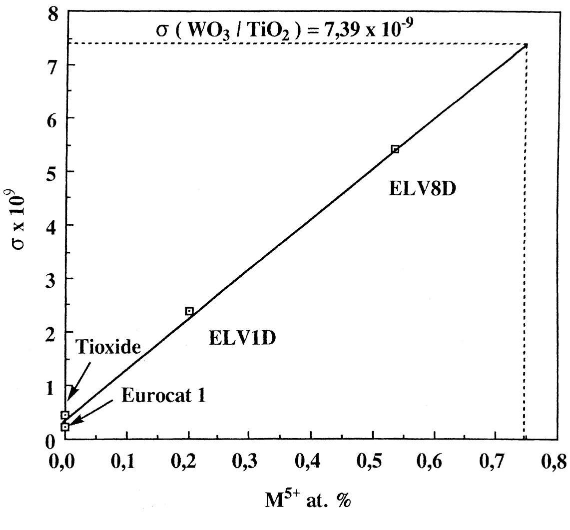


Fig. 1. Linear correlation between electrical conductivity σ and the amount of pentavalent cations dissolved in the lattice of titania (EUROCAT, ELVID and ELV8D from Ref. [6] and Ti-oxide from Ref. [18]).

Table 4
ICP elemental chemical analyses (in element wt.%) of EUROCAT catalysts after total dissolution in ($H_2SO_4 + HNO_3 + HF$)

Samples	Ti (%)	W (%)	Si (%)	V (%)	Al (%)	Ca (%)
Support	44	6.5	4.2	0.1	1.6	1.6
Fresh catal.	43.2	6.3	4.7	2.1	1.6	1.6
Used catal.	43.5	6.9	4.5	2.1	1.0	1.5

Table 5
Ionic radii of the various cations involved

Cation	Ionic radius (Å)
Ti^{4+}	0.68
W^{6+}	0.64
V^{5+}	0.59
V^{4+}	0.63

(0.37 at.%) actually represents the content in W^{6+}, since dissolved hexavalent W^{6+} cation are double electron donors (Scheme 2). This corresponds to 1.07×10^{20} W^{6+} ions dissolved/cm^3.

If the calibration curve of Fig. 1 is used to titrate the number of pentavalent-equivalent impurities dissolved in titania from the value of $\sigma(V_2O_5\text{–}WO_3/TiO_2)$ on the *fresh* catalyst, one gets a [M^{5+}] mean concentration of 6.61×10^{20} M^{5+} ions/cm^3, which corresponds to 4.47×10^{20} V^{5+} ions and 1.07×10^{20} W^{6+} ions.

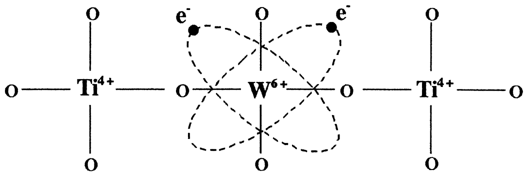
The same calculation for the *used* catalyst gives a total M^{5+} dissolved amount equal to 9.56×10^{20} M^{5+} ions/cm^3. The increase Δn of M^{5+} ions dissolved corresponds mainly to the increase in [V^{5+}] dissolved: $\Delta n = 2.9 \times 10^{20}$. Therefore, the used catalyst which is still active in SCR reaction can be characterized by a higher value of heterocations dissolved in titania. They correspond mainly to V^{5+} cations, since vanadia is more reducible with more anionic vacancies, which favour the mass transfer of small V^{5+} cations (Table 5).

Since fresh and used catalysts have similar compositions and similar catalytic behaviours, the only manifestation of ageing observable by conductivity was a supplementary progressive dissolution of 2.9×10^{20} V^{5+} cations in titania.

3.3. *Electrical conductivity variation under various atmospheres*

3.3.1. *Under 2000 ppm NO*

After reaching the steady state under oxygen (400 Torr) at 300°C, oxygen was promptly removed and 2000 ppm NO (1.5 Torr) were introduced over $V_2O_5/WO_3/TiO_2$ and over WO_3/TiO_2. The kinetic variations are presented in Fig. 2. A small decrease was observed during ca. 2 h on the EUROCAT sample. A similar variation was observed for tungsta/titania after a slight initial increase. For both solids, as explained in the introduction, the conductivity measured is that of the support.



Scheme 2. Substitutional doping of titania by W^{6+}.

For titania the decrease in electron concentration can be accounted for by two simultaneous and/or consecutive phenomena:

1. Ionosorption of NO with electron capture

$$NO(g) + e^- \rightarrow NO^-(ads) \tag{15}$$

   Such a ionosorbate has already been observed on UV-illuminated titania at room temperature by photoconductivity before being decomposed into N_2 and N_2O [27]. Actually, the photoconductivity σ of UV-irradiated titania, measured at steady state, was found to vary with NO pressure as $\sigma = kP_{NO}^{-1}$. It has also been suggested to be formed on SnO_2 [28].

2. Reoxydation of the surface of the trioxidic catalyst by filling of surface anionic vacancies

$$NO(g) + e^- \rightarrow NO^-(ads) \tag{16}$$

$$V_O^+ + NO^- \rightarrow N^o + O_s^{2-} \tag{17}$$

$$N^o + N^o \rightarrow N_2(g) \tag{18}$$

Eq. (15) is plausible since NO has an electron affinity of 0.024 eV, which is not nil. Eq. (17) is thermodynamically favourable with a substantially negative enthalpy (−102.6 kcal/mol or −429.4 kJ/mol), calculated within the frame of the Born–Haber cycle for titania with the enthalpies of formation of NO (+21.59 kcal/mol) and of V_O^+ (+82 kcal/mol from Ref. [39]). For $V_2O_5\text{–}WO_3/TiO_2$, the same reaction can occur on the deposited phases but more pronounced. By comparison of the two curves in Fig. 2, it can be

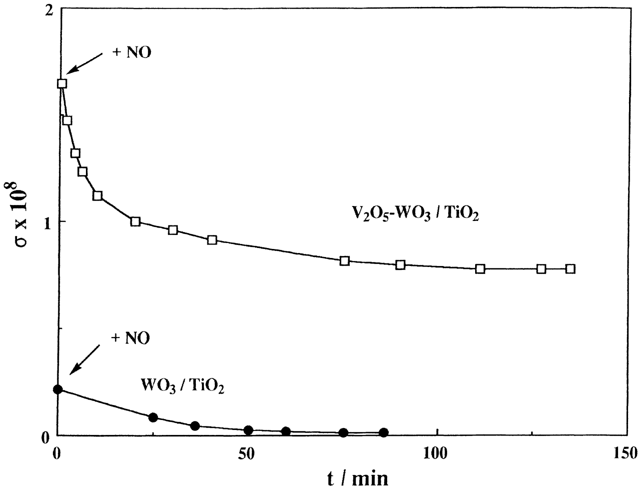


Fig. 2. First exposure to 2000 ppm NO of WO_3/TiO_2 and V_2O_5–WO_3/TiO_2 in an oxidized state and after a prompt outgassing, recorded at 573 K.

concluded that there are substantially more anionic vacancies on vanadia than on the other two oxides. It can be suggested that the ionosorption of NO as NO^- or the reoxidation of the surface of these phases require electrons which are withdrawn from titania support through the interface according to the equation

$$e^-(TiO_2) \Leftrightarrow e^-(V_2O_5 - WO_3/TiO_2) \qquad (19)$$

This reversible electron transfer is induced by the alignment of the Fermi levels of differently reduced solid phases [1,7,31,32,38]. This electronic interaction had previously been postulated in Ref. [33].

The oxidized state of the EUROCAT sample is confirmed by the orange colour of the solid observed in situ in the cell at 300°C. Since the catalyst containing vanadia has a higher conductivity (Fig. 2), this means that vanadia is the more easily reducible oxide. The filling of anionic vacancies by NO is supported by previous results on pure V–Mg–O phases [29]. In addition, Eqs. (16) and (18) can interfere and give birth to N_2O detected by IR spectroscopy [30,40]

$$N^0 + NO \rightarrow N_2O \qquad (20)$$

3.3.2. Electrical conductivity variation under ammonia

After a prompt outgassing of NO, 2000 ppm of NH_3 were introduced (Fig. 3). A sharp increase of σ was observed for both V_2O_5–WO_3/TiO_2 and WO_3/TiO_2 by more than one order of magnitude. This increase in $\sigma(TiO_2)$ can be ascribed to the reducing character of ammonia with respect to titania with the production of anionic vacancies according to the overall reaction

$$2NH_3 + 3(O_s^{2-}) \rightarrow 3H_2O + 3V_O^{+} + 3e^- \qquad (21)$$

where (O_s^{2-}) represents a surface anion (neutral entity with respect to the lattice) and V_O^{+} represents a singly ionized anionic vacancy (once positively charged entity with respect to the lattice).

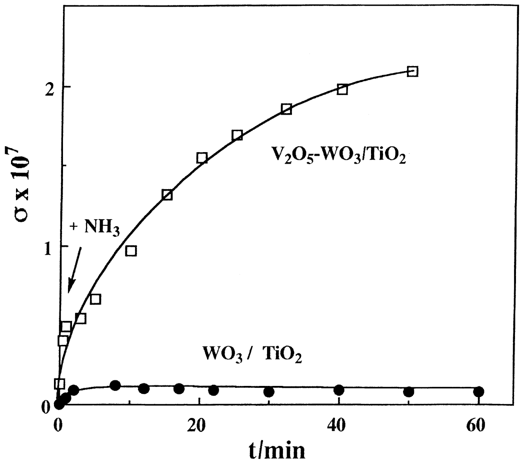


Fig. 3. First exposure to 2000 ppm NH_3 of WO_3/TiO_2 and V_2O_5–WO_3/TiO_2 in an oxidized surface state resulting from the first exposure to NO, recorded at 573 K.

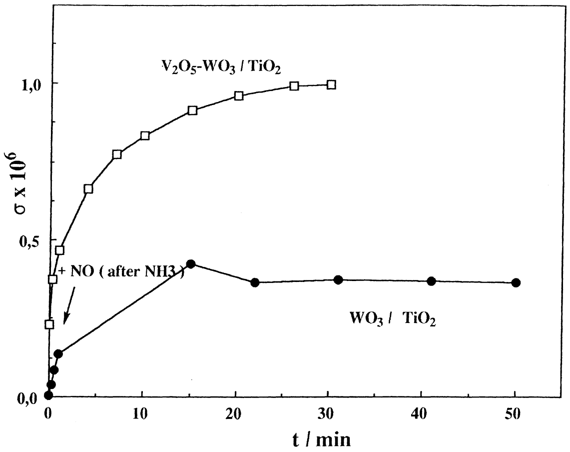


Fig. 4. Exposure to 2000 ppm NO of WO_3/TiO_2 and $V_2O_5/WO_3/TiO_2$ after exposure to ammonia, recorded at 573 K.

The enrichment in conduction electrons produced in Eq. (21) is responsible for the increase in σ observed. Since σ measured is that of the support, this means that there is an electron transfer from the reduced oxides to titania

$$e^-(V_2O_5\text{–}WO_3/TiO_2) \Leftrightarrow e^-(TiO_2) \qquad (22)$$

This reversible electron transfer is induced by the alignment of the Fermi levels of differently reduced solid phases [1,7,31,32,38]. From Fig. 3, it can be easily observed that vanadia is substantially more reducible than tungsta in line with Ref. [33]. Therefore, vanadia will constitute the more reactive phase with respect to ammonia.

3.3.3. Electrical conductivity variations in NO atmosphere subsequently to NH_3 exposure

After the sequence under NH_3, the gas phase was promptly removed and 2000 ppm NO were introduced at 300°C (Fig. 4). By contrast to the initial admission of NO, the second one produced a substantial increase, mainly on the fresh V_2O_5–WO_3/TiO_2. The initial acceptor character of NO apparently disappeared and was replaced either by a donor character or by a reducing character of NO with respect to the surface of both V_2O_5–WO_3/TiO_2 and WO_3/TiO_2 catalysts. Actually the surface of the solids is initially in a reduced state, induced by the previous sequence under NH_3 as indicated by the electrical conductivity, which is higher by two orders of magnitude. Actually, the initial acceptor character has not changed but presently NO is in presence of a reduced surface containing residual NH_3 and/or some of its fragments. Therefore, the increase in σ shown in Fig. 4 is indicative of a reaction occurring in the adsorbed phase between NH_x and NO. This reaction will be better analyzed in the next section under reaction mixture.

The increase of $\sigma(V_2O_5\text{–}WO_3/TiO_2)$ which is significantly higher than $\sigma(WO_3/TiO_2)$ clearly indicates once more that V_2O_5 *is more reducible than* WO_3 [33] since more electrons arising from anionic vacancies are produced and transferred to titania support.

3.3.4. Electrical conductivity variations under (2000 ppm NO + 2000 ppm NH_3) reaction mixture after the second exposure to NO and in absence of oxygen

The catalysts having previously undergone the subsequent exposures (i) to pure NO, (ii) to pure ammonia and (iii) to pure NO again at 300°C, were promptly evacuated and the reaction mixture (2000 ppm NO + 2000 ppm NH_3) was introduced *in the absence of oxygen*. After the second exposure to NO, the electrical conductivity still continued to increase, especially for V_2O_5–WO_3/TiO_2, whose conductivity monotonously increased for 1 h (Fig. 5). By comparison of the two curves, it can be observed that the reactivity (or reducibility) of vanadia is substan-

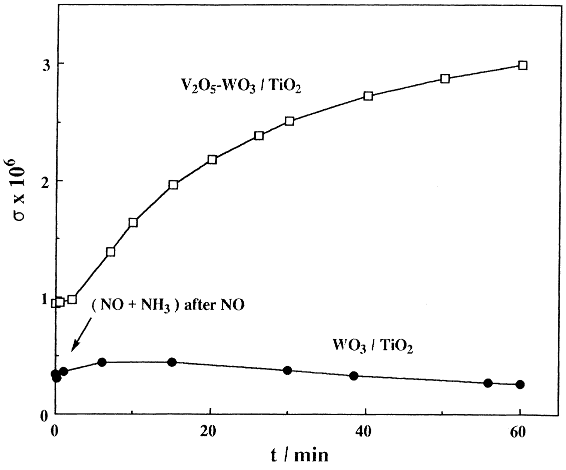


Fig. 5. Exposure to the reaction mixture (2000 ppm NO + 2000 ppm NH_3) *without oxygen* of WO_3/TiO_2 and V_2O_5–WO_3/TiO_2 after exposure to NO, recorded at 573 K.

tially higher than that of tungsta. The initial electron acceptor character of NO has completely disappeared. The increase in conductivity observed is in line with those obtained in NH_3 (Fig. 3) and in NO after exposure to ammonia (Fig. 4). Additionally, it can be also ascribed to the reductor character of excess ammonia which obeys the following stoichiometry:

$$6NO + 6NH_3 \rightarrow 5N_2 + 6H_2O + 2NH_3$$

Actually, such a reaction mixture does not correspond to the real world, which always involves the presence of oxygen, whose influence has been studied in the next section.

3.3.5. Electrical conductivity variations under (2000 ppm NO + 2000 ppm NH_3) reaction mixture in the presence of 500 ppm of oxygen

The same sample was used to keep the same geometrical factor. It was regenerated by an oxygen treatment under 400 Torr O_2 at 300°C overnight. Oxygen pressure was then decreased to a fraction of 1 Torr corresponding to approximately to 500 ppm. Initially, the catalyst was beige-yellow. It became grey at the end of the ($NO + NH_3 + O_2$) sequence.

In the presence of oxygen, the electrical conductivity of fresh EUROCAT V_2O_5–WO_3/TiO_2 catalyst increased similarly as in the absence of oxygen (Fig. 6). However, the initial conductivity was an order of magnitude smaller than that of the catalyst without oxygen. This means that the anionic vacancies are preferentially filled and/or refilled by oxygen from the gas phase, in line with the electron affinity of oxygen, which is much higher than that of NO. In agreement with previous Refs. [33–37], this indicates that the initial acceptor character of NO alone will not be acting anymore and that NO will preferentially react in a non-ionosorbed state and more precisely in a neutral state with a donor character, evidenced by the results of its second exposure (Fig. 4). Once more, the peculiar reactivity of vanadia with respect to the reaction mixture ($NO + NH_3 + O_2$) is underlined by the difference of the two curves in Fig. 6 relative to V_2O_5–WO_3/TiO_2 and WO_3/TiO_2 catalysts, respectively.

The fresh catalyst seems to have a faster rate of reducibility than the used one. This does not mean that the former catalyst is necessarily more active that the latter but that before reaching its steady state, the initial freshly oxygen-treated catalysts has more numerous labile surface oxygen species.

In these conditions, the stoichiometry of the reaction can be considered as

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

with no more excess of ammonia.

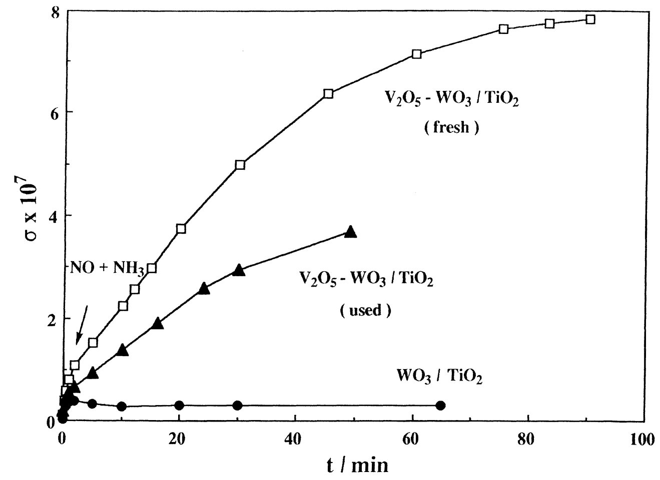


Fig. 6. Exposure to the reaction mixture (2000 ppm NO + 2000 ppm NH_3 + 500 ppm O_2) of WO_3/TiO_2 and V_2O_5–WO_3/TiO_2 (fresh and used) catalysts in an oxidized state, recorded at 573 K.

3.4. Consequences for redox catalysis

Since both titania and deposited oxides are n-type semiconductor oxides, all the different measurements of σ in the subsequent experiments clearly put into evidence the following points:

- NO *alone and in the absence of oxygen* has an electron acceptor character since $\partial\sigma/\partial P_{NO} < 0$, forming NO^- ionosorbate and/or filling anionic vacancies.
- NH_3 has a reducing character since $\partial\sigma/\partial P_{NH_3} > 0$.
- The SCR reaction mixture (1 NO (2000 ppm) + 1 NH_3 (2000 ppm)) has also a reducing character with respect to the surface of $V_2O_5/WO_3/TiO_2$ catalyst, either in a slightly reduced state (Fig. 5) or in an oxygen-containing atmosphere (Fig. 6).

Therefore, two different cases have to be envisaged.

3.4.1. SCR reaction in a reducing atmosphere (without oxygen)

The following reaction mechanism can be proposed.

1. Initial electrophilic ionosorption of NO on a reduced surface with consumption of conduction electrons

$$NO(g) + e^- \rightarrow NO^-(ads) \quad (23)$$

2. Dissociative chemisorption of NH_3 on acidic sites with release of a proton and of a conduction electron

$$NH_3(g) \rightarrow NH_2^o + H^+ + e^- \quad (24)$$

3. Formation of hydroxyl groups with surface anions O_s^{2-}

$$H^+ + O_s^{2-} \rightarrow O_s\text{–}H^- \quad (25)$$

4. Dehydroxylation of the surface with formation of water and an empty anionic vacancy (i.e. doubly ionized and thence *doubly positively charged with respect to the solid*)

$$2O_s\text{–}H^- \rightarrow H_2O(g) + V_O^{2+} \quad (26)$$

5. Capture of one conduction electron by an empty anionic vacancy to form the thermodynamically stable singly ionized anionic vacancy

$$V_O^{2+} + e^- \rightarrow V_O^+ \quad (27)$$

6. Filling of a singly ionized anionic vacancy by oxygen from NO^-

$$V_O^+ + NO^- \rightarrow N^o + O_s^{2-} \quad (28)$$

7. Reaction of NH_2 with ionosorbed NO^- via the formation of an activated complex, already postulated in Refs. [33–36] with release of nitrogen, water and of a conduction electron

$$NH_2^o + NO^- \rightarrow [\text{activated complex}]^* \rightarrow N_2 + H_2O + e^- \quad (29)$$

and/or

8. reaction of NH_2^o with freshly renewed surface anions from Eq. (28). This reaction corresponds to the oxidation of the nitrogen atom from the oxidation degree −2 to the oxidation degree 0 and to the reduction of the solid with the formation of an anionic vacancy

$$NH_2^o + O^{2-} \rightarrow N + H_2O + V_O^+ + e^- \quad (30)$$

9. Recombination of two N^o atoms into dinitrogen

$$N^o + N^o \rightarrow N_2(g) \quad (31)$$

This mechanism is supported by the electrical conductivity measurements performed on a partly reduced surface.

3.4.2. SCR reaction in the presence of oxygen

In the presence of oxygen, the following reaction mechanism can be proposed:

1. Dissociative chemisorption of NH_3 on acidic sites with release of a proton and of a conduction electron

$$NH_3(g) \rightarrow NH_2^o + H^+ + e^- \quad (24a)$$

2. Formation of hydroxyl groups with surface anions O_s^{2-}

$$H^+ + O_s^{2-} \rightarrow O_s\text{–}H^- \quad (25a)$$

3. Dehydroxylation of the surface with formation of water and an empty anionic vacancy (i.e. doubly ionized and thence *doubly positively charged with respect to the solid*)

$$2O_s\text{–}H^- \rightarrow H_2O(g) + V_O^{2+} \quad (26a)$$

4. Capture of one conduction electron by an empty anionic vacancy to form the thermodynamically stable singly ionized anionic vacancy

$$V_O^{2+} + e^- \rightarrow V_O^+ \tag{27a}$$

5. Filling of a singly ionized anionic vacancy by *oxygen from the gas phase*

$$V_O^+ + \tfrac{1}{2}O_2 + e^- \rightarrow O_s^{2-} \tag{28a}$$

6. Reaction of NH_2^o with neutral molecular NO and formation of water and of molecular nitrogen via the formation of an activated complex, already postulated in Refs. [33–36]

$$NH_2^o + NO^- \rightarrow [\text{activated complex}]^* \rightarrow N_2 + H_2O \tag{29a}$$

Therefore, the stoichiometric reaction

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

can be summarized in two steps:

- redox reaction between ammonia and vanadia, whose anionic vacancies are directly refilled by O_2;
- reaction of NH_2 with undissociated and neutral NO to directly form water and nitrogen.

This mechanism is supported by the electrical conductivity measurements performed in presence of oxygen.

3.5. *Role of the support*

Why is TiO_2 up to now the best support for SCR deNO$_x$ reaction? From electrical conductivity measurements, it can be seen that titania is an n-type semiconductor whose semiconductivity arises from its reducibility with the formation of singly ionized anionic vacancies. The lability of its surface anions enables it to participate to redox processes occurring on the oxides deposited on it. In addition, there is an easy reversible electron transfer between deposited tungsta and vanadia and their support. In addition, from the results of Section 2.2, it appeared that titania was doped by W^{6+} ions first and by additional V^{5+} ions during the preparative calcination. These solid state dissolution can be described by

$$(1-x-y)TiO_2 + xWO_3 + \tfrac{1}{2}yV_2O_5 \rightarrow Ti_{1-x-y}W_xV_yO_{2+x+y/2}$$

The incorporation of heterocations (W^{6+} and V^{5+}) in the lattice of titania is compensated by $(x+\frac{1}{2}y)$ extra-anions in the stoichiometry of doubly doped titania. It can be suggested that anionic vacancies can be more easily formed among these extra anions as formulated in Ref. [6], thus producing more labile surface oxygen species. This is in line with the TPR results obtained in this special issue of Catalysis Today.

$$Ti_{1-x-y}^{4+}W_x^{6+}V_y^{5+}O_{2+x+(y/2)}^{2-} \rightleftarrows [Ti_{1-x-y}^{4+}W_x^{6+}V_y^{5+}O_{(2+x+(y/2)-\varepsilon)}^{2-}\square_\varepsilon] + \tfrac{1}{2}\varepsilon O_2$$

4. Conclusions

The in situ electrical conductivity measurements on EUROCAT V_2O_5–WO_3/TiO_2 catalyst and on the biphasic WO_3/TiO_2 precursor allowed the following conclusions:

1. As soon as one or two oxide phases are deposited on titania, the calcination treatment, necessary to convert the impregnated precursors into supported oxides, directly induces a partial dissolution of the cations into the lattice of the oxide support detected by a substitutional doping effect by substitution. Presently, the intermediate catalyst WO_3/TiO_2 contains W^{6+} cations dissolved in the sublattice of titania. The subsequent deposition of V_2O_5 induces an additional dissolution of heterocations V^{5+}. The conductivity of the used catalyst indicated an increase of 2.9×10^{20} V^{5+} cations/cm^3 dissolved in the lattice of titania support as a manifestation of ageing of the solid phases without any apparent effect on activity.
2. Vanadia and tungsta are in electronic equilibrium with the titania support. In reducing atmospheres (NH_3, $NO+NH_3$), these oxides, which are more reducible than titania, loose some surface anions O^{2-} with the creation of singly ionized anionic vacancies and of conduction electrons, which are transmitted to titania in relation with the alignment of the Fermi levels of the reduced solid phases.
3. NO alone chemisorbs on the slightly reduced EUROCAT with an electron acceptor character. This has to be ascribed to the filling of anionic vacancies by the oxygen atom of NO. NO looses its acceptor character as soon as oxygen is present and

as soon as water is formed by the SCR reaction in the absence of oxygen.

4. Ammonia reduces the surface of tungsta and mainly that of vanadia by creation of anionic vacancies induced by the concerted elimination of one water molecule from two vicinal OH^- groups.
5. In $(NO + NH_3)$ atmosphere *without oxygen*, the surface of vanadia is acting as a redox relay: the H atoms originating from ammonia dissociation create singly ionized anionic vacancies which result from the dehydroxylation and the dehydration of the surface and which are subsequently filled by the oxygen atom from NO. Nitrogen atoms which result from these reactions recombine into dinitrogen.
6. Under $(4\,NO + 4\,NH_3 + O_2)$ stoichiometric ratio, ammonia reduces vanadia and forms anionic vacancies, which are filled directly by oxygen from the gas phase.

Finally, the activity of V_2O_5–WO_3/TiO_2 catalyst in SCR deNO_x reaction is basically a redox process assisted by acidic sites necessary to a dissociative chemisorption of ammonia.

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