**Promotional effect of ceria on the catalytic behaviour of new V₂O₅-WO₃-
TiO₂ aerogel solids for the DeNO_x process**

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Abstract

New cerium and/or tungsten modified V₂O₅-TiO₂ aerogel catalysts (V₂O₅-TiO₂, V₂O₅-WO₃-TiO₂, V₂O₅-CeO₂-TiO₂ and V₂O₅-WO₃-CeO₂-TiO₂) were successfully developed, by associating the sol gel procedure and supercritical drying approach. A combination of various analytical techniques, including XRD, N₂-Physisorption at 77 K, DRUV-Vis spectroscopy, NH₃-TPD and H₂-TPR, was used to characterize the obtained solids. Their catalytic performances were evaluated in the low temperature NO-SCR by NH₃. The results reveal that all the materials exhibit high cristallinity of TiO₂ anatase phase and developed mesoporous texture. The addition of tungsten (W) increases the surface acidity of V₂O₅-TiO₂ and thereby enhances its reactivity at high temperatures (> 420 °C). However, the addition of cerium (Ce) improves the redox properties of the latter catalyst and increases significantly its NO-SCR reactivity, especially at low temperatures. The NO-SCR activity increases over the aerogel systems, in the 200-400 °C temperature range, following this order: V₂O₅-WO₃-TiO₂ < V₂O₅-TiO₂ < V₂O₅-CeO₂-TiO₂ < V₂O₅-WO₃-CeO₂-TiO₂. The new V₂O₅-WO₃-CeO₂-TiO₂ system was found to be the most active catalyst for converting NO into N₂ (with 60 % and 90 % NO conversions at 250 °C and between 320 and 420 °C, respectively). The highest SCR activity of this new aerogel solid if compared to the other samples was essentially correlated with a good reactivity of its acidic and redox sites which in turn was related to the existence of

strong interactions between cerium and the other active elements (mostly $\text{Ce} \leftrightarrow \text{V}$ and $\text{Ce} \leftrightarrow \text{W}$).

Key words: Environmental remediation, DeNO_x process, Transition metals, Rare earths, New aerogel solids, Modified $\text{V}_2\text{O}_5\text{-TiO}_2$

1. Introduction

Simple/complexed oxides are a wide class of materials, with diverse crystal structures, which can be synthesized via different methods and are characterized by amazingly diverse properties (acidic, basic, redox, electric, dielectric, optical, magnetic, photocatalytic, catalytic, electrochemical, ferroelectric, piezoelectric, semiconductivity, ionic conductivity ...) which make them quite useful in a large range of applications including electro-optical, electro-mechanical, electronics, energy storage, drug delivery, magnetic resonance imaging, biosensors and catalysis [1-14]. Recently, transition metal oxides have demonstrated high catalytic performance in the selective catalytic reduction (SCR) of nitrogen oxides (NO_x) by ammonia (NH_3) [15].

Nitrogen oxides (NO_x , $x = 1, 2$), discharged from power plants, waste incinerators, industrial boilers, engines and automobiles, can cause adverse effects to the human health (bronchitis, pneumonia...) and contribute to a series of environmental issues (photochemical smog, acid rain, ozone decline in middle to high latitudes from spring to fall, biological death of lakes and rivers...) [16,17]. Many control technologies have been developed in order to reduce NO_x emissions. Among them, the NH_3 -SCR has been proved to be one of the most successful methods for the purification of NO_x from stationary sources and diesel vehicles [18-20]. A variety of NH_3 -SCR catalysts, including noble metals, zeolites, carbon-based catalysts and transition metal oxides have been explored [21-23]. Especially, $\text{V}_2\text{O}_5/\text{TiO}_2$ systems, promoted by WO_3 or MoO_3 , have been extensively used in the industry and demonstrated an excellent NO_x removal efficiency in the 300-400 °C temperature range [24-29]. For such catalysts: TiO_2 is employed as a carrier because of its high surface area and porosity which are beneficial for the catalytic reactions and reactants adsorption. V_2O_5 is the main active substance, which generates active redox sites and exhibits strong catalytic activity and stability, while WO_3 or MoO_3 act as ‘chemical’ and ‘structural’ promoter by enlarging the

temperature window of the SCR reaction, limiting the oxidation of SO_2 and improving the mechanical strength of catalysts [30].

Generally, the high activity and stability of supported metal oxide catalysts depend on the active sites dispersion and metal-support interactions. In this respect, the preparation method is a vital factor to determine the phase composition, configuration and dispersion of the active components. Therefore, it is crucial to find the appropriate preparation method to optimize the SCR performances of catalysts [31]. According to the literature reports, the main synthesis methods of V_2O_5 - TiO_2 -based SCR catalysts are (wet, dry, incipient wetness and ultrasound- assisted)-impregnation [27,32-35], co-precipitation [34] and deposition-precipitation [35-37]. Pang et al. [35] showed that the ultrasound- assisted impregnation method produced a stronger interaction between the vanadium species and WTi support, which stabilized these species in the reduced state and leads to more active VWTi SCR catalyst compared to the same one obtained via the conventional impregnation method. On the other hand, He et al. [34] concluded that the SCR activity is always greater for the VWTi co-precipitated catalysts compared to the impregnated VWTi ones for the same catalyst composition and surface area.

In recent years, cerium has been extensively studied as an accessory element for NH_3 -SCR catalysts because of its high oxygen storage capacity (OSC) and remarkable redox properties [38-40]. CeO_2 is also considered as the active component in the SCR reaction due to its ability to enhance the oxidation of NO to NO_2 [41]. In addition, oxygen vacancies exist on the CeO_2 surface which facilitates the adsorption and activation of NO and NH_3 , and subsequently increases the NH_3 -SCR activity [42]. Chen et al. [42] investigated the effect of the additive Ce on V_2O_5 - WO_3 / TiO_2 system for the selective catalytic reduction (SCR) of NO_x with NH_3 . Their results showed that adding Ce could enhance the NO_x adsorption and then accelerate the SCR reaction due to the synergetic interaction between the Ce and V, W

species. Cheng et al. [43] demonstrated that the SCR activity of $V_2O_5-WO_3/TiO_2$, elaborated by the homogeneous precipitation method, was greatly enhanced by Ce doping (molar ratio of $Ce/Ti = 1/10$) in the TiO_2 support. However, Hu et al. [44], reported that $CeO_2-V_2O_5-WO_3/TiO_2$ catalysts, obtained via the impregnation method, exhibited a higher NH_3 -SCR activity and better Na resistance than the $V_2O_5-WO_3/TiO_2$ catalyst.

Based on the above discussion, and taking into account (i) the advantages of using the sol gel method for the preparation of highly active aerogel catalysts for the DeNO_x process ([45-48] and (ii) that until now, any research work has not been devoted to the investigation of VWTi and VWCeTi aerogel solids in the NH_3 -SCR reaction, it appeared interesting to develop in this work a new $V_2O_5-WO_3-TiO_2$ and $V_2O_5-WO_3-CeO_2-TiO_2$ aerogel catalysts, containing V and W amounts representative of $V_2O_5-WO_3/TiO_2$ commercial SCR catalyst (2% wt. V_2O_5 and 10 % wt. WO_3), for the selective catalytic reduction of NO by NH_3 from diesel engine exhaust. It is worth mentioning that Ce and W species were added in order to improve the redox and acidic performances to $V_2O_5-TiO_2$ system, respectively. In fact, it is established that both acidic and redox properties of catalyst are the key factors which govern its SCR activity [49]. It was revealed that the surface acidity plays an important role in the adsorption and activation of ammonia, especially at high temperature. However, the reactivity of catalyst is controlled, at low temperature, by its redox behaviour [49].

2. Material and methods

2. 1. Aerogel catalysts preparation

It is well known that, several advantages distinguish the sol-gel procedure including a simple technology, low processing temperature and flexible control of the structure and size of final products via many operating parameters [50,51]. Therefore, this method was adopted in this work for the elaboration of aerogel samples (TiO_2 , $V_2O_5-TiO_2$, $V_2O_5-WO_3-TiO_2$, $V_2O_5-CeO_2-TiO_2$ and $V_2O_5-WO_3-CeO_2-TiO_2$) according to the same procedure described in our

previous works [45,46]. Vanadyl acetylacetonate ($V(C_5H_7O_2)_2$, Fluka, 95%), ammonium metatungstate hydrate ($(NH_4)_6H_2W_{12}O_{24}.xH_2O$, Sigma Aldrich, > 99.9%) and cerium nitrate ($Ce(NO_3)_3.6H_2O$, Aldrich) were used as V, W and Ce precursors. Theoretical loading of V_2O_5 , WO_3 and CeO_2 were fixed to 2, 10 and 10 % wt., respectively. All the aerogel mixed oxides were calcined at 500 °C for 3 h under O_2 flow (30 mL.min⁻¹).

2. 2. Aerogel catalysts characterization

The powder X ray diffraction (XRD) patterns were registered, between 2 and 80 °, by means of a Brüker AXS D8 diffractometer, using $CuK\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The Scherrer formula ($D = 0.89 (\lambda / \beta \cos\theta)$) [43], applied to the most intense peak of TiO_2 anatase phase ($\sim 2\theta = 25^\circ$), was used for the calculation of the crystallites size (D) of samples. λ is the wavelength of XR radiation, β is the corrected peak width at half-maximum intensity (FWHM in radians), and θ is the peak position of the main reflection.

The textural properties of solids (specific surface area (S_{BET}), total pore volume (V_{PT}) and pore size diameter (Φ_{pore})) were determined by N_2 adsorption-desorption at 77 K with a Micromeritics ASAP 2020 equipment. Prior to adsorption measurement, the sample was degassed in an evacuation chamber at 200 °C.

The UV-vis diffuse reflectance absorption spectra of powder aerogels were collected at room temperature on a PerkinElmer spectrophotometer type lambda 45 equipped with an integrating sphere type RSA-PE-20. The scanning range was between 200 nm and 900 nm.

The NH_3 temperature-programmed desorption (NH_3 -TPD) analyses were performed using an AUTOCHEM 2920 (Micromeritics) equipped with a TCD detector. A 0.05 g of each catalyst was loaded in the reactor and was pretreated in air flow (30 mL min⁻¹) at 500 °C (ramp 10 °C min⁻¹) for 30 min, and then cooled to 100 °C in the same stream. Afterward, the pretreated sample was exposed to NH_3 (5 vol% NH_3 in He, flow rate = 30 mL min⁻¹) for 45 min. The physisorbed NH_3 was removed by flushing the catalyst with He at a flow rate of 30

mL min⁻¹ for 2 h before starting the TPD experiment. The NH₃-TPD curves were recorded by heating the samples in He (30 mL min⁻¹) from 100 to 600 °C at a heating rate of 10 °C min⁻¹.

The H₂ temperature-programmed reduction (H₂-TPR) experiments were carried out in an AUTOCHEM 2910 (Micromeritics) using 0.05 g of catalyst. Prior to the analysis, the sample was pretreated at 500 °C with 5 vol % O₂ in He (30 mL min⁻¹) for 30 min (ramp 10 °C min⁻¹). The TPR experiments were realized using a stream of 5 vol % H₂ in Ar (30 mL min⁻¹) from 50 to 800 or 900 °C at a heating rate of 10 °C min⁻¹. The hydrogen consumption was measured by a thermal conductivity detector.

2. 3. Catalytic performance test

The selective Catalytic Reduction (SCR) tests were done in a fixed-bed quartz flow reactor, operating at atmospheric pressure, using the following reaction conditions: 400 ppm NO, 400 ppm NH₃, 8 % O₂ in He and 100 mL min⁻¹ total flow rate yielding a gas hourly space velocity (GHSV) of 120,000 h⁻¹. Before measurements, the catalyst (0.05 g) was activated in situ at 200 °C for 30 min under O₂/He (20/80, v/v) flow then cooled to 100 °C. Afterward, the NO conversion curves were recorded between 100 and 500 °C with the heating rate of 6 °C min⁻¹. The reactants and products gases were continuously analyzed by an online Pfeiffer Omnistar quadrupole mass gas spectrometer equipped with Channeltron and Faraday detectors (0-200 amu).

3. Results and discussion

3. 1. Characterization of aerogel catalysts

The structural properties of samples were examined by XRD, the results are given in Fig 1 and Table 1. As shown in Fig 1, the dominant phase in all the XRD patterns is TiO₂ anatase which is identified by its characteristic peaks located at $2\theta \approx 25.3^\circ$ (hkl:101); 36.9° (103); 37.8° (004); 38.6° (112); 48.2° (200); 53.9° (105); 55.2° (211); 62.7° (204); 69.0°

(116); 70.4° (220) and 75.2° (215) [ICSD 01-083-2243]. Additional minor peak is observed at $2\theta = 27.2^\circ$ (110) in the diffractograms of V_2O_5 -TiO₂ and V_2O_5 -WO₃-CeO₂-TiO₂ catalysts and is attributed to a trace amount of the TiO₂ rutile phase [ICSD 01-076-1941]. Noting that a low amount of cubic CeO₂ seems to be formed at the surface of V_2O_5 -WO₃-CeO₂-TiO₂, since a new peaks of low intensity are detected at $2\theta \approx 28.5^\circ$ (hkl: 111) and 32.9° (200) [ICSD 00-034-0394] on the diffractogram of the previous cited sample. It is worth mentioning that the absence of reflections related to crystalline phases V₂O₅ (major one at $2\theta = 20.2^\circ$ (001) [ICSD 01-089-2482]) and WO₃ (major one at $2\theta \approx 23.7^\circ$ (hkl: 110) [ICSD 01-089-8053]) for all the catalysts and the presence of a low quantity of cubic CeO₂ in the case of V_2O_5 -WO₃-CeO₂-TiO₂ only indicate, in line with the results already obtained by Hu et al. [44], for comparable systems, that V, W and Ce species are well dispersed and exist in the form of monolayer species at the surface of TiO₂ carrier. Based on the above XRD results and taking into account the values of the crystallites size of powder aerogels (ranging between ~ 9 and 29 nm, Table 1), it can be concluded that all the obtained catalysts are well structured materials with a nanometer size of grain. It should be mentioned the addition of vanadium, tungsten and cerium contributes to the growth of the TiO₂ crystallites size. This may be due to the agglomeration of the metal clusters to form larger particle size [52]. Furthermore, the formation of trace amount of the TiO₂ rutile phase, in the case of V_2O_5 -TiO₂ and V_2O_5 -WO₃-CeO₂-TiO₂ catalysts, contributes also to the increase of the crystallites size of titania carrier [53].

Table 1. XRD phases and TiO₂ crystallites size of aerogel catalysts.

Aerogel mixed oxides	XRD phases	FWHM (°)	TiO ₂ crystallites size D (nm)
TiO ₂	A	0.892	8.6
V ₂ O ₅ -TiO ₂	A + R (t)	0.626	12.4
V ₂ O ₅ -CeO ₂ -TiO ₂	A	0.761	10.2
V ₂ O ₅ -WO ₃ -TiO ₂	A	0.808	9.5
V ₂ O ₅ -CeO ₂ -WO ₃ -TiO ₂	A + R (t) + CeO ₂ (t)	0.266	28.8

Figure 1. Powder XRD patterns of aerogel catalysts.

The textural properties of samples are given in Table 2. It is clearly seen that all the aerogel oxides, except for the V₂O₅-WO₃-CeO₂-TiO₂ solid, display a developed texture with a high surface area ($82 \leq S_{\text{BET}} \leq 128 \text{ m}^2/\text{g}$) and total pore volume ($0.33 \leq V_{\text{PT}} \leq 0.41$). The lowest values of the S_{BET} and V_{PT} , obtained in the case of V₂O₅-WO₃-CeO₂-TiO₂ catalyst,

could reveal the blockage of some pores of TiO₂ carrier by V, W and/or Ce supported species. This is consistent with the result already obtained by Hu et al. [44] demonstrating that the BET surface area and total pore volume of VWTi catalysts tend to decrease after doping CeO₂, and this tendency is more obvious with the higher amount of CeO₂. The authors suggested that the highly dispersed CeO₂ blocks the micropores of catalysts.

Table 2. Textural properties of aerogel catalysts.

Aerogel mixed oxide	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average Pore diameter (Φ_{pore} , Å)
TiO ₂	122	0.33	79
V ₂ O ₅ -TiO ₂	101	0.37	117
V ₂ O ₅ -CeO ₂ -TiO ₂	82	0.33	133
V ₂ O ₅ -WO ₃ -TiO ₂	128	0.41	111
V ₂ O ₅ -CeO ₂ -WO ₃ -TiO ₂	43	0.21	158

The N₂ adsorption-desorption isotherms at 77 K and pores size distribution curves of samples are displayed in Fig. 2. It is clearly seen that, all the catalysts are characterized by a type IV isotherm, typical of mesoporous materials according to the IUPAC classification [54], and unimodal porous distribution with diverse types of hysteresis loops. So, the H1 type of hysteresis, revealing the presence of cylindrical mesoporous channels [55], is obtained in the case of V₂O₅-TiO₂, V₂O₅-CeO₂-TiO₂ and V₂O₅-WO₃-CeO₂-TiO₂ samples. However, the hysteresis loop of H2 type is found for the TiO₂ and V₂O₅-WO₃-TiO₂ solids and it indicates the presence of ink-bottle pores in their mesoporous texture [56].

Figure 2. N₂ Adsorption-desorption isotherms and pore size distribution curves of aerogel catalysts.

Fig. 3 shows the UV-Vis diffuse reflectance spectra of different catalysts. According to the literature reports [45,57], the typical absorption bands of TiO_2 are situated between 200 and 400 nm, which are attributed to the $\text{O}^{2-} \rightarrow \text{Ti}^{4+}$ charge transfer corresponding to the excitation of electrons from the O2p valence band to the Ti3d conduction band. Additional bands with different intensities are observed in the 350-400 nm range for the catalysts containing vanadium and/or cerium which could be assigned to $\text{O}^{2-} \rightarrow \text{V}^{5+}$ charge transfer (CT) transitions in various VO_x surface species [57,58] and/or $\text{O}^{2-} \rightarrow \text{Ce}^{4+}$ CT transitions of hexacoordinated cerium species [45,59]. It is worthy to note that, tungsten, vanadium and cerium species can display absorption bands corresponding to $\text{O}^{2-} \rightarrow \text{M}^{n+}$ CT transitions ($\text{M} = \text{W}, \text{V}$ or Ce) in the same region than those of TiO_2 support as it was indicated in table 3. It should be noted also that the weak bands located at around 520 nm and 665 nm on the UV spectra of all the catalysts can be ascribed to a low amount of crystalline V_2O_5 , probably too small to be detected by XRD technique, and to V^{4+} d-d transitions, respectively [60]. Nevertheless, no band related to the crystalline phase of WO_3 (usually at 430-450 nm [61]) is detected in the UV spectra of aerogels containing tungsten. Based on the obtained UV-vis results, it can be suggested the presence of a diversity of highly dispersed cerium, vanadium and tungsten species at the TiO_2 surface.

Figure 3. DRUV-Vis spectra of aerogel catalysts.

Table 3. UV-vis diffuse reflectance band positions and assignments found in the literature for M species (M = V, Ce and W).

M	DRUV-vis band Position: λ (nm)	Type of transition	Assignments	Ref.
V	240-280	$O^{2-} \rightarrow V^{4+}$ LMCT	Monomeric tetrahedral V^{4+} species	[46,62]
	280-340	$O^{2-} \rightarrow V^{5+}$ LMCT	Monomeric tetrahedral V^{5+} species	[46,62]
Ce	220-250	$O^{2-} \rightarrow Ce^{3+}$ LMCT	tetracoordinated Ce^{3+}	[63,64]
	280-300	$O^{2-} \rightarrow Ce^{4+}$ LMCT	tetracoordinated Ce^{4+}	[63,64]
W	220-240	$O^{2-} \rightarrow W^{6+}$ LMCT	Isolated tetrahedral W^{6+}	[55]
	320-340	$O^{2-} \rightarrow W^{6+}$ LMCT	Polymeric octahedral W^{6+}	[55]

Acid sites are the adsorption and activation sites for ammonia during the NH_3 -SCR reaction. Therefore, the surface acidity of samples was examined by NH_3 -TPD technique and the results are depicted in Fig. 4. As it can be seen the strength and the number of acid sites are clearly affected by the type of the elements added to titania oxide. So, the highest total acidity is obtained in the case of $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ catalyst which displays the most intense and large NH_3 desorption peaks between 100 and 550 °C corresponding to the ammonia desorbed from weak, medium and strong acid sites [47,65]. As shown also in Fig. 4, a higher number of acid sites, related to NH_3 desorption in the 100-400 °C temperature range, exist at the surface of $\text{V}_2\text{O}_5\text{-CeO}_2\text{-TiO}_2$ compared to that of $\text{V}_2\text{O}_5\text{-TiO}_2$. This result reveals, in agreement with many previous reports [4,66-69], that cerium and, particularly, tungsten species contribute to the creation of new and diverse acid sites at the surface of $\text{V}_2\text{O}_5\text{-TiO}_2$ catalyst. It seems that these new acid sites are generated by the presence of W and Ce species and through the interactions developed between them and with Ti and/or V elements. Noting that the lowest acidity is registered in the case of $\text{V}_2\text{O}_5\text{-WO}_3\text{-CeO}_2\text{-TiO}_2$ solid suggesting that the simultaneous presence of V, W and Ce species had a negative effect on the surface acidity of this aerogel catalyst. This is probably due to the existence of concurrent interactions between V, W and Ce species or between these supported species and the TiO_2 support which influence the surface acidity of solid. Similar result, revealing a visible decrease of the surface acidity of the zirconia after adding cerium, molybdenum and tungsten species, was reported in our previous work and was related to the existence of diverse interactions between the support and the supported active species which cover or change the nature of acidic sites at the ZrO_2 surface [47].

Figure 4. NH₃-TPD profiles of aerogel catalysts.

In addition to the surface acidity, the redox behaviour of catalyst had a great influence on the SCR reaction. Herein, the H₂-TPR analyses were done to examine the redox properties of aerogel solids and the obtained results are shown in Fig. 5. As it can be noticed, two unresolved peaks, maximizing at 430 and 500 °C, are observed for the binary V₂O₅-TiO₂ and can be ascribed to the reduction of highly dispersed VO_x species [42,46]. When W or Ce species were introduced into V₂O₅-TiO₂ system, a new H₂ consumption peaks are appeared at different temperatures indicating the creation of new and various redox sites at the catalysts surface. Hence, the well resolved peak beginning at ~ 370 °C, with a maximum at 537 °C, detected in the H₂-TPR profile of V₂O₅-CeO₂-TiO₂ can be related to the reduction of surface oxygen of cerium, vanadium and cerium species [45,70-71]. For the V₂O₅-WO₃-TiO₂ sample, the peaks observed in the 400-600 °C temperature range and at 770 °C can be correlated with the reduction of vanadium [42,46] and tungsten [42,46,70] species, respectively. The V₂O₅-CeO₂-WO₃-TiO₂ sample displays similar (but less intensive) H₂ consumption peaks compared

to those obtained in the case of $V_2O_5-WO_3-TiO_2$ solid. This indicates the presence of reducible O, V, Ce and W species at the $V_2O_5-WO_3-CeO_2-TiO_2$ surface. Nevertheless, the reduction of tungsten species occurred at higher temperature in the presence of cerium (at 860 °C for VWCeTi and 770 °C for VWTi). This could confirm, in line with the NH_3 -TPD results, the existence of strong interactions between the supported elements which affect the reducibility of catalysts.

Figure 5. H_2 -TPR profiles of aerogel catalysts.

3. 1. *NO-SCR activity of aerogel catalysts*

The NO conversion versus reaction temperature recorded for the aerogel catalysts are displayed in Fig 6. As it can be noticed, the $V_2O_5-TiO_2$ catalyst is more active than TiO_2 support for the NO reduction, particularly between 200 and 400 °C. This is due to the presence of active redox sites generated by vanadium species at the catalyst surface, which improves the SCR activity of solid, especially below 400 °C [46]. Nevertheless, only a

maximum of ~ 67 % NO conversion into N₂ is obtained over the V₂O₅-TiO₂ catalyst at 450 °C. The addition of tungsten into V₂O₅-TiO₂ sample decreases the SCR activity between 200 and 410 °C but it increases the NO conversion (~ 68 %) into N₂ at high temperatures (T > 420 °C). The enhancement of the SCR activity of the V₂O₅-WO₃-TiO₂ sample at high temperature can be correlated with the reactivity of acidic sites created by tungsten species. In fact, it was reported that tungsten oxide acts as a promoter owing to its Brønsted acidity which enhances ammonia adsorption on the catalyst during the SCR reaction [34]. The V₂O₅-CeO₂-TiO₂ solid demonstrates much higher SCR activity than those obtained over V₂O₅-TiO₂ and V₂O₅-WO₃-TiO₂. It exhibits, thanks to the redox sites created by cerium species, more than 80 % NO conversion into N₂ between 320 and 410 °C. This underlines, in agreement with our previous study [45], the crucial role of the OSC and redox performance of cerium species for DeNOxing at low temperature. Markedly, the DeNOx activity of V₂O₅-WO₃-CeO₂-TiO₂ catalyst is clearly higher than those obtained over all the other samples, in the whole temperature range of the experiment (150-500 °C). Hence, the T 50 and T 90 (temperatures for which 50 % and 90 % of NO conversions into N₂ are achieved) are: 245 and 320 °C, respectively. Taking into account the characterization results, demonstrating that V₂O₅-WO₃-CeO₂-TiO₂ develops the lowest surface area and acidity, it can be suggested, in line with the result already obtained by Hu et al. [44] for comparable systems (CeO₂-V₂O₅-WO₃/TiO₂) that, in this case, the BET surface area is not responsible for the catalytic activity. Therefore, the superior SCR performance of the new V₂O₅-WO₃-CeO₂-TiO₂ catalyst can be essentially related to a good mobility of surface oxygen species and a high reactivity of surface acid and redox sites, most probably due to the existence of strong interactions between the supported actives elements, mainly Ce↔V and Ce↔W. It should be also mentioned that the decrease of the NO conversion at high temperature for all the samples, except for V₂O₅-WO₃-TiO₂ solid, can be explained by the absence of active acidic sites for high temperature at their surfaces. In

fact, it was reported that the surface acidity of catalyst plays an important role in the adsorption and activation of ammonia, especially at high temperature [72].

Figure 6. NO conversion versus reaction temperature over the aerogel catalysts.

4. Conclusion

In this study, new W and/or Ce modified V₂O₅-TiO₂ aerogel catalysts (V₂O₅-TiO₂, V₂O₅-WO₃-TiO₂, V₂O₅-CeO₂-TiO₂ and V₂O₅-WO₃-CeO₂-TiO₂) were prepared, characterized and tested in the DeNO_x process. The results show that the addition of WO₃ improves the surface acidity and, consequently, the high temperature SCR-activity of V₂O₅-TiO₂ derived sol gel catalyst. However, the presence of CeO₂ enhances the redox performance of the later catalyst and obviously increases its SCR activity at low temperature. Among all the samples investigated, the new aerogel V₂O₅-WO₃-CeO₂-TiO₂, which exhibits the lowest surface area and acidity, was found to be the most active catalyst for the NO removal with 60 % and above 90 % of NO conversions into N₂ at 250 °C and in the 320-420 °C temperature range,

respectively. The highest SCR activity of this novel aerogel system was correlated with a high reactivity of surface acid and redox sites, most probably induced by the strong interactions developed between the supported active elements, mainly $\text{Ce} \leftrightarrow \text{V}$ and $\text{Ce} \leftrightarrow \text{W}$.

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