A new V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-} nanostructured aerogel catalyst for Diesel DeNOx technology

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Abstract

New V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-} nanostructured aerogel catalyst, containing V and Mo amounts representative of V_2O_5 - MoO_3 / TiO_2 commercial SCR catalyst, was developed via the one step sol gel method combined to supercritical drying approach for the low temperature selective catalytic reduction of NO by NH_3 , in excess O_2 . The new V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-} system was analysed by XRD, N_2 -Physisorption, H_2 -TPR, NH_3 -TPD, Raman, XPS and DRUV-Vis spectroscopy. The elaboration and characterization of TiO_2 , V_2O_5 - TiO_2 , MoO_3 - TiO_2 , V_2O_5 - MoO_3 - TiO_2 , TiO_2 - SO_4^{2-} , V_2O_5 - TiO_2 - SO_4^{2-} and MoO_3 - TiO_2 - SO_4^{2-} aerogel samples were reported also in this work. The results proved the successful synthesis of nanostructured aerogel materials with a good cristallinity of TiO_2 anatase phase, developed mesoporous texture and nanometer size as a new SCR catalysts. V, Mo and SO_4^{2-} were found highly dispersed on the TiO_2 surface, their presence and the diverse interactions, developed between them, strongly affect the physicochemical properties and catalytic behaviour of the derived sol-gel solids. Among all the samples investigated, the new aerogel V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-} was found to be the most efficient catalyst for the low temperature NO-SCR: compared to a V_2O_5 - WO_3 / TiO_2 commercial catalyst (EUROCAT), it demonstrates a similar SCR activity in the 200-375 °C temperature range, but, at higher temperatures (375-500 °C), it exhibits superior catalytic efficiencies. A total NO conversion into N_2 is achieved in the 450-500 °C temperature range

over the new $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ nanostructured aerogel catalyst, when the $\text{NH}_3\text{-SCR}$ reaction was realized using 1000 ppm NO and 1000 ppm NH_3 , in the presence of 3.5 % H_2O .

Key words: Aerogel; $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2$; Sulfate; V- SO_4^{2-} -Mo interactions; Commercial SCR catalyst; Diesel De- NO_x technology.

1. Introduction

Nitrogen oxides (NO_x), emitted from stationary and mobile sources are the major air pollutants which can cause seriously adverse environmental and human health problems, including ozone depletion, acid rain, greenhouse effects, haze, photochemical smog, eye and throat irritation, chest tightness, nausea and headache, respiratory diseases like bronchitis, pneumonia, etc. [1,2]. Selective catalytic reduction of NO_x by ammonia (NO-SCR or NH₃-SCR), in excess O₂, has been considered as the most efficient available technology for nitrogen oxide removal from stationary sources and diesel exhausts [3-4]. V₂O₅-WO₃(MoO₃)/TiO₂ commercial catalysts, containing ~ 0.1-2 wt. % V₂O₅ and 10 wt. % WO₃ or 6 wt. % MoO₃ (generally deposited by the impregnation method), are still widely used in thermal power plants and coal-fired boilers [5-7]. V₂O₅ represents the most active phase, while, WO₃ and MoO₃ act as ‘chemical’ and ‘structural’ promoter by enlarging the temperature window of the SCR reaction, limiting the oxidation of SO₂ and improving the mechanical strength of catalysts [8,9]. Analogous catalytic systems, optimized for Diesel vehicle applications, contain higher amount of vanadia (1.5-2 wt. %) to achieve high DeNO_x activity [10]. Nevertheless, the high starting temperature, the narrow active temperature window (300-400 °C) and the low N₂ selectivity at high temperature remain the major drawbacks of V₂O₅-WO₃ (MoO₃)/TiO₂ industrial systems [11,12].

It is estimated that diesel engines contribute to about 85 % of all the NO_x emissions from mobile sources, principally in the form of NO [13,14]. Therefore, the emission of NO_x from vehicle is limited by various standards, such as Euro V and Euro VI. In Euro V, it is limited to < 180 mg/Km for diesel-driven engine and 60 mg/Km for petrol-driven engine. However, the NO_x emissions from Euro VI is 55 % lower than that from Euro V [15,16].

According to the literature, the SCR process for mobile applications can be summarized by the followings main reaction [17-18]:

In diesel engine, this process requires a highly efficient catalyst operating in oxygen rich exhaust gas, at high gas hourly space velocity (GHSV) over a wide temperature range (200-500 °C) [19]. The three way catalysts (TWC) have been successfully used by the automotive industry for the simultaneously elimination of harmful emissions (NO_x, CO and unburned hydrocarbon (HC)) from gasoline-powered engines that work in stoichiometric air-to-fuel ratio. However, this system cannot be used for diesel vehicles, because of the oxygen-rich atmosphere where NO_x reduction cannot be easily achieved [20-22]. Zeolite-based catalysts promoted by transition metals such as Fe and Cu are being considered for practical applications in diesel emission control [19]. Nevertheless, the insufficient low-temperature activity of Fe-ZSM-5 and the poor hydrothermal stability of Cu-ZSM-5 are neither satisfactorily solved [23].

Owing the required higher De-NO_x efficiency and in order to meet the increasingly stringent legislations for NO_x emission in mobile applications, a lot of efforts have been recently concentrated on the optimization of SCR catalysts for broadening the active De-NO_x temperature window as widely as possible, enhancing the catalysts durability and reducing the cost of De-NO_x systems [24]. Despite the low cost of Mo (in comparison with W "for which the price has risen about 30 times compared to ten years ago") and in spite of the fact that V₂O₅-MoO₃/TiO₂ SCR catalysts have been introduced on the commercial scale, only a few studies related to this subject have been reported in the literature [25-29,30-33]. In this framework, L. Lietti *et al.* [25,26] studied the V₂O₅-MoO₃/TiO₂ De-NO_x SCR catalysts, prepared by the incipient wetness method, and suggested that molybdenum oxide acts as “chemical” promoter

for SCR reaction besides playing “structural” promoter for the catalyst. Moreover, L. Zhu *et al.* [28] showed that the addition of 5 wt. % MoO₃ enhances the low temperature (150-300 °C) NH₃-SCR activity of VWTi catalysts. Recently, Xu *et al.* [30] studied the SO₂ tolerance of V₂O₅-MoO₃/TiO₂ catalyst. They concluded that a high proportioned stable tridentate sulfates on VMoTi-S surface act as strong Brønsted acid sites which liberates more active polymeric vanadates to activate the adsorbed NH₄⁺ to form -NH₂ species as a crucial intermediate for NH₃-SCR reaction. More recently, Wu *et al.* [32], investigated the effect of doping of expanded graphite (EG) with different methods on SCR performance over V₂O₅-MoO₃/TiO₂ [32]. Their results demonstrated that doping of EG by high shear method enhances the surface area, increases Brønsted and Lewis acid sites, raises the VO²⁺ and adsorbed surface oxygen species and consequently leads to the most active SCR catalyst.

Over the last few years, several studies proved that the direct sulfating of SCR catalysts (such as: V₂O₅-CeO₂-TiO₂-SO₄²⁻ [34], V₂O₅-SO₄²⁻/TiO₂ [35], V₂O₅-WO₃-TiO₂-SO₄²⁻ [36] and CeO₂-ZrO₂-NiO-SO₄²⁻ [37]) improves their acidity, enhances their stability and, thus, increases both their high temperature activity and N₂ selectivity. Nevertheless, up to date any direct modification of V₂O₅-MoO₃/TiO₂ SCR catalyst by sulfate ions has not been investigated.

Taking into account the key role of sulfate groups in increasing the high temperature SCR activity (NO conversion and N₂ selectivity) and that until now no studies devoted to the direct sulfating of V₂O₅-MoO₃/TiO₂ SCR catalyst has been described in the literature, we have developed in this work, using the one step sol gel method combined to supercritical drying approach, a new V₂O₅-MoO₃-TiO₂-SO₄²⁻ aerogel catalyst, containing V and Mo loadings representative of V₂O₅-MoO₃/TiO₂ commercial SCR one (2 wt. % V₂O₅ and 6 wt. % MoO₃), for De-NO_xing in Diesel Engines in a wide temperature range (150-500 °C), under oxygen rich conditions and at relatively high GHSV (120.000 h⁻¹).

2. Experimental

2. 1. Synthesis of aerogel catalysts

The TiO₂ support and the aerogel mixed oxides (V₂O₅-TiO₂, MoO₃-TiO₂, V₂O₅-MoO₃-TiO₂, TiO₂-SO₄²⁻, V₂O₅-TiO₂-SO₄²⁻, MoO₃-TiO₂-SO₄²⁻ and V₂O₅-MoO₃-TiO₂-SO₄²⁻) were prepared via the one step sol-gel method using a similar procedure to that reported in our previous work [34]: First, Ti(IV) isopropoxide (Ti(OiC₃H₇)₄, Sigma-Aldrich, 97%) was dissolved in anhydrous ethanol (C₂H₆O, Aldrich, 99.8 %). Then, Ethyl acetoacetate (C₆H₁₀O₃, Fluka, > 99.5%) was added to the mixture (with a molar ratio Etacac /Ti = 1) for the control of the reaction kinetics. After ageing under stirring, at room temperature, a dilute solution of HNO₃ (0.1 M) was added to accomplish hydrolysis according to the molar ratio H₂O/Ti = 10. Finally, the obtained gel was transformed into TiO₂ aerogel oxide by supercritical drying in the autoclave (at T = 243 °C and P = 63 bar). For the elaboration of V₂O₅-TiO₂, MoO₃-TiO₂, V₂O₅-MoO₃-TiO₂, TiO₂-SO₄²⁻, V₂O₅-TiO₂-SO₄²⁻, MoO₃-TiO₂-SO₄²⁻ and V₂O₅-MoO₃-TiO₂-SO₄²⁻ aerogel samples, the appropriate amounts of vanadyl acetylacetonate (V(C₅H₇O₂)₂, Fluka, 95 %) and Molybdenyl acetylacetonate (MoO₁₀H₁₄O₆, Merck Schuchardt), corresponding to theoretical contents 2 % wt. and 6 % wt. of V₂O₅ and MoO₃, respectively, were introduced in the slurry before the hydrolysis. To obtain the sulfated catalysts, a suitable volume of H₂SO₄ solution (Scarlaw, 95-97 %), giving a molar ratio S/Ti rate = 0.2, was added to the organic mixture before the hydrolysis step. All the aerogel oxides were calcined for 3 h at 500 °C under O₂ flow (30 mL.min⁻¹).

2. 2. Characterization of aerogel catalysts

2. 2. 1. N₂ adsorption-desorption at 77 K

N₂ Physisorption was carried out at 77 K using a Micromeritics ASAP 2020 apparatus. Prior to N₂ adsorption, the samples were degassed at 200 °C for 6 h. The residual pressure reached during the degassing step was 10⁻⁵ torr.

2. 2. 2. X-ray diffraction (XRD)

Powder X-ray diffraction measurements were performed on a Brüker AXS D8 diffractometer with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The data of 2θ were collected from 2 to 80 ° with a step size of 0.02 °. The crystallites size (D) of solids was calculated using the Scherrer formula [38] based on TiO₂ anatase specific peak ($\sim 2\theta = 25^\circ$): $D = 0.89 (\lambda / \beta \cos\theta)$

Where, 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

2. 2. 3. Raman spectroscopy

Raman spectra were collected under ambient conditions in backscattering configuration using a T64000 Jobin-Yvon Spectrometer. The light excitation is provided by the 488 nm line of an Ar⁺ laser. The incident power is taken equal to 5mW at the surface of sample.

2. 2. 4. X-ray Photoelectron Spectroscopy

XPS experiments were realized with the device ESCALAB 250 of thermo electron with a monochromatic ray Al K α (1486.6 eV) as the excitation source. The analyzed surface has a diameter of 400 μm and the X-ray Photoelectron spectra are calibrated in binding energy with regard to the binding energy of the C-C bond of carbon C1s at 284.8 eV. The charge is compensated with an electron beam (-2 eV).

2. 2. 5. DRUV-Vis spectroscopy

Ultraviolet visible diffuse reflectances spectroscopy (DR-UV-vis) was done over the aerogel powder on a PerkinElmer spectrophotometer type instrument lambda 45 coupled to an integration sphere type RSA-PE-20. The UV spectra were recorded in the 200-900 nm range with a speed of 960 nm min⁻¹ and an aperture of 4 nm.

2. 2.6. Temperature Programmed Desorption by Ammonia (NH₃-TPD)

The NH₃-TPD experiments were performed using an AUTOCHEM 2920 (Micromeritics) equipped with a TCD detector. Prior to NH₃ adsorption, the catalyst powder (m= 0.05 g) was activated under air flow (30 mL min⁻¹) at 500 °C (ramp 10 °C min⁻¹) for 30

min. After cooling to 100 °C, the sample was saturated with ammonia (5 vol% NH₃ in He, flow rate = 30 mL min⁻¹) for 45 min. Then, it was flushed with He (30 mL min⁻¹) during 2 h to remove physisorbed NH₃. Finally, the ammonia was desorbed in He flow (30 mL min⁻¹) from 100 °C to 600 °C using a heating rate of 10 °C min⁻¹.

2. 2. 7. Temperature Programmed Reduction by Hydrogen (H₂-TPR)

The H₂-TPR analyses were realized on a Micromeritics AUTOCHEM 2910 equipped with a TCD detector. Briefly, the aerogel powder (m = 0.05 g) was pre-treated under 5 vol % O₂ in He (flow rate = 30 mL min⁻¹) at 500 °C (ramp 10 °C min⁻¹) for 30 min. After being cooled down to 50 °C in the same atmosphere, the sample was flushed with He (30 mL min⁻¹) then exposed to a flow containing 5 vol % H₂ in Ar (30 mL min⁻¹) and heated between 50 and 800 °C (10 °C min⁻¹).

2. 3. NO-SCR catalytic test

The selective catalytic reduction (SCR) of NO by NH₃ was carried out in a fixed-bed quartz flow reactor operating at atmospheric pressure. 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 150 °C. A feed gas stream, containing 400 ppm NO, 400 ppm NH₃ and 8 % O₂ in He as a balance gas, was supplied through mass flow controllers to the micro-reactor with a total flow rate of 100 cm³ min⁻¹ yielding a gas hourly space velocity (GHSV) of 120,000 h⁻¹. The SCR was performed out on programmed temperature from 150 to 500 °C with the heating rate 6 °C min⁻¹. The reactants and products were analyzed by a quadruple mass gas spectrometer (Pfeiffer Omnistar) equipped with Channeltron and Faraday detectors (0-200 amu).

3. Results and discussion

3. 1. N₂-Adsorption-desorption at 77 K

Table 1 summarizes the values of specific surface areas (S_{BET}), BJH desorption pore volumes (V_{PT}) and pore size diameters (Φ_{pore}) of samples. As it can be noted, all the aerogel

materials calcined at 500 °C exhibit a high surface area ($73 \text{ m}^2/\text{g} \leq S_{\text{BET}} \leq 122 \text{ m}^2/\text{g}$) and large porosity ($0.15 \text{ cm}^3/\text{g} \leq V_{\text{PT}} \leq 0.37 \text{ cm}^3/\text{g}$) which reflect their developed texture and good thermal stability. It is worthy to note that, a comparable systems (e.g: $\text{MoO}_3(6)/\text{TiO}_2$ and $\text{V}_2\text{O}_5(2.3)\text{MoO}_3(6)/\text{TiO}_2$) with lower surface area (79.4 and 64 m^2/g) and total pore volume (0.28 and 0.27 cm^3/g) has been previously obtained by Nova et al. [39] and Lietti et al. [25] via the incipient wetness method. This point out the determining effect of the preparation method on the textural properties of solids and underlines the advantages of the use of aerogel materials as catalytic systems. In fact, it is recognized that large specific surface area implies more active sites exposed on the surface of catalyst and more contact opportunities with gas molecules, which can promote the SCR activity [40].

It should be also mentioned that a partial blockage of TiO_2 support's pores by the supported active species seems to be occurred, since a slight decrease of the surface area and pore volume of TiO_2 is observed (Table 1) after V, Mo and/or SO_4^{2-} addition [34,41].

Table 1. Textural properties of aerogel catalysts.

Sample	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average Pore diameter (Φ_{pore} , Å)
TiO_2	122	0.33	79
$\text{V}_2\text{O}_5\text{-TiO}_2$	101	0.37	117
$\text{MoO}_3\text{-TiO}_2$	118	0.33	87
$\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2$	75	0.26	116
$\text{TiO}_2\text{-SO}_4^{2-}$	108	0.34	116
$\text{V}_2\text{O}_5\text{-TiO}_2\text{-SO}_4^{2-}$	73	0.15	62
$\text{MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$	98	0.18	64
$\text{V}_2\text{O}_5\text{- MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$	92	0.20	71

N_2 adsorption-desorption isotherms and pore size distribution curves of aerogel solids are displayed in Fig. 1 and Fig. 2, respectively. The data show that all the samples are

mesoporous materials displaying a type IV isotherm and H1 or H2 hysteresis loops, according to the IUPAC classification (Fig. 1)[42]. It is well known that the occurrence of the capillary hysteresis loop depends on the pore sizes. Therefore, the H1 type, registered for V_2O_5 - TiO_2 and V_2O_5 - MoO_3 - TiO_2 samples reveals the presence of cylindrical mesoporous channels [42,43]. However, H2 type, observed in the case of TiO_2 , MoO_3 - TiO_2 , V_2O_5 - TiO_2 - SO_4^{2-} , MoO_3 - TiO_2 - SO_4^{2-} and V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-} indicates, in agreement with several previous reports [41,44-46], the existence of an inkbottle-type pores. Finally, the hysteresis loop obtained over TiO_2 - SO_4^{2-} cannot be classified into any type of the IUPAC classification and mostly resembles to H3 type conforming to mesoporous solids with a broad distribution of the pores size [47,48]. Similar unusual shape of capillary hysteresis loop has been previously registered for $NiCoO_2$ and $Mn/Ce/TiW$ systems and was attributed also to H3 type [47,48].

The shape of pore size distribution curves presented in Fig 2, confirm the existence of unimodal pore for TiO_2 , MoO_3 - TiO_2 , V_2O_5 - TiO_2 - SO_4^{2-} , MoO_3 - TiO_2 - SO_4^{2-} , V_2O_5 - MoO_3 - TiO_2 and V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-} samples and bimodal pore for TiO_2 - SO_4^{2-} catalyst. Noting that the modification of the nature and size of Titania pores, induce by V, Mo and/or SO_4^{2-} incorporation (Fig. 2 and Table 1), could provide evidence about the existence of strong interactions between TiO_2 and the supported species which affects the textural properties of aerogel catalysts [34].

Figure 1. N_2 Adsorption-desorption isotherms of nanostructured aerogel catalysts: (A) unsulfated samples and (B) sulfated samples.

Figure 2. Pore size distribution curves of nanostructured aerogel catalysts: (A) unsulfated samples and (B) sulfated samples

3. 2. X-ray diffraction

The XRD patterns of samples are illustrated in Fig. 3. As it can be seen, all the aerogel are well structured materials and show only the typical reflections of TiO₂ anatase phase 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 peaks of very low intensity, corresponding to a trace amount of TiO₂ rutile phase [ICSD 01-076-1941], are detected at $2\theta = 27.2^\circ$ (110), 35.7° (101) and 53.9° (211) in the diffractogram of V₂O₅-TiO₂ only. Remarkably, no characteristic peaks of VO₂; V₂O₅ ; MoO₃ and MoO₂ crystalline phases, principally identified at $2\theta = 27.7^\circ$ (110) [ICSD 01-079-1655] ; $2\theta = 20.2^\circ$ (001) [ICSD 01-089-2482]; $2\theta = 25.8^\circ$ (210) [PDF 00-021-0569] and $2\theta = 26.0^\circ$ (-111) [ICSD 01-076-1807], respectively, are perceived for all the catalysts implying the highly dispersion state of V and Mo species on the TiO₂ surface [25,28]. It should be also mentioned that no typical peaks related to MoS₂ compound, principally identified at $2\theta \approx 14.2^\circ$ (002); 32.5° (100) and 39.4° (103) [JCPDS 37-1492], are seen for the samples containing both Mo and sulfate evidencing that no reaction has been produced between molybdenum and sulfate, during the synthesis or the thermal treatment of catalysts, to form molybdenum disulfide crystalline phase (MoS₂).

The average crystallites size, which influences the surface areas and subsequently the catalytic performances of samples [49], was estimated based on the strong anatase diffraction peak (101, at $2\theta \approx 25^\circ$) and the values are listed in table 2. Noticeably, all the aerogel materials are characterized by a nanometer size ranging between 7.66 and 12.93 nm. This confirms the successful synthesis of a new generation of highly structured nanocatalysts for the NO-SCR reaction.

Figure 3. XRD patterns of nanostructured aerogel catalysts: (A) unsulfated samples and (B) sulfated samples.

Table 2. XRD phases and TiO₂ crystallites size of aerogel catalysts.

Sample	XRD phases	FWHM (°)	TiO ₂ crystallite size D (nm)
TiO ₂	Anatase	0.8920	8.66
V ₂ O ₅ -TiO ₂	Anatase + Rutile (*t)	0.6259	12.41
MoO ₃ -TiO ₂	Anatase	0.7576	10.47
V ₂ O ₅ -MoO ₃ -TiO ₂	Anatase	1.0356	7.66
TiO ₂ -SO ₄ ²⁻	Anatase	0.6160	12.93
V ₂ O ₅ -TiO ₂ -SO ₄ ²⁻	Anatase	0.6452	12.30
MoO ₃ -TiO ₂ -SO ₄ ²⁻	Anatase	0.6513	12.19
V ₂ O ₅ - MoO ₃ -TiO ₂ -SO ₄ ²⁻	Anatase	0.7467	10.63

With *t = *trace amount*.

It is established that the controllable regulation of the size and surface features of catalysts, which is possible through a suitable preparation method and synthesis parameters, is an effective way to enhance their catalytic performances [50]. On the other hand, it is recognized that numerous advantages distinguish the sol gel procedure including a simple technology, low process-temperatures and flexible control of the structure and size of final products via many operating parameters [51]. Based on the above XRD and N₂ physisorption results, it can be concluded the successful synthesis of new aerogel SCR catalysts with a developed mesoporous texture (high surface area and porosity), nanometer size and good cristallinity of TiO₂ anatase phase (~ 100 %). This highlights the appropriate choice of both the preparation method (one step sol-gel procedure-supercritical drying) and optimized synthesis conditions (such as: Molar ration Etacac /Ti = 1, and H₂O/Ti = 10, temperature...) for adjusting the physicochemical properties of the final aerogel products.

3. 3. Raman spectroscopy

Raman spectroscopy has proven to be a valuable tool in elucidating the structure of complex transition metal oxides, presenting either as bulk or two dimensional supported phases.

Vibrational spectra of solids are presented in Fig. 4. The bands at 145, 197, 396, 515 and 637 cm^{-1} are observed for all the samples and are assigned to E_g , E_g , B_{1g} , A_{1g} and E_g modes of TiO_2 anatase, respectively [4,34,38,52]. For the catalysts containing molybdenum, a new weak and broad band is generated at around 950 cm^{-1} and is attributed to Mo=O terminal stretching mode of dispersed molybdenum species [39,53-54]. The slightly changes of the terminal Mo=O frequency, registered after vanadia or sulfate addition, may serve as a proof about the existence of $\text{V} \leftrightarrow \text{Mo}$; $\text{Mo} \leftrightarrow \text{SO}_4^{2-}$ and/or $\text{V} \leftrightarrow \text{Mo} \leftrightarrow \text{SO}_4^{2-}$ interactions which probably modify the structure and/or the polymerization degree of Mo surface species. Many researchers have studied by Raman spectroscopy the relationship between the terminal Mo=O frequency and the state of Mo species dispersed on several supports [53-54]. W. Yu *et al.* [54] demonstrated that the isolated tetrahedral molybdena gradually changes into the octahedral polymolybdate species and the terminal Mo=O stretching frequency shifts from 921 to 964 cm^{-1} when molybdena loadings increases from 0.2 to 0.8 mmol/100 m^2 CeO_2 on $\text{MoO}_3/\text{CeO}_2$ systems. Accordingly, the octahedral polymeric molybdena species seem to be the major form in the case of our samples. Noting that the terminal Mo=O vibration is hardly detectable in the $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ Raman spectrum. This may be due to its very low intensity since a visible decrease in the Raman peaks intensity of TiO_2 is seen in the case of $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ and $\text{V}_2\text{O}_5\text{-TiO}_2\text{-SO}_4^{2-}$ catalysts. This decrease has been already observed for many supported metal oxides ($\text{V}_2\text{O}_5/\text{TiO}_2$, $\text{MoO}_3/\text{TiO}_2$, $\text{SiO}_2/\text{TiO}_2$, Cu/TiO_2 and $\text{V}_2\text{O}_5\text{-MoO}_3/\text{TiO}_2$ [25]) and it was explained by three different factors: increase disorder of the surface, increase absorption of the excitation radiation and more complex solid-state phenomena [25].

As shown also in Fig. 4, no typical Raman bands related to crystalline phases of V_2O_5 (994 cm^{-1} [55,56]) and MoO_3 (818, 995 cm^{-1} [25,54]) are detected for all the aerogel samples suggesting, in line with the XRD results and in perfect agreement with the results already

obtained by Lietti *et al.* [25] for similar SCR systems, the highly dispersed state of vanadium and molybdenum on the catalysts surface. In addition, no typical bands of well dispersed VO_x species (between 800 and 1050 cm⁻¹ [25]) are found in the Raman spectra of our samples most probably due to the low loading of vanadium [34,57,58]. The absence of VO_x characteristic peaks on the Raman spectra of several V-based catalysts (like: V₂O₅-CeO₂-TiO₂-SO₄²⁻ [34], V₂O₅/CeO₂ [57], V₂O₅/TiO₂ and V₂O₅/TiO₂-SO₄²⁻ [58], VTS and VTCeS [59]) has been already remarked and explained by the low quantities of vanadium.

Figure 4. Raman spectra of nanostructured aerogel catalysts: (A) unsulfated samples and (B) sulfated samples.

3. 4. X-ray photoelectron spectroscopy

The XPS analysis was exclusively applied to the new $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ catalyst to provide information about the surface interaction and chemical state of active elements at the surface. The XPS spectra of Ti, O, Mo, V and S are depicted in Fig. 5.

The Ti 2p_{3/2} and Ti 2p_{1/2} binding energy, corresponding to the typical Ti^{4+} oxidation state in a tetragonal structure [60], are detected at 459.1 and 464.8 eV, respectively, in the Ti 2p XPS spectra (Fig. 5 a). These values are slightly higher compared to those characterizing pure TiO_2 (458.1 and 463.8 eV) [61] due to strong interactions developed between the TiO_2 support and active species (V, Mo and/or SO_4^{2-}) [34,60,61].

Two peaks are detected in the XPS spectra of O1s (Fig. 5b): the first peak, centred at 530.2 eV, could be assigned to the lattice oxygen O^{2-} (reference as O β) [62] and the second one, maximizing at 531.8 eV, can be ascribed to several O1s states of surface adsorbed oxygen (referenced as O α) [60, 62, 63]. It was considered that O α is beneficial to oxidize NO to NO_2 which could improve the De NO_x activity at low temperatures [64].

According to the literature, the binding energies of oxidation states of Mo are: 235.85 and 232.65 eV for MoO_3 ; 234.9 and 231.7 eV for Mo_2O_5 and 232.3, 229.1 eV for MoO_2 [65]. The XPS spectra of Mo3d (Fig 5c) shows principally two peaks centred at around 235.4 and 232.4 eV which can be essentially ascribed to Mo^{6+} state (Mo 3d_{3/2} and Mo 3d_{5/2}, respectively). This suggests that molybdenum mainly exists at its highest oxidation state (+6) on the $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ surface.

The intense peak centered at 515.6 eV in the V 2p_{3/2} XPS spectrum (Fig. 5 d), is assigned to V^{4+} surface species [34,66], whereas, the weak shoulder localized at around 517.8 eV is linked to V^{5+} species [34,66]. Similar results, indicating the stabilization of vanadium at

its 4+ oxidation state and suggesting the existence of $V \leftrightarrow SO_4^{2-}$ has been obtained in a previous work [34].

An asymmetric peak with binding energies of 169.0 eV were measured for the S 2p line (Fig. 5 e). According to similar previous data [55,61-68], these binding energy are typical of S^{6+} oxidation state in the $-SO_4^{2-}$ groups. The S^{6+} species might be present in the form of bidentate sulfate on the surface of TiO_2 , either chelating or bridging, as proposed in the literature [67,68]. Nevertheless, no peaks attributable to sulfide (at 161-162.8 eV) and elemental sulfur (at 164 eV) [55,68] are detected confirming, in line with the XRD results, that no molybdenum sulfide (MoS_2) is formed on the $V_2O_5-MoO_3-TiO_2-SO_4^{2-}$ surface.

It is worth mentioning that the presence of highly dispersed vanadium and sulfate species on the $V_2O_5-MoO_3-TiO_2-SO_4^{2-}$ surface, which was not proven by Raman technique, is evidenced by using XPS analysis. This point out the importance to use several consistent technique for the structure examination of catalysts.

Figure 5. XPS results over the novel V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-} nanostructured aerogel catalyst.

3. 5. DR UV-vis spectroscopy

To discern the chemical state and obtain more information regarding the dispersion of V and Mo species at the catalysts surface, diffuse reflectance UV-vis spectra of samples are showed in Fig. 6. The spectrum of all the aerogel materials (Fig. 6 A) shows a broad absorption band in 200-400 nm range which is related to $O^{2-} \rightarrow M^{n+}$ charge transfer transitions ($M = Ti; V; Mo$), corresponding to the excitation of electrons from the valence band (having the $O2p$ character) to the conduction band (having the $Ti\ 3d, V\ 3d$ and/or $Mo\ 3d$ character) [69]. The presence of this band identify the anatase phase of TiO_2 and can reveal the presence of highly dispersed V and Mo species on its surface [34,69-75]. Additional peaks have appeared in 350-400 nm range for the catalysts containing vanadium and/or molybdenum and can be associated with $O^{2-} \rightarrow V^{5+}$ and $O^{2-} \rightarrow Mo^{5+}$ charge transfer (CT) transitions in a new types of VO_x and MoO_x surface species, respectively [34,70,76,77]. For clearness purposes, the attribution of Ti, V and Mo characteristic bands, based on the literature, is stated in Table 3.

This literature report (Table 3) shows that there is a significant overlap of spectral regions of the investigated elements. Therefore, on the basis of UV-absorption bands, it can be supposed the coexistence of a variety of highly dispersed vanadium and molybdenum species on the TiO_2 surface.

Noting that the decrease of the intensity of band located at around 378-385 nm, most probably related to Mo^{5+} CT transition [77], after sulfate addition (Fig. 6B), could demonstrates (in line with the XPS result) the predominance of Mo^{6+} species on the surface of sulfated systems like $V_2O_5-MoO_3-TiO_2-SO_4^{2-}$. The weak broad bands situated at around 600 and 665 nm can be ascribed to Mo^{5+} and V^{4+} d-d transitions, respectively [78-80], while, the shoulders localized at ~ 320 and 520 nm, more visible in the case of unsulfated samples, could be

(A)

attributed to MoO_3 [74] and V_2O_5 [78] crystalline phases, respectively which exist in a trace amounts and seem to be too small to be detected by the XRD technique.

Figure 6. DRUV-Vis spectra of nanostructured aerogel catalysts: (A) unsulfated samples and (B) sulfated samples.

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

Species	DRUV-vis band Position: λ (nm)	Type of transition	Assignments	Ref.
Ti	217	$O^{2-} \rightarrow Ti^{4+}$ LMCT	Tetrahedral Ti^{4+} species	[34,70]
	275	$O^{2-} \rightarrow Ti^{4+}$ LMCT	Octahedral Ti^{4+} species	[34,70]
	320 and 350	$O^{2-} \rightarrow Ti^{4+}$ LMCT	TiO_2 Anatase phase	[34,70]
V	240-280	$O^{2-} \rightarrow V^{4+}$ LMCT	Monomeric tetrahedral V^{4+} species	[34,71]
	280-340	$O^{2-} \rightarrow V^{5+}$ LMCT	Monomeric tetrahedral V^{5+} species	[34,71]
	350-400	$O^{2-} \rightarrow V^{5+}$ LMCT	Oligomeric tetrahedral VO_x chain	[34,76]
			Low polymeric tetrahedral VO_x chain	[34,70]
			V in square pyramidal configuration	[34,70]
	500-550	LMCT	Crystalline V_2O_5	[78]
	545-800	d-d transition	Vanadium (IV)	[78]
Mo	200-270	$O^{2-} \rightarrow Mo^{6+}$ LMCT	Isolated tetrahedral Mo^{6+}	[72-75]
	260-280	$O^{2-} \rightarrow Mo^{6+}$ LMCT	Polymeric octahedral Mo^{6+}	[73-75]
	300-350			
	360-385	$O^{2-} \rightarrow Mo^{5+}$ LMCT	-	[77]
	320	-	Crystalline MoO_3	[74]
	400-900	d-d transition	Molybdenum (V)	[79,80]
	600-750			

3. 6. H_2 -TPR and NH_3 -TPD analysis

The acid and redox properties of catalyst play a crucial role in the $DeNO_x$ process [11,18, 81,82]. It was recognized that the SCR activity is governed, at low temperature by the reducibility of catalyst, and by its acidity at high temperature [82].

H_2 -TPR analysis was carried out to investigate the redox properties of aerogel oxides. The obtained H_2 -TPR profiles are illustrated in Fig. 7. As it is well known, TiO_2 support is

characterized by a very low reducibility [68] which was confirmed in this work by the very weak H₂ consumption peak detected at around 540 °C in its H₂-TPR profile (Fig. 7 A). The addition of vanadium, molybdenum and/or sulfate influences differently the redox properties of aerogel catalysts. In fact, two unresolved peaks maximizing at 430 and 500 °C are observed for the binary V₂O₅-TiO₂ and are associated with the reduction of highly dispersed VO_x species [34,62]. Two well resolved peaks are detected also in the case of MoO₃-TiO₂ system; the low temperature hydrogen consumption (~ 401 °C) is assigned to the first-step reduction of polymeric octahedral Mo species (weakly bounded to the support) from Mo⁶⁺ to Mo⁴⁺ [75,83]. However, the peak at higher temperature (~ 717 °C) is ascribed to the second-step reduction, from Mo⁴⁺ to Mo⁰, of polymeric octahedral Mo species with different aggregation degree and to the reduction of highly dispersed tetrahedral Mo⁶⁺ species, in strong interaction with the support [75,83].

The V₂O₅-MoO₃-TiO₂ ternary catalyst displays different reduction behaviour if compared to corresponding binary samples (V₂O₅-TiO₂ and MoO₃-TiO₂), since a several peaks centred at around 380, 450, 523, 727 and 756 °C are detected and could be attributed to the reduction of V and Mo species, toward different temperatures reduction with respect to binary systems. This observation may serve as a proof about the existence of strong interaction between vanadium and molybdenum (V↔Mo) which probably affects the nature, dispersion and/or polymerization degree of V and Mo co-supported species and, thus, influences the reducibility of ternary catalyst.

Fig. 7 B shows a twin peaks at 627 and 653 °C in the H₂-TPR profile of TiO₂-SO₄²⁻ support which correspond to the reduction of SO₄²⁻ groups [35,58,84]. The reduction of SO₄²⁻ anions is moved to lower temperature and completely hides both the reduction of vanadium and the first reduction peak of molybdenum for all the sulfated catalysts. In addition, a decrease in

the intensity and temperature reduction of the second H₂ consumption peak of Mo is noted in the H₂-TPR profile of MoO₃-TiO₂-SO₄²⁻ (from 717 to 676 °C), while, this peak has completely disappeared for V₂O₅-MoO₃-TiO₂-SO₄²⁻ catalyst. This can be correlated with the existence of diverse interactions between sulfate ions and the supported transition metals (V $\leftrightarrow$ SO₄²⁻, Mo $\leftrightarrow$ SO₄²⁻ and V $\leftrightarrow$ SO₄²⁻ $\leftrightarrow$ Mo) which make easy the sulfate reduction and influence the reducibility of Mo and V species. Accordingly, it can be suggested that these interactions modify the nature, coordination, polymerization degree, dispersion and/or oxidation state of the supported transition metals and, consequently, affect the redox properties of the aerogel mixed oxides.

(A)

Figure 7. H₂-TPR profiles of the nanostructured aerogel catalysts: (A) unsulfated samples and (B) sulfated samples.

In the NH_3 -SCR reaction, it is important to adsorb and activate NH_3 reductant on the catalyst surface. Adsorption and desorption of NH_3 molecules are greatly influenced by the acidic properties of catalysts which control their reactivity in the NO-SCR reaction, especially at high temperature [82]. The surface acidity of aerogel samples was examined via the temperature programmed desorption of ammonia and the obtained NH_3 -TPD profiles are given in Fig. 8. For all the unsulfated catalysts (Fig. 8 A), two broad peaks with different intensities are recorded: the first one, located in the 100-250 °C temperature range, is attributed to ammonia desorption from weak acid sites and the second one, situated in the 250-450 °C temperature range, corresponds to desorbed ammonia from medium strong acid sites [34,69]. It is known that that NH_3 adsorbs as ammonia coordinatively held over Lewis acid sites and as ammonium ions produced by protonation of ammonia at Brønsted sites. According to P. Forzatti et al. [86], vanadyls ($\text{V}=\text{O}$) and molybdenyls ($\text{Mo}=\text{O}$) act as adsorption sites for ammonia, Ti^{4+} could also coordinate ammonia. The authors reported that the NH_3 coordinated at Lewis sites is associated with Ti, V and Mo oxide surface species, but, Brønsted acid sites are absent on the surface of pure titania and can be generated from V-OH and Mo-OH groups [86].

Beside the former peaks, a new well resolved peak is appeared at higher temperatures (> 450 °C) in the NH_3 -TPD profiles of the sulfated samples (Fig. 8 B) indicative of the creation of a new type of strong acid sites at the catalysts surface, by the presence of sulfate groups. This result is consistent with that obtained in our previous work for $\text{V}_2\text{O}_5\text{-CeO}_2\text{-TiO}_2\text{-SO}_4^{2-}$ aerogel catalyst [34]. The positive effect of sulfate groups on the acidity and, thus, on the SCR activity of various catalysts has been also reported by Z. Si *et al.* [37] , R. Khodayari *et al.* [87] and J. P. Chen *et al.* [88]. Noticeably, the temperature of new NH_3 desorption peak, which is strongly influenced by the acid sites strength, is affected by the chemical composition of samples and

decreases following this order: 520 °C ($\text{TiO}_2\text{-SO}_4^{2-}$), 500 °C ($\text{MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$), 490 °C ($\text{V}_2\text{O}_5\text{-TiO}_2\text{-SO}_4^{2-}$) and 470 °C ($\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$). This confirms the existence of strong interactions between the supported transition metals and sulfate groups. Depending on the nature of element present in the sample, these interactions modify not only the redox properties of the aerogel solids (as verified by H_2 -TPR analysis) but also the strength and most probably the nature of surface acid sites. Markedly, a higher total acidity, in the 100-500 °C temperature range, is obtained in the case of new $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ aerogel catalyst.

Figure 8. NH_3 -TPD profiles of nanostructured aerogel catalysts: (A) unsulfated samples and (B) sulfated samples

3. 7. Catalytic test

The curves of the NO conversion as a function of temperature, over the unsulfated aerogel catalysts, are depicted in Fig. 9 A. It is clearly seen that TiO₂ support exhibits a low NO conversion. The addition of vanadium, molybdenum or both of them increases the SCR activity, especially at low temperature: around 0, 10, 28 and 77 % of NO conversions are achieved at 300 °C over TiO₂, MoO₃-TiO₂, V₂O₅-TiO₂ and V₂O₅-MoO₃-TiO₂ samples, respectively. This underlines the crucial role of redox sites created by molybdenum (Mo⁶⁺/Mo⁵⁺) and, particularly, by vanadium (V⁵⁺/V⁴⁺) on the MoO₃-TiO₂, V₂O₅-TiO₂ and V₂O₅-MoO₃-TiO₂ surface for the low temperature NH₃-SCR reaction. Noticeably, the reactivity of the ternary catalyst (V₂O₅-MoO₃-TiO₂) is significantly higher than that of corresponding binary systems; In fact, the reaction temperature window is extended and shifted towards lower temperatures over this ternary catalyst: around 3, 9 and 30 % of NO conversions are reached at 250 °C using MoO₃-TiO₂, V₂O₅-TiO₂ and V₂O₅-MoO₃-TiO₂, respectively. This result is in perfect agreement with those already obtained by L. Lietti *et al.* [25,26] and D. W. Know *et al.* [29] for VMoTi systems prepared by the impregnation method. It indicates that the co-existence of vanadium and molybdenum species and most likely the interactions developed between them, which affect the reducibility and surface acidity of V₂O₅-MoO₃-TiO₂ catalyst, play a key role in improving the reactivity of V and Mo active sites (acid and redox ones) and lead to more active catalyst for DeNO_xing at low temperatures. At high temperature, NO conversion and N₂ selectivity decrease over V₂O₅-TiO₂ and V₂O₅-MoO₃-TiO₂ catalysts due to the secondary reaction of NH₃ oxidation. The NO conversion does not exceed 75 %, in the 400-500 °C temperature range, over all the unsulfated catalysts.

(A)

The addition of SO_4^{2-} groups enhances both NO conversion and N_2 selectivity at high temperature ($> 350\text{ }^\circ\text{C}$) leading to more active and N_2 selective catalysts with respect to sulfate free ones (Fig. 9B). Interestingly, more than 90 % of NO conversions are achieved in the 435-500 $^\circ\text{C}$, 390-500 $^\circ\text{C}$ and 350-500 $^\circ\text{C}$ temperature ranges over $\text{TiO}_2\text{-SO}_4^{2-}$, $\text{MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ and $\text{V}_2\text{O}_5\text{-TiO}_2\text{-SO}_4^{2-}$ catalysts, respectively. More interestingly, the best SCR activity on the whole temperature range (150-500 $^\circ\text{C}$) is obtained over the sulfated ternary sample ($\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$). Using this new aerogel catalyst, around 60 % and more than 90 % of NO conversions, with a high N_2 selectivity (between 75 and 100 %), are achieved at 250 $^\circ\text{C}$ and in the range of 300-500 $^\circ\text{C}$, respectively (Table 4). The increase of the high temperature SCR activity by sulfating the catalysts is in perfect agreement with the most reports existing in the literature [34,35-37,89-91]. It is obviously linked to the enhancement of the surface acidity and acid sites reactivity of catalysts by (i) the presence of sulfate groups and (ii) the interactions developed between the SO_4^{2-} ions and the supported active species.

For the SCR reaction, it is recognized that both acidity and redox properties of catalysts are the key factors governing its reactivity [11,81,82]. Accordingly, it can be suggested that the simultaneous presence of V, Mo and sulfate allows a good balance between the actives redox and acid sites leading to an excellent new catalyst ($\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$) for DeNOxing in a wide temperature range (150-500 $^\circ\text{C}$). The reactivity of these active sites seems to be improved by divers interactions developed between the supported species (like $\text{V}\leftrightarrow\text{Mo}$, $\text{V}\leftrightarrow\text{SO}_4^{2-}$, $\text{Mo}\leftrightarrow\text{SO}_4^{2-}$ and $\text{V}\leftrightarrow\text{SO}_4^{2-}\leftrightarrow\text{Mo}$). A synergism in the SCR reaction, related to the existence of V-Mo and V-W electronic interactions has been reported earlier for $\text{V}_2\text{O}_5\text{-MoO}_3/\text{TiO}_2$ and $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ systems [26,92,93]. Recently, X. Hu et al. [7] concluded that a synergistic effect between Mn and Mo species might exist in the $\text{NH}_3\text{-SCR}$ reaction using Mo(x)-MnO_x nanorods.

Table 4. Catalytic performances of V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-} nanostructured aerogel catalyst calcined at 500 °C in NO-SCR by NH_3 : $[NO] = [NH_3] = 0.04 \%$, $[O_2] = 8.00 \%$ balance with He and $(GHSV) = 120\,000\ h^{-1}$.

Aerogel catalyst	Temperature (°C)	NO Conversion (%)	Selectivity (%)		
			N ₂	N ₂ O	NO ₂
V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-}	200	18.7	100	0	0
	250	59.1	100	0	0
	300	89.0	100	0	0
	350	96.4	100	0	0
	400	96.3	96	4	0
	450	95.4	88	12	0
	500	95.8	75	25	0

As it can be seen in Fig. 10, compared to V_2O_5 - WO_3 / TiO_2 commercial catalyst (EUROCAT containing 3.15 wt % V_2O_5 , 9 wt % WO_3 , 6.5 wt % SiO_2 , 1.5 wt % Al_2O_3 , 1 wt % CaO , 0.85 wt % SO_4^{2-} and 78 wt % TiO_2 [94]), and under the same experimental conditions ($[NO] = [NH_3] = 400$ ppm), the new V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-} aerogel catalyst demonstrates a similar SCR activity, in the 200-375 °C temperature range, but exhibits a superior catalytic performances at higher temperature (375-500 °C). After adding water (3.5 % H_2O) in the reaction gas mixture, the NO conversion over the two catalysts slightly decreases, especially at low temperatures (< 350 °C) for the aerogel V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-} . At high temperatures (> 400 °C), the new aerogel system shows a better resistance to water vapour than the V_2O_5 - WO_3 / TiO_2 commercial one which in turn demonstrates a higher resistance to water vapour at lower temperature (< 400 °C).

Figure 10. NO conversion versus reaction temperature over $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ aerogel catalyst and $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ commercial one, $[\text{NO}] = [\text{NH}_3] = 0.04 \%$; $[\text{O}_2] = 8.00 \%$ and balance with He, $(\text{GHSV}) = 120\,000 \text{ h}^{-1}$, without H_2O and with 3.5% H_2O .

The effect of the NO concentration (400 and 1000 ppm) on the SCR activity of new $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ aerogel catalyst, in the presence of water (3.5% H_2O), was investigated and the results are represented in Fig. 11. Noticeably, using a mixture containing 400 ppm NO and 400 ppm NH_3 , a high NO conversions ($\geq 88 \%$) are obtained, in the 400-500 °C temperature range, over the $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ aerogel catalyst. The NO-SCR activity is clearly improved at high temperature by increasing the NO concentration. Surprisingly, 100 % NO conversion with 100 % N_2 selectivity are achieved, in the 450-500 °C temperature range, when the NO-SCR reaction was carried out using the concentrations $[\text{NO}] = [\text{NH}_3] = 1000 \text{ ppm}$ (Table 5).

Figure 11. Effect of NO concentration (0.04 or 0.1 %) on the SCR activity of V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-} aerogel catalyst, $[NO] = [NH_3] = 0.04$ or 0.1 %, $[O_2] = 8.00$ % and balance with He, 3.5 % H_2O , (GHSV) = $120\,000\ h^{-1}$.

Table 5. Catalytic performances of V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-} nanostructured aerogel catalyst calcined at 500 °C in NH_3 -SCR of NO: $[NO] = [NH_3] = 0.1 \%$, $[O_2] = 8.00 \%$ balance with He, 3.5 % H_2O and $(GHSV) = 120\,000\ h^{-1}$.

Aerogel catalyst	Temperature (°C)	NO Conversion (%)	Selectivity (%)		
			N_2	N_2O	NO_2
V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-}	200	3.4	100	0	0
	250	12.9	100	0	0
	300	51.3	100	0	0
	350	89.9	100	0	0
	400	99.2	100	0	0
	450	100	100	0	0
	500	100	100	0	0

The turnover frequency (TOF, h^{-1}) was calculated for all the samples, at 220 °C, and the results are illustrated in Fig. 12. A visible increase in the TOF values is noted by adding V, Mo or both of them and by sulfating the catalysts, particularly the ternary one (Fig. 12 A). This highlight the crucial role of V and Mo redox sites and the synergistic effect of the interactions developed between them (V-Mo) and with sulfate groups (V- SO_4^{2-} -Mo) for DeNO_xing at low temperature. The inhibiting role of H_2O and the non-beneficial effect of increasing NO concentration ($[NO]$) for the low temperature SCR-NO (< 220 °C) over V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-} are verified through the decrease of the TOF value after adding water and increasing NO concentration (Fig 12 B).

(A) Effects of the nature of transition metals (V; Mo) and sulfate addition (SO_4^{2-})

T = 220 °C

(a) TiO_2 ; (b) $\text{V}_2\text{O}_5\text{-TiO}_2$; (c) $\text{MoO}_3\text{-TiO}_2$; (d) $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2$

Figure 12. TOF values, defined at 220 °C, over the nanostructured aerogel catalysts: (A)

Effects of the nature of transition metal and sulfate addition: $[\text{NO}] = [\text{NH}_3] = 0.04\%$ without

H_2O and (B) Effect of NO concentration (0.04 or 0.1 %) with 3.5 % H_2O .

4. Conclusions and perspectives

New $\text{V}_2\text{O}_5\text{-TiO}_2$, $\text{MoO}_3\text{-TiO}_2$, $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2$, $\text{TiO}_2\text{-SO}_4^{2-}$, $\text{V}_2\text{O}_5\text{-TiO}_2\text{-SO}_4^{2-}$, $\text{MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ and $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ nanostructured and mesoporous aerogel catalysts were developed for the first time in this study for DeNO_xing in Diesel Engine. All the obtained aerogels calcined at 500 °C, are characterized by a nanometer size (~ 8-13 nm), a good crystallinity of TiO_2 anatase phase, high surface area and porosity ($S_{\text{BET}} \geq 73 \text{ m}^2/\text{g}$ and $V_{\text{PT}} \geq 0.15 \text{ cm}^3/\text{g}$) reflecting their developed mesoporous texture and good thermal stability. The nature of supported transition metal (V or Mo), the addition of sulfate groups (SO_4^{2-}) and the existence of diverse interactions between V, Mo and SO_4^{2-} active species clearly influence the physicochemical properties of aerogel catalysts and strongly affect their SCR activity.

In the SCR-NO by NH_3 , the synergistic effect between V and Mo has led to a more reactive $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2$ ternary catalyst (with maximum of 90 % NO conversion at 350 °C) compared to corresponding binary samples ($\text{V}_2\text{O}_5\text{-TiO}_2$ and $\text{MoO}_3\text{-TiO}_2$). The addition of sulfate enhances the SCR activity of aerogel catalysts, mainly at high temperature, as a consequence of (i) the creation of new strong acid sites by the presence of SO_4^{2-} species and (ii) the modification of the nature and reactivity of actives acid and redox sites by the diverse interactions developed between V, Mo and sulfate.

The simultaneous presence of V, Mo and sulfate allows a good balance between the actives acid and redox sites and leads to a new $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ catalyst with excellent SCR activity in 150-500 °C temperature range. This new nanostructured aerogel catalyst demonstrates a similar SCR activity, in the 200-375 °C temperature range, compared to a $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ commercial catalyst (EUROCAT), but exhibits a superior catalytic performances at higher temperature (375-500 °C) with respect to the commercial one. It helps to reduce more than 96 % of NO with a high N_2 selectivity (75-100 %) using a reaction mixture containing 400 ppm NO and 400 ppm NH_3 .

The $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ aerogel system shows a better resistance to water vapour, at high temperature ($> 400\text{ }^\circ\text{C}$), than the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ commercial one. Conversely, this later catalyst was found more resistant to H_2O at lower temperature ($< 350\text{ }^\circ\text{C}$).

In the presence of water vapour (3.5 %), the SCR activity of $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ catalyst is considerably improved, at high temperature, by increasing the NO concentration. Interestingly, 100 % NO conversion with 100 % N_2 selectivity are achieved, in the $450\text{-}500\text{ }^\circ\text{C}$ temperature range, when the NO-SCR reaction was carried out using $[\text{NO}] = [\text{NH}_3] = 1000$ ppm.

Further studies are in progress *(i)* to study the effects of the concentrations of the water vapour and nitrogen oxide on the SCR activity of $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ and $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts, *(ii)* to investigate the hydrothermal stability of new $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2\text{-SO}_4^{2-}$ aerogel catalyst in order to improve more its reactivity at low temperatures and *(iii)* to evaluate the effect of SO_2 on its SCR activity.

There are no conflicts of interest to declare

Acknowledgements

The authors wish to express their sincere thanks to Thomas Cacciaguerra, Valérie Flaud and Prof. Meftah Abdelaziz for XRD, XPS and Raman analysis, respectively. Financial support by Laboratory of Chemistry of Materials and Catalysis (LCMC) of Tunisia and Franco-Tunisian Cooperation (French Institute of Tunisia, SSHN grant) are gratefully acknowledged.

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