Effect of vanadia and tungsten loadings on the physical and chemical characteristics of V_2O_5-WO_3/TiO_2 catalysts

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Abstract

Titania-supported tungsten and vanadia oxides with different W and V loadings and calcined at different temperatures have been prepared by the sol–gel method and characterized. Large amount of tungsten (9%; w/w) provides thermal stability to WO_3/TiO_2 systems upon addition of vanadia. It is found that WO_3 and V_2O_5 crystallites are formed when their concentrations are higher than those corresponding to three monolayers. DTA analyses have shown that the presence of V_2O_5 crystallites is not essential for the transformation of titania anatase into rutile. High reactivity in limited temperature range (225–350 °C) has been observed for the catalyst with 8% (w/w) V_2O_5 with a high formation of N_2O amount during the SCR reaction. The catalyst with 3% (w/w) V_2O_5 exhibits a slight lower reactivity but with a high selectivity to N_2 preserved in all working temperature.
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Keywords: Titania; Vanadium oxide; Catalyst characterization; Monolayers; SCR reaction

1. Introduction

Among the various catalysts which have been tested for the selective catalytic reduction (SCR) of NO by ammonia, V_2O_5–WO_3/TiO_2 gained wide technical application. Several studies [1,2] have shown that the catalytic properties as well as the chemical and physical structure of such products are markedly influenced by parameters, such as the method of preparation, the concentration of the active component, and the nature of the support. In the previous studies carried out on V-W/Ti catalysts prepared by several methods (grafting, impregnation), the formation of V_2O_5 crystallites occurs after the TiO_2 anatase is covered with a complete monolayer vanadia species. The sol–gel process is known as a method of preparation of a highly pure and homogeneous multicomponent metal oxides. This method leads to the increase in the interactions between V and Ti which strongly enhance the catalytic properties. The objective of the present paper is first to investigate whether or not the sol–gel method leads to the formation of V_2O_5 crystallites when the V content is higher than the surface coverage as it is known in literature, and secondly to study the effect of high vanadia loading on the selective catalytic reduction of NO_x. For this purpose, X-ray diffraction (XRD), surface area (S_a), thermal analysis (TG/DTA) and SCR activity were employed to investigate the structural and physico-chemical characteristics of V_2O_5-WO_3/TiO_2 catalysts with high and low vanadia loading.

2. Experimental

2.1. Catalyst preparation

The TiO_2 and V_2O_5–WO_3/TiO_2 samples with different loadings of WO_3 (3–5–9%; w/w) and V_2O_5 (3–8%; w/w) have been prepared by a sol–gel method using titania(IV)-*bis*-ethylacetoacetato-isopropyl at ($C_{18}H_{32}O_8Ti$, 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, ethylene glycol and water were added in appropriate amounts to the ternary mixture. After stirring the mixture for ca: 15 min at ambient temperature, the excess

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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 for 2 h at calcination temperatures from 400 to 800 °C.

X-ray diffraction patterns were obtained with a Siemens D-500 powder X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å) in step mode between 20 and 80°, using a step size of 0.02 step/s. The anatase and rutile relative contents were determined according to the equation reported in literature [3].

$$A\,(\%) = \frac{1}{1 + (1.4 I(1\,1\,0)_{R}/I(1\,0\,1)_{A})}$$

where I is the intensity of the corresponding XRD peak. The crystallite dimensions were calculated using the Shirrer method.

BET measurements were performed with a quantochrome autosorb 1C using Nitrogen. Mesopores distribution measurements have been obtained by mercury penetration method using a porosimeter (Autopore III).

Thermal analysis (TG/DTA) was performed in a Netzsch STA 409. Catalytic measurements have been carried out in a quartz tubular fixed bed micro-reactor (i.d. 10 mm) containing 200 mg catalyst. A feed consisting of ~400 ppm NO, ~100 ppm NO$_2$, ~500 ppm NH$_3$, and ~6% (v/v) O$_2$ with N$_2$ being a carrier gas (total flow rate = 100 N cm^3/min). The flow was accurately measured and controlled by means of mass flow meters and controllers. Activity data have been collected at different temperatures in the range 150–500 °C, each temperature was maintained until steady-state condi-

tions were reached. NO and NO$_2$ conversions were measured using chemiluminescence method with apparatus type "CLD 700 EL hat" while NH$_3$ and N$_2$O were measured using NDIR Spectrometers type BINOS 4b.1 and Ultramat 5E, respectively.

3. Results

3.1. XRD and morphology

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 500 °C, all samples 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 in all cases. The mean pore radius increases and the pore volume decreases even with high WO$_3$ loading. For pure TiO$_2$, the anatase to rutile phase transformation ($2\theta = 27.5$–36–$54.5°$) is detected starting from 600 °C and is complete at 800 °C (Fig. 1a). For TiO$_2$ doped with WO$_3$, the increase in tungsten loading leads to inhibit this transformation (Fig. 1b–d). The W and V surface coverages have been calculated from values of S_a and from the nominal oxide loading by assuming a monolayer capacity of 7 μmol/m^2 for WO$_3$ [4] and of 0.145% (w/w) for V$_2$O$_5$/m^2 [5]. No rutile phase has been observed in all

Table 1
Morphological properties

Catalyst	T calculated (°C)	S_a (m^2/g)	Phase	D_c (Å)	V_p (cm^3/g)	$r_{p_{exp}}$ (Å)
Ti	400	47	A	285	0.267	18.6
	500	19	A	427	0.266	21.6
	600	10	77% A + 23% R	773	–	–
	800	–	R	983	–	–
W3/Ti	400	97	A	250	0.293	18.2
	600	22	A	511	0.284	25.2
	800	–	68% A + 32% R	919	–	–
W5/Ti	400	95	A	227	0.31	17.3
	600	40	A	475	0.255	29
	800	10	90% A + 10% R	919	–	–
W9/Ti	400	124	A	199	0.283	18
	600	54	A	404	0.257	25.6
	800	15	A	766	0.25	31
V3W9/Ti	400	115	A	265	0.336	16.6
	500	77	A	319	0.289	20
	600	22	A	579	0.248	23.2
	800	7	R	783	–	–
V8W9/Ti	400	154	A	265	0.31	30
	500	22	A	682	0.29	72
	600	14	43% A + 57% R	1068	–	–
	800	–	R	–	–	–

A: anatase, R: rutile.
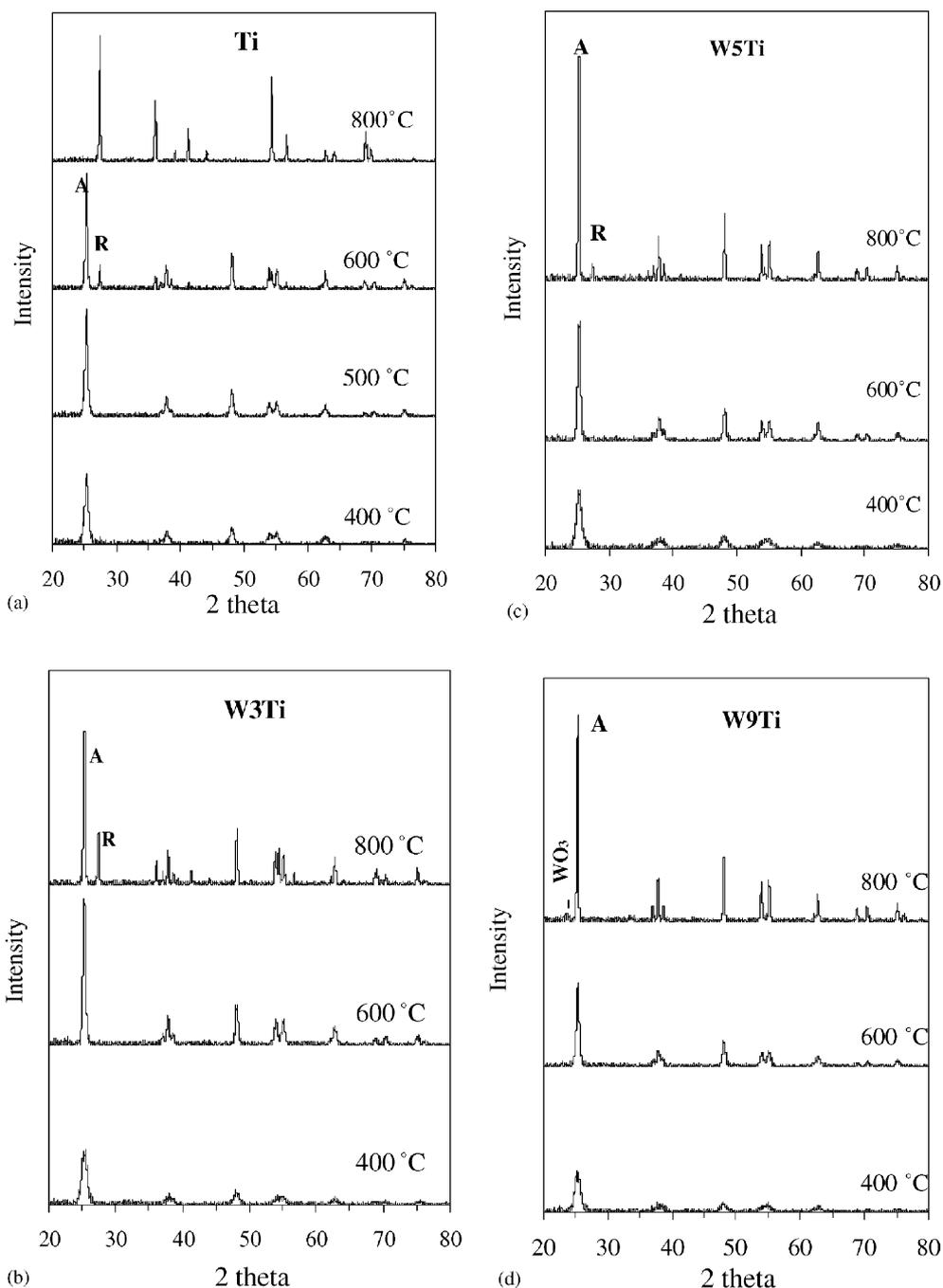
Fig. 1. X-ray powder diffraction patterns of: (a) Ti; (b) W3Ti; (c) W5Ti; (d) W9Ti calcined from 400 to 800 °C.

calcination temperatures for sample W9Ti, however WO_3 segregation was evidenced by XRD ($2\theta = 17.8$–20.2–23.1°) (Fig. 1d). This formation occurs, normally, as is described in literature, after the TiO_2 anatase is covered with a complete monolayer tungsten species [6]. The calculations of W coverages for samples W–Ti show that WO_3 crystallites are detected when the W concentration is higher than the one corresponding to three monolayers. This was the case for W9Ti at 800 °C. However, W5 sample exhibits an excess of monolayer at 800 °C without showing any WO_3 crystallites,

this is probably due to the W amount which is below the XRD detection limits.

Crystallite dimensions increase with increasing calcination temperature for all samples. No significant differences are observed in the crystallite dimensions of anatase on samples WO_3/TiO_2 with the only exception of the sample with the highest tungsten loading (9%; w/w) where smaller crystallites have been measured comparatively to the other W-containing samples. The mean pore radius and anatase phase are preserved even at 800 °C for sample W9Ti. These

results demonstrate that WO_3 hinders the sintering process to higher calcination temperatures. W9Ti is thus more suited to stabilize the anatase phase and preserves the surface characteristics. Catalyst W9Ti has been used for further investigations.

To investigate the effect of V loading on morphological and catalytic properties of the catalyst, two different loadings of V_2O_5 have been prepared (3 and 8%; w/w) V_2O_5 on W9Ti. The morphological data of Table 1 indicates that vanadia affects both the initial sintering of TiO_2 and the anatase to rutile transformation which are faster especially at high vanadia loadings and high calcination temperatures. At 400 °C, V8 exhibits higher surface area than V3. This is probably due to the high amount of vanadia alkoxide used in the preparation of V8 catalyst comparatively to that of V3. Higher amount of organic residues thus remains on the titania surface after calcination at this low temperature, which leads to a product with lower cristallinity and consequently with higher surface area. However, the increasing in the calcination temperature over 400 °C leads to the dramatical decrease of the surface area of V8 comparatively to that of V3 (Table 1), and high amount of rutile (57%) is already formed at 600 °C. At the same temperature V_2O_5 crystallites ($2\theta = 26.18$–20.31–$31.06°$) appear (Fig. 2b). This is consistent with the well-known promoting effect of vanadia on both the TiO_2 sintering and the anatase to rutile transformation.

As the calcination temperature is further increased above 600 °C, the crystalline V_2O_5 content is diminished and is not present at 800 °C which indicates that most of the vanadia is incorporated into the titania support as $V_xTi_{1-x}O_2$ (rutile) [7].

On V3, no V_2O_5 crystallites, even before the total transformation of the titania anatase into rutile, have been observed, probably because vanadia was highly dispersed as isolated VO_x species. However, WO_3 crystalline has been detected at 800 °C on V3 catalyst (Fig. 2a).

The presence of WO_3 without V_2O_5 crystallites on Ti support at high calcination temperatures on both V3 and V8 catalysts suggests that titania interacts more strongly with vanadia than with tungsten [8].

Low intensity of rutile and WO_3 crystallites peaks on V8 at 800 °C have been observed comparatively to those of V3. This could be due to the destruction of the surface structure of titania because of the modification of rutile structure and the loss of its crystallinity, promoted by high vanadia loading.

3.2. Thermal analysis

The samples (~15 mg) were heated in flowing air (100 ml/min) from ambient temperature to 1000 °C at a rate of 5 °C/min. The thermoanalytical results of the samples (Ti, W9Ti, V3W9Ti, V8W9Ti) are illustrated in Figs. 3 and 4. DTA curves for all samples show endothermal peaks in temperature range (104–108 °C) originated mainly from the evaporation of water (desorption of physical water,
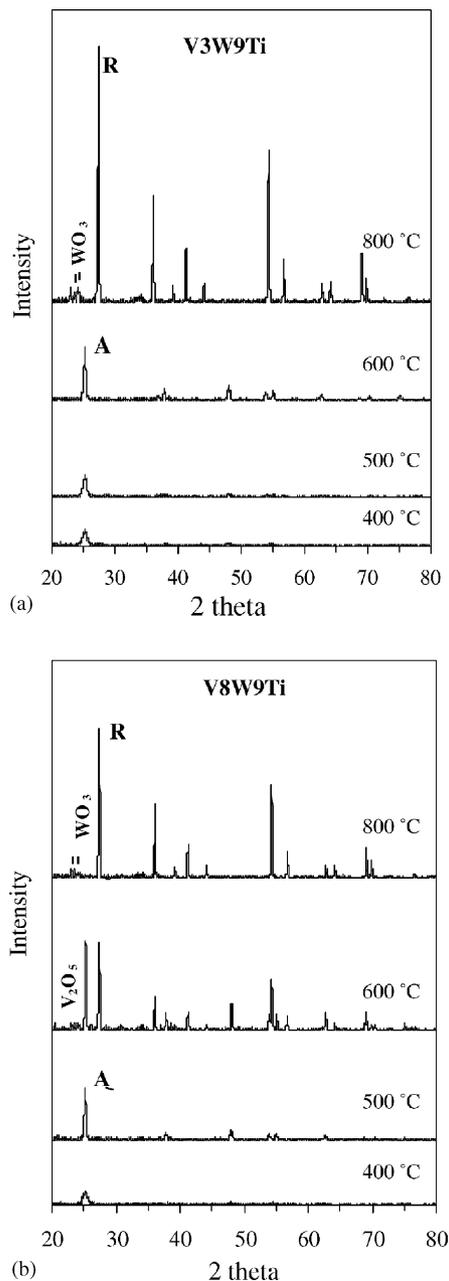
Fig. 2. X-ray powder diffraction patterns of: (a) V3W9/Ti; (b) V8W9/Ti calcined from 400 to 800 °C.

dehydroxylation) which was already present in the samples, followed by two exothermal peaks at ~(127–134 °C) and at ~(298–309 °C) with shoulders at ~(219–228 °C), respectively, due to the oxidation of organic residues and formation of CO_2. It is worth noting to mention that the sample A is still completely amorphous after this oxidation process for all samples (not shown). The exothermal peaks located at (469, 482, 446 and 442 °C) for the four samples (TiO_2, W9Ti, V3W9Ti and V8W9Ti), respectively, reflect the crystallization of titania anatase. The oxidation of organic residues and the crystallization of titania anatase are accompanied with a weight loss in all cases.
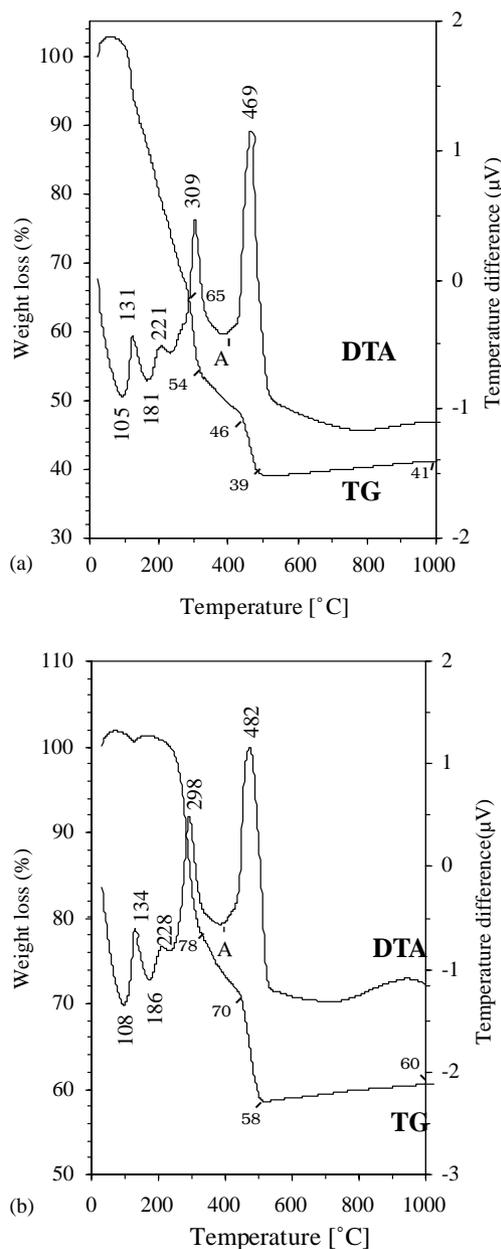
Fig. 3. Thermoanalytical curves of: (a) Ti and (b) W9Ti gels heated under air. Heating rate 5 °C/min; sample weight 15 mg; air flow rate 100 cm^3/min.

On samples Ti and W9Ti, the anatase peak intensity is higher than that of CO$_2$ peak (Fig. 3a and b), possibly because inorganic precursor for WO$_3$ is used in different tungsten loadings and has more significant effect on the formation of a strong anatase crystallites, which was confirmed by XRD. When vanadia is introduced, the inverse occurs (Fig. 4a and b), especially in case V8 where the intensity of anatase peak is lower than that of all other samples. The CO$_2$ peak in case V8 is also much larger, probably because vanadia is generated from an alkoxide which increases the amount of organic residues, which need larger window of temperature to be oxidized. By adding vanadia to W9Ti,

the appearance of anatase peak shift to lower temperatures (446 °C for V3 and 442 °C for V8). A very weak and broad exothermal DTA signal which has a maximum at ~600 °C observed on V8 indicates a slight crystallization of V$_2$O$_5$, followed by a weak and broad endothermal peak at ~695 °C, corresponding to the vanadia melting. This agrees with our results obtained by XRD where only small crystallites of V$_2$O$_5$ have been detected on V8 calcined at 600 °C which disappear fastly over this temperature.

On V3 catalyst, no V$_2$O$_5$ crystallization has been observed and only a very weak endothermal DTA peak at 673 °C has been detected. This behavior of both catalysts could be due as reported in literature by mean of XPS analysis [7], to the strong interaction between vanadia and titania support which leads to formation of V(IV) ions situated in the substitution points of Ti(IV) ions in TiO$_2$ anatase lattice. Thus only weak population of V(V) species is enable to grow. Heat treatment may promote diffusion of V(IV) into titania crystal structure generating substitutional defects which induce formation of rutile phase. Thus, the endothermal peaks corresponding to the melting of vanadia crystallites which should be observed by DTA analysis on both V3 and V8 are left and are replaced by a very weak DTA signal at 673 and 695 °C, respectively.

On samples V3 and V8, a slight increasing in the weight (5 and 3%, respectively) is observed over 500 °C, probably because of the oxidation of vanadia, which confirms our supposition that vanadia is still present in a partly reduced state even with high V loading.

An explicit and precise evaluation of the content of V(IV) and V(V) in the ternary V-W/Ti catalyst is not the aim of the present paper. However, in the literature, the role and the presence of V(IV) on TiO$_2$-supported systems have been the object of long debate. While several authors on the basis of EXAFS, TPR and XPS data [9,10] concluded that pentavalent vanadium is the only component of the overlayer on TiO$_2$, other authors showed the presence of nonnegligible amounts of vanadium(IV) [11–13], but their quantitative evaluation is however not easy to attempt. Previous studies have shown that the alkoxide route leads to the formation of V(IV) [14,15] which agree with our observations.

3.3. Catalytic activity measurements

The results of the catalytic tests in the reduction of (NO + NO$_2$) by NH$_3$ performed over V3 and V8 samples are shown in Fig. 5.

The reaction stoichiometry in typical SCR conditions are the following [15]:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{R1}$$

$$4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O \tag{R2}$$
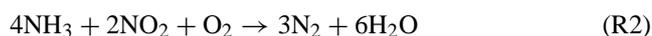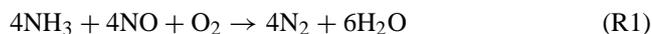
The reaction between NO and ammonia can also proceed in a different way, giving rise to the unwanted product N$_2$O

$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \tag{R3}$$
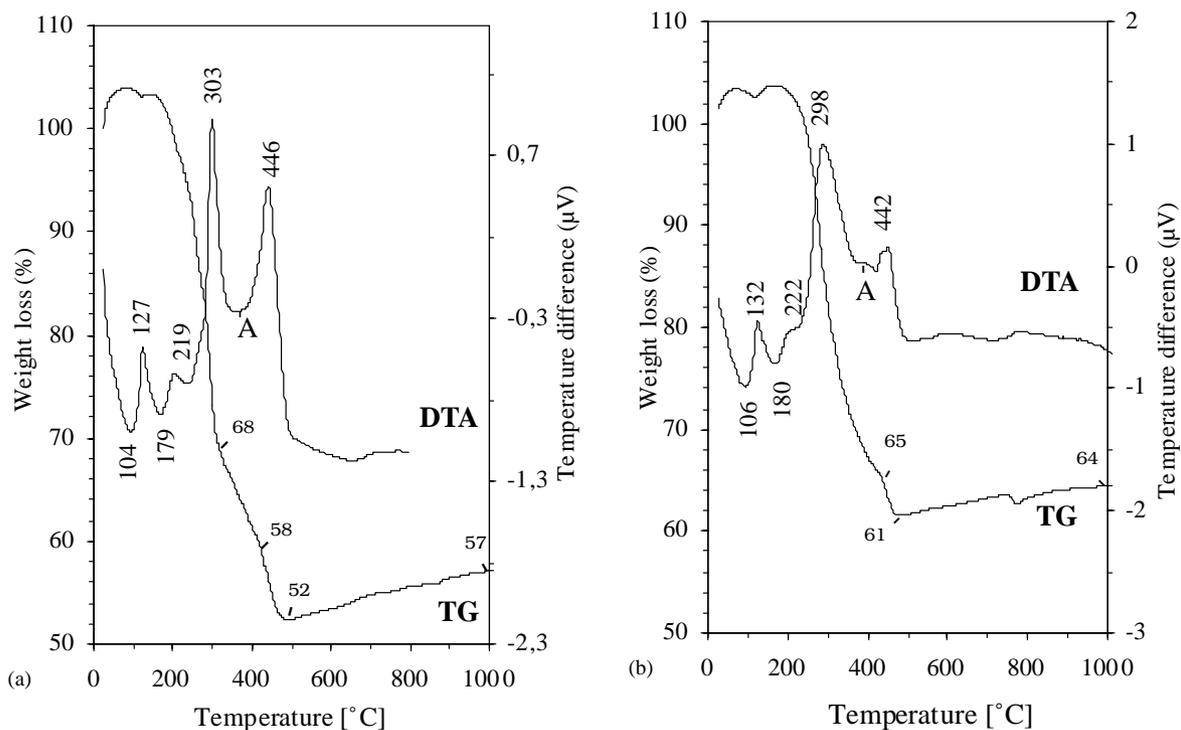
Fig. 4. Thermoanalytical curves of: (a) V3W9Ti; (b) V8W9Ti gels heated under air. Heating rate 5 °C/min; sample weight 15 mg; air flow rate 100 cm³/min.
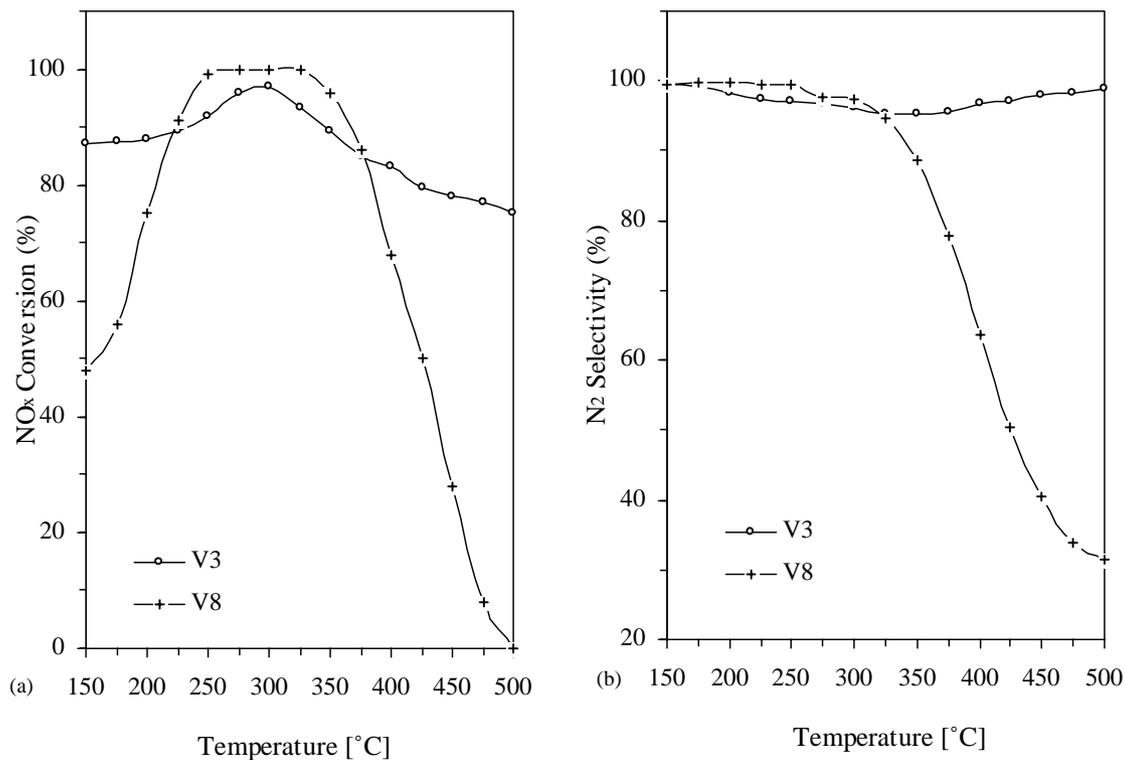
Fig. 5. NO$_x$ conversion (a) and N$_2$ selectivity (b) vs. temperature over V3W9Ti and V8W9Ti.

Ammonia can also be oxidized by oxygen instead of NO through one of the following ways:

$$2NH_3 + \tfrac{3}{2}O_2 \rightarrow N_2 + 3H_2O \tag{R4}$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \tag{R5}$$

$$2NH_3 + \tfrac{5}{2}O_2 \rightarrow 2NO + 3H_2O \tag{R6}$$

$$4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O \tag{R7}$$
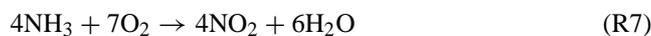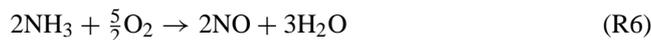
The reaction parameters were kept the same for SCR reaction and ammonia oxidation experiments to facilitate combination of the two studies in drawing conclusions for the side reactions.

The conversion of NO_x and the N_2 selectivity were calculated as

$$X_{NO_x} = 1 - \frac{[NO_x]_{out}}{[NO_x]_{in}}$$

and

$$S_{N_2} = \frac{[N_2]}{[N_2] + [N_2O]}$$

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

$$\begin{aligned} N_{2,out} =\ & \tfrac{1}{2}([NO_x]_{in} - [NO_x]_{out}) \\ & + \tfrac{1}{2}([NH_3]_{in} - [NH_3]_{out}) - [N_2O]_{out} \end{aligned}$$

The results of the steady-state reaction on V3 and V8 calcined at 500 °C as a function of temperature show that V3 catalyst exhibits a significant activity at 150 °C (87%) which increases upon increasing the temperature up to 300 °C (97%) (Fig. 5a). Below 325 °C, the amount of N_2O produced is weak (Fig. 6a), resulting in a high nitrogen
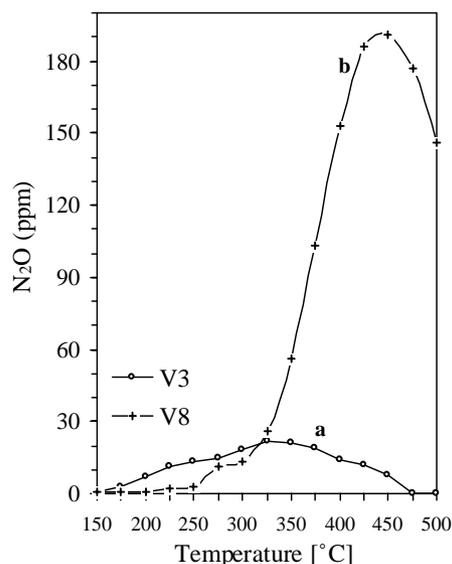
selectivity. Over 325 °C, NO_x conversion slightly decreases and reaches 75% at 500 °C and the N_2 selectivity remains high up to 500 °C.

On V8 catalyst, the NO_x conversion increases abruptly with temperature, reaching 100% conversion in temperature range (250–325 °C). At a temperature lower than 225 °C, its activity is significantly weaker than that of V3, this low reactivity explains the low formation of N_2O during the SCR reaction (Fig. 6b). The selectivity to nitrogen remains high up to 325 °C before dropping. Over 325 °C, NO_x conversion dramatically decreases and high amount of N_2O is produced due probably to the greater relative importance of the side reactions. Over 450 °C, N_2O amount further decreases.

N_2O may be formed from oxidation of ammonia by O_2 (R5) or from oxidation by $NO + O_2$ (R3). The question is, which reaction is prevailing over each catalyst. Comparing experiments carried out with and without NO_x, have shown that N_2O is formed through different ways. In fact in case V3, the amount of nitrous oxide produced in SCR reaction is weak in all working temperature and exhibits a maximum of 22 ppm at 325 °C (Fig. 6a). In ammonia oxidation, only 6 ppm of N_2O have been formed at the same temperature (Fig. 7c). The sum of the selectivity for the standard SCR reaction and for N_2O formation is lower than 100% in case V3, the missing difference is attributed to the ammonia oxidation into N_2 (R4).

In case V8, SCR reaction produces considerable amount of N_2O which reaches 186 ppm at 450 °C (Fig. 6b). High amount of N_2O was also produced during NH_3 oxidation reaching 128 ppm as a maximum at 425 °C and 125 ppm at 450 °C (Fig. 7d). The small difference in the N_2O formed during both reactions (SCR and NH_3 oxidation) indicates

Fig. 6. N_2O formation during SCR reaction over V3W9Ti (a) and V8W9Ti (b).
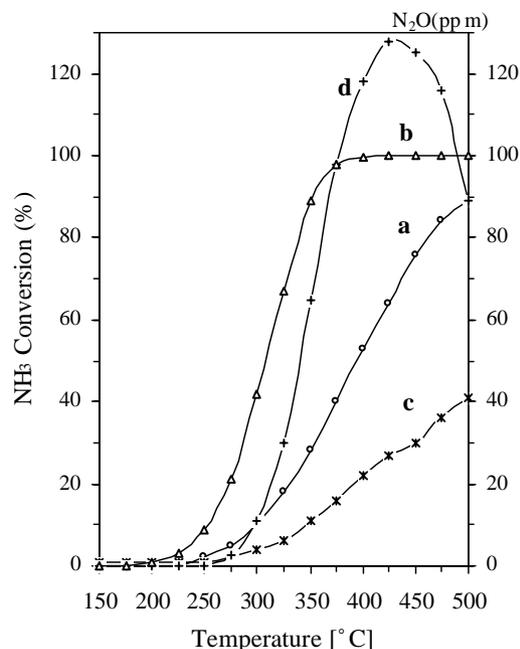
Fig. 7. Ammonia conversion (a, b) and N_2O formation (c, d) during NH_3 oxidation over V3W9Ti and V8W9Ti, respectively.

that during the SCR reaction, N_2O is mainly formed according to reaction R5.

It is interesting to note that in spite of the relatively low surface area of V8 ($22\,m^2/g$), comparatively to that of V3 ($77\,m^2/g$), its activity reaches 100% in temperature range (250–325 °C), which indicates the presence of highly active vanadia on titania support. However, the strong decrease in the activity over 325 °C suggests the presence of microcrystalline vanadia which is known to promote ammonia oxidation. During ammonia oxidation, higher selectivity to NO than to N_2O (not shown) was measured in temperature range (275–500 °C) over V3, on the contrary of V8 where high amount of N_2O was produced comparatively to NO which decreases again over 400 °C.

No adsorption of NO has been observed over both V3 and V8 catalysts under the reaction conditions, this suggests that the selective reduction of NO over both catalysts occur by an Eley–Rideal mechanism.

The decrease of N_2O amount observed at high temperature over V3 could be due to its decomposition by way [15]

$$N_2O \rightarrow N_2 + \tfrac{1}{2}O_2$$
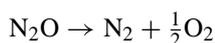
In case V8, N_2O could also be oxidised to NO by way [16]

$$N_2O + \tfrac{1}{2}O_2 \rightarrow NO,$$
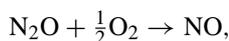
which explains the high amount of NO formed at high temperatures during ammonia oxidation. This is probably due to transition metal oxides as V–W/Ti used in our case which could also be active as catalyst for N_2O decomposition as reported by Ramanujachary and Swamy [17].

Similar experiments (SCR and ammonia oxidation) have been carried out on V3 and V8 catalysts without WO_3. The results have shown a lower activity of both catalysts over the whole temperature range and a high selectivity to N_2O and NO which indicates the effect of WO_3 on the stability of titania upon addition of vanadia. But this point will be discussed in the forthcoming paper.

4. Discussion

The results in Table 1 and Figs. 1 and 2 show that WO_3 has an influence on the crystallite growth process, providing thermal stability by inhibiting initial sintering process. The presence of large amounts of tungsten ($\sim$9%; w/w) are essential to preserve the structural and morphological properties of W/Ti samples upon addition of vanadia.

Up to 500 °C, all samples are monophasic and consist of the anatase polymorphic form of TiO_2. By increasing the calcination temperature and in the presence of vanadia, the TiO_2 anatase support exhibited a simultaneous loss in surface area and the increase of mean pore radius. Formation of crystalline WO_3 for sample with 9% (w/w) tungsten was observed at a high calcination temperature. However, only small V_2O_5 crystallites are formed at 600 °C for sample with

high vanadia loading (V8), and disappear fastly at higher calcination temperature.

Additional structural information come from the calculations of V and W concentrations which show that above the theoretical monolayer, crystalline V_2O_5 and WO_3 are not formed as it is usually observed for V_2O_5-WO_3/TiO_2 catalysts. In our case this occurs only when W and V concentrations are higher than those corresponding to three monolayers.

With our TG/DTA and XRD results we found only a very weak evidence for a clear formation of crystalline vanadia in sample V8. This characteristic feature differs from the one reported in literature [16] where crystalline vanadia has been well detected at high vanadia content. This behavior could be due to the sol–gel method which leads to a well dispersion of V on Ti support due to a strong V–Ti electrostatic interactions involving these two oxides [16], on the contrary of other methods where crystalline V_2O_5 is formed even at low vanadium content [5]. It thus seems that alkoxide route leads to immobilized vanadia layers with a higher degree of disorder and the formation of crystalline domains is strongly lowered. These results suggest the presence of a solid state solution of vanadium in anatase [8] where the V(IV) species are stabilized by interaction with titania support and further stabilization occurs at high calcination temperatures by their localisation in titania rutile lattice [7].

Some previous findings have shown that the presence of crystalline V_2O_5 appears to be essential for the formation of $V_xTi_{1-x}O_2$ (rutile) from the supported vanadia phase on the TiO_2 anatase [18]. Kozlowski et al. showed that the monolayer of surface vanadia species was first converted into crystalline V_2O_5 prior to the formation of $V_xTi_{1-x}O_2$ rutile [19]. However, in our case, V3 calcined at high temperature which was in excess of monolayer did not show any V_2O_5 crystallites before the transformation into rutile. Furthermore, in case V8, high amount of rutile (57%) was formed at 600 °C and very small crystallites of V_2O_5 have been observed at the same temperature which disappear rapidly. These results indicate that the solid state reaction between vanadia and titania anatase to form rutile outweights the V_2O_5 crystallites formation. We therefore conclude that it is not necessary to have the rutile after the formation of crystalline V_2O_5 on titania support.

Both V3 and V8 catalysts exhibit high reactivity in the selective catalytic reduction of NO_x. More significant changes in activity occurred on sample with high vanadia content. In fact, total NO_x conversion was observed at 250 °C on catalyst V8 and preserved only up to 325 °C. Over 325 °C, its SCR activity was lower than that of V3 because part of ammonia was consumed in side reactions (R5) leaving less ammonia to react in the standard SCR reaction which leads to the increase in NO concentration. In case V3, N_2 was not formed only by SCR reaction but also by ammonia oxidation which explains the slight decrease in SCR activity due to consumption of the reducing agent and the increase in the selectivity to nitrogen observed over 325 °C.

Over V3, very low amount of N_2O was formed during the SCR reaction which was found to result mainly from the unwanted SCR reaction, while over V8, N_2O was formed mainly through direct oxidation of ammonia and on the contrary of V3, the N_2O amount was considerable. This indicates the different nature of active sites present over both catalysts. Several previous findings have shown that the polymeric metavanadate species which are formed in the case of high vanadia loading, are more reactive than those of monomeric species [20]. These agree with our results which show higher reactivity of V8 catalyst comparatively to V3, indicating the presence of high fraction of polymeric vanadia. However, the dramatic decrease in the NO_x reduction occurring upon increasing the working temperature indicates the presence of microcrystalline V_2O_5 particles which are known to promote ammonia oxidation. Low vanadia loading leads to well dispersion of vanadia on Ti support, which improves the selectivity to N_2 [21]. With high vanadia loading, segregation into bulk V_2O_5 takes place decreasing the interaction with titania and results in a significant change of its catalytic performances. From these results, we can conclude that V3 catalyst has the widest temperature window for high NO_x conversion and N_2 selectivity than V8.

5. Conclusions

The results presented above show that the state of V_2O_5-WO_3/TiO_2 catalyst is strongly dependent on calcination temperature and V_2O_5 content. High vanadia loading decreases the temperature required for conversion of titania anatase into rutile. It has been observed that crystallites of V_2O_5 and WO_3 are formed when their concentrations are greater than those corresponding to three monolayers and that the anatase to rutile transformation did not occur necessary after V_2O_5 crystallites formation. This suggests the existence of high electronic interactions between V and Ti species due probably to the alkoxid route used for the preparation of the catalysts in our case.

Vanadia content strongly influences the catalytic behavior of V-W/Ti catalyst. Indeed, the well dispersed and isolated vanadium oxide species were found to be weakly active for the SCR reaction but with a high selectivity to N_2. Increasing vanadia loadings leads to the sintering of the TiO_2 support and to aggregation of isolated vanadium ions which favours the activity in the SCR reaction but only in a narrow temperature window and promotes the undesired ammonia oxidation at high temperatures.

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