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# **New SCR catalysts based on Mn supported on simple or mixed aerogel oxides: Effect of sulfates addition**

**Jihene ARFAOUI<sup>1</sup>, Abdelhamid GHORBEL<sup>1</sup>, Carolina PETITTO<sup>2</sup>, Gérard DELAHAY<sup>2</sup>**

<sup>1</sup>Université Tunis El Manar, Laboratoire de Chimie des Matériaux et Catalyse, Département de Chimie, Faculté des Sciences de Tunis, Campus Universitaire Farhat Hached d'El Manar, 2092, Tunis, Tunisia.

<sup>2</sup>ICGM, Université de Montpellier, CNRS, ENSCM, Montpellier, France

\* Corresponding author: E-mail address: [jihenar@yahoo.fr](mailto:jihenar@yahoo.fr), [jihene.arfaoui@fst.utm.tn](mailto:jihene.arfaoui@fst.utm.tn)

Jihene ARFAOUI ORCID: <https://orcid.org/0000-0003-2158-1185>

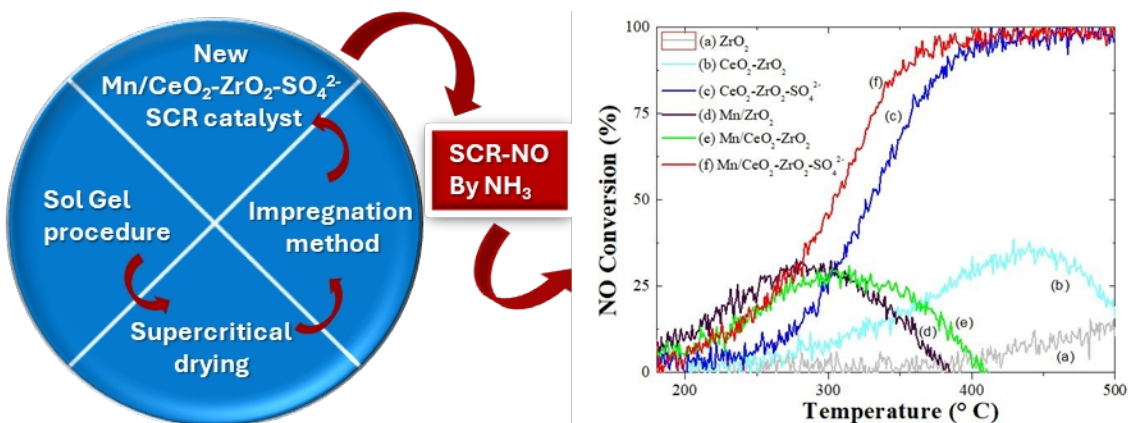
Gérard DELAHAY ORCID: <https://orcid.org/0000-0002-7146-5281>

## Abstract

New SCR catalysts based on Mn supported on simple or mixed aerogel oxides ( $\text{Mn/ZrO}_2$ ,  $\text{Mn/CeO}_2\text{-ZrO}_2$  and  $\text{Mn/CeO}_2\text{-ZrO}_2\text{-SO}_4^{2-}$ ) were prepared for selective catalytic reduction of nitrogen oxide by ammonia (NO-SCR by  $\text{NH}_3$ ). One step sol gel method followed by supercritical drying process were used for elaborating the catalytic supports, however, Mn species were incorporated into aerogels via impregnation method. Structural, textural, acidic and redox properties of samples were studied using XRD; BET and porosity measurements;  $\text{NH}_3\text{-TPD}$  and  $\text{H}_2\text{-TPR}$  techniques. The results revealed that  $\text{Mn/ZrO}_2$  and  $\text{Mn/CeO}_2\text{-ZrO}_2$  solids develop mesoporous texture, good crystallinity of zirconia tetragonal phase and nano-sized particles but exhibit a poor NO-SCR activity. The addition of  $\text{SO}_4^{2-}$  induces a disorder in  $\text{ZrO}_2$  structure but it generates very active strong acid sites for the high temperature NO reduction. 100 % NO conversion into  $\text{N}_2$  was achieved above 400 °C over the new  $\text{Mn/CeO}_2\text{-ZrO}_2\text{-SO}_4^{2-}$  catalytic system.

**Key words:** Transition metals, Aerogels, Mixed oxides, Catalysis, NO-SCR, Air depollution.

## Graphical Abstract



## Highlights

- New  $\text{Mn/ZrO}_2$ ,  $\text{Mn/CeO}_2\text{-ZrO}_2$  and  $\text{Mn/CeO}_2\text{-ZrO}_2\text{-SO}_4^{2-}$  SCR catalysts
- Unsulfated  $\text{Mn/CeO}_2\text{-ZrO}_2$  catalyst with 2 % wt. Mn exhibits poor SCR activity
- Sulfates generate new strong acid sites and a disorder of tetragonal structure of  $\text{ZrO}_2$ .
- 100 % NO conversion into  $\text{N}_2$  was obtained at  $T > 400$  °C over  $\text{Mn/CeO}_2\text{-ZrO}_2\text{-SO}_4^{2-}$

## 1. Introduction

“Aerogels” is a term describing any material derived from organic, inorganic or hybrid molecular precursors that are usually obtained by sol-gel method followed by an appropriate drying process with which the liquid filled pores have been replaced by gas and the three-dimensional and highly porous network is conserved [1]. These materials are currently known as a light solids because of its nano-porous structure (1-100 nm), low density ( $0.003 \sim 0.5 \text{ g cm}^{-3}$ ), high porosity (80 ~ 99.8 %), high specific surface area ( $500 \sim 1200 \text{ m}^2/\text{g}$ ), ultra-low dielectric constant (1.0 ~ 2.0), low thermal conductivity ( $0.005 \sim 0.1 \text{ W/ m.K}$ ), low index of refraction ( $\sim 1.05$ ) [2-4] and other exclusive characteristics, showing unique properties in heat, mechanics, optics, acoustics and other aspects. Aerogels have broad and huge application prospects in many fields like aerospace, building sectors, catalysis, energy storage devices, chemical sensors, adsorption and environmental clean-up, biomedical and pharmaceutical sectors [5]. They are called "the magical materials that change the world".

Recently, aerogels and their composites have demonstrated high efficiencies in environmental remediation applications such as:  $\text{CO}_2$  capture, removal of volatile organic compounds (VOCs) from air and elimination of heavy metals, oil and toxic products from water [1]. Kong et al. [6] showed that, using amine modified hybrid resorcinol-formaldehyde/silica composite aerogels (AH-RFSA), the maximum adsorption capacity of  $\text{CO}_2$  was attained at  $25^\circ\text{C}$  and is maintained after 30 adsorption-desorption regeneration cycles. In addition, the removal of Mn (II), Ni (II), Cd (II), Cu (II), Hg (II), and Pb(II) from water, over a carbon aerogel sorbent, was investigated by Kumar Meena et al. [7]. The authors stated that the highest adsorption capacity ( $400.8 \text{ mg/g}$ ) was obtained in the case of Cd (II) and the lowest one ( $0.70 \text{ mg/g}$ ) for Pb (II).

More recently, we have showed that various aerogel mixed oxides, prepared via the one step sol gel route, such as  $\text{MoO}_3\text{-CeO}_2\text{-ZrO}_2$ ,  $\text{WO}_3\text{-CeO}_2\text{-ZrO}_2$  and  $\text{V}_2\text{O}_5\text{-WO}_3\text{-CeO}_2\text{-TiO}_2$  display high catalytic performance in the selective catalytic reduction of NO by  $\text{NH}_3$  (NO-SCR by  $\text{NH}_3$ ) [8-9]. This process, consisting on the reaction between  $\text{NO}_x$  and  $\text{NH}_3$  to obtain  $\text{N}_2$  and  $\text{H}_2\text{O}$ , has been commonly known as the most suitable technology to reduce  $\text{NO}_x$  emissions due to the high efficiency and cost-benefit. It was confirmed that the redox ability and surface acidity of catalyst play key roles at low and high temperatures, respectively [10].

The commercially used SCR catalysts are principally  $\text{WO}_3$ -or  $\text{MoO}_3$ -doped  $\text{V}_2\text{O}_5/\text{TiO}_2$ , which exhibit excellent SCR performances between  $300$  and  $400^\circ\text{C}$  but they have several drawbacks such as narrow reaction temperature range, production of  $\text{N}_2\text{O}$  at high temperature, volatility, and toxicity of vanadium [11-13]. In recent years, much attention was devoted to Mn-Ce/ $\text{TiO}_2$  SCR catalysts due to their nontoxicity and exceptional low-temperature activity. These systems showed extraordinary SCR-activity between  $100$  and  $200^\circ\text{C}$  which was essentially correlated with the important quantity of active oxygen generated by Mn species (that is necessary to complete the SCR cycle), oxygen storage capacity (OSC) and redox performances of Ce species [14–20]. On the other hand, Khodayari et al. [21] was demonstrated that sulfating  $\text{TiO}_2/\text{V}_2\text{O}_5/\text{WO}_3$  commercial SCR catalyst reinforced the Bronsted acidity and, hence, improved activity and stability of solid. Moreover, we have evidenced in our previous works that adding sulfates to  $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2$ ,  $\text{V}_2\text{O}_5\text{-CeO}_2\text{-TiO}_2$  or  $\text{Ce-Mn-TiO}_2$  aerogel solids contributes to the creation of strong acid sites and enhances significantly NO conversion and  $\text{N}_2$  selectivity at high temperature [22–24].

In this work, we investigate for the first time the synthesis and characterization of new SCR catalysts based on Mn supported on simple or mixed aerogel oxides (Mn/ZrO<sub>2</sub>, Mn/CeO<sub>2</sub>-ZrO<sub>2</sub> and Mn/CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup>). These new systems were prepared by combining the one step sol gel process and impregnation method. Noting that the use of aerogel oxides as catalytic supports could be justified by their attractive properties for catalytic applications such as: highly crystalline structure with superior textural properties (high specific surface area and porosity), which can provide more active sites in the catalyst surface and consequently enhance its NO-SCR activity [25]. It should be mentioned that CeO<sub>2</sub> and Mn were used to enhance oxygen storage capacity, redox and oxidative properties of Mn/CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup> catalyst, while ZrO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> were chosen for the generation of acidic sites at its surface.

## 2. Material and methods

Zirconium (IV) butoxide, (Zr(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, Sigma-aldrich, 80 %), absolute ethanol (C<sub>2</sub>H<sub>5</sub>OH, 99,8%, Aldrich), ethyl acetoacetate (C<sub>6</sub>H<sub>10</sub>O<sub>3</sub>, 99.5%, Fluka), Manganese nitrate (Mn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, 98 %, Aldrich), Cerium nitrate (Ce(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O, Aldrich), H<sub>2</sub>SO<sub>4</sub> (Scarlau, 95-97 %) and an aqueous solution of nitric acid HNO<sub>3</sub> (0.1 M) are the chemical products used for the catalysts preparation.

Aerogel oxides (ZrO<sub>2</sub>, CeO<sub>2</sub>-ZrO<sub>2</sub> and CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup>) were elaborated via the one-step sol-gel method using the same procedure described in ref [8]. So, for the preparation of a desired mass of pure zirconia, a suitable quantity of Zr precursor was dissolved, at room temperature and under continuous stirring, in an appropriate volume of anhydrous ethanol (the molar ratio  $n_{\text{Ethanol}}/n_{\text{Zr}}$  and the final concentration of ethanol were fixed to 1 and 1 M, respectively). Then, the needed amount of a complexing agent, yielding a molar ratio  $n_{\text{Etacac}}/n_{\text{Zr}} = 1$ , was introduced into the mixture to control the reactions rate. After 1 h, a dilute solution of HNO<sub>3</sub> (0.1 M) was gradually added, with a molar ratio  $n_{\text{H}^+}/n_{\text{Zr}} = 10$ , to accomplish hydrolysis, and the slurry was kept under stirring until the formation of gel which was transformed into ZrO<sub>2</sub> aerogel powder by drying in an autoclave under the supercritical conditions of ethanol (T = 243 °C and P = 63 bar). The catalytic supports were prepared using the same methodology. The appropriate amount of Ce precursor, giving a theoretical loading of 10% wt. CeO<sub>2</sub>, was introduced in the slurry and stirred 1 h before the hydrolysis step. For the sulfated samples, sulfate groups were introduced by adding H<sub>2</sub>SO<sub>4</sub> solution with a molar ratio S/Ti = 0.2, at a final step before hydrolysis. The addition of Mn (theoretical content of 2 % wt.) was done by impregnation method. Hence, the required quantity of Mn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O was dissolved in water (H<sub>2</sub>O) and the obtained aqueous solution was mixed under stirring with ZrO<sub>2</sub>, CeO<sub>2</sub>-ZrO<sub>2</sub> or CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup> powder to obtain Mn/ZrO<sub>2</sub>, Mn/CeO<sub>2</sub>-ZrO<sub>2</sub> or Mn/CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup> samples. All the solids were calcined under O<sub>2</sub> at 500 °C for 3 h.

Powder X-ray diffraction (XRD) patterns were recorded between  $2\theta = 2^\circ$  and  $80^\circ$  with a step size of  $0.02^\circ$  on a Brüker AXS D8 XRD system (CuK $\alpha$  radiation,  $\lambda = 1.5406 \text{ \AA}$ ). N<sub>2</sub> Physisorption was realized at 77 K on an ASAP 2020 (Micromeritics). Before analysis, the powder (m = 0.1 g) was degassed at 200 °C for 6 h. Acidic and redox performances of samples were explored, using an AUTOCHEM 2910 (Micromeritics), by temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD, 5 vol % NH<sub>3</sub> balanced with He) and temperature programmed reduction by hydrogen (H<sub>2</sub>-TPR, 3 % H<sub>2</sub> in Ar), respectively.

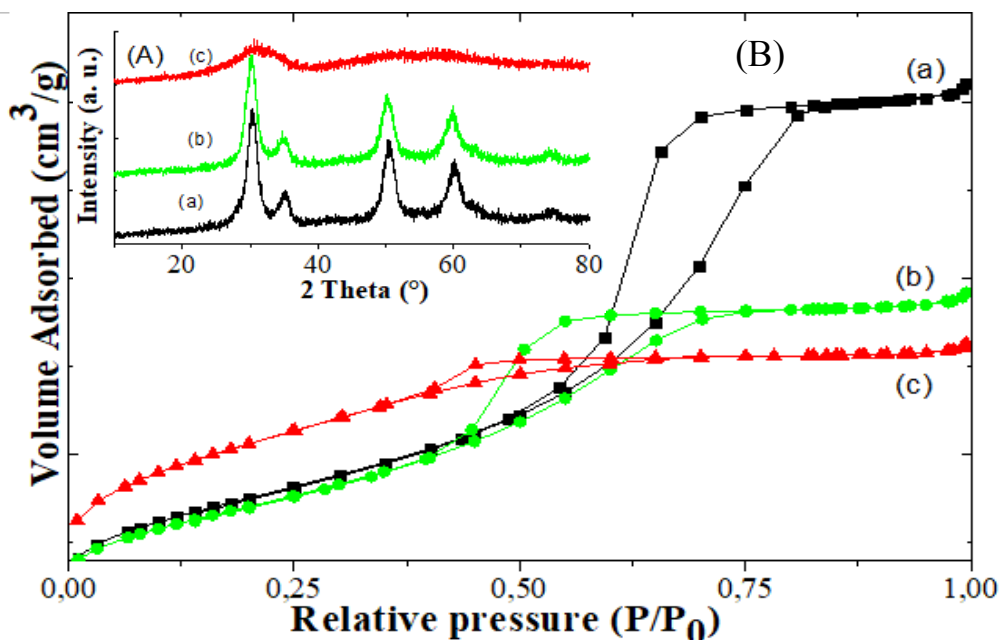
Before catalytic test, the powder (0.05 g) was activated in situ at 200 °C for 30 min under O<sub>2</sub>/He flow (20/80, v/v) then cooled to 150 °C. The SCR reaction was carried out from 150 to 500 °C using a feed gas stream

containing 1000 ppm NO, 1000 ppm NH<sub>3</sub>, 8 % O<sub>2</sub> balanced with He and 3.5 % H<sub>2</sub>O. The reactants and products were continuously analyzed by a quadruple gas mass spectrometer (Pfeiffer Omnistar).

### 3. Results and discussion

Structural and textural properties of catalysts were examined by XRD and N<sub>2</sub>-physisorption at 77 K, respectively. The results are presented in Fig. 1 and table 1. Fig 1 A reveals that the unsulfated solids demonstrate a high crystalline structure of zirconia tetragonal phase (t-ZrO<sub>2</sub>). This form is identified by its typical diffraction peaks at  $2\theta = 30.18^\circ$  (hkl:101),  $34.89^\circ$  (002),  $50.34^\circ$  (112),  $60.12^\circ$  (211),  $62.86^\circ$  (202) and  $74.60^\circ$  (220) [ICSD #: 066787]. After sulfation process, we noted a remarkable decrease in the intensity of t-ZrO<sub>2</sub> diffraction peaks and some of them disappeared leading to more amorphous than crystalline structure for the sulfated sample. This could indicate, according to Abd El Aziz A. Said et al. [26], an increase in the disorder of the structure caused by the strain, a less ordered crystalline or amorphous ZrO<sub>2</sub> phase. The absence, in XRD diffractograms, of reflections corresponding to Mn metal and its oxides, on one hand, and CeO<sub>2</sub>, on the other hand, demonstrates the high dispersion state of Mn and Ce species at catalysts surface [24].

The crystallites size (D) of catalysts was calculated by Scherrer formula based on the most intense peak of t-ZrO<sub>2</sub> ( $2\theta \sim 30.20^\circ$ ):  $D = 0.89 (\lambda/\beta\cos\theta)$  [8], where  $\theta$  is the peak position,  $\beta$  is the corrected peak width at half-maximum intensity (FWHM in radians) and  $\lambda$  is the wavelength of XR radiation. The obtained values are listed in table 1 and are equal to 4.2 and 4.4 for Mn/ZrO<sub>2</sub> and Mn/CeO<sub>2</sub>-ZrO<sub>2</sub>, respectively. This result proves the successful preparation of unsulfated catalysts with nano-sized particles.



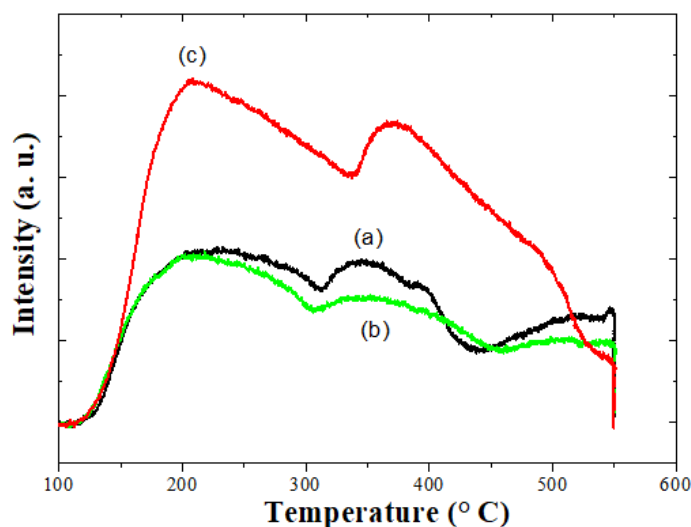
**Figure 1.** (A) XRD patterns and (B) N<sub>2</sub>-adsorption-desorption isotherms of catalysts: (a) Mn/ZrO<sub>2</sub>, (b) Mn/CeO<sub>2</sub>-ZrO<sub>2</sub> and (c) Mn/CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup>.

N<sub>2</sub> adsorption-desorption isotherms of samples (Fig. 1B) show a profile corresponding to type IV of the IUPAC classification, characteristic of mesoporous materials. In addition, the results given in table 1 indicates that all the catalytic systems develop high surface area ( $S_{\text{BET}} > 130 \text{ m}^2/\text{g}$ ) whereas, a decrease of the pores volume is noted, particularly, after incorporation of both ceria and sulfate. It can be associated with the pore's blockage of support by Ce, Mn and/or  $\text{SO}_4^{2-}$  species [27].

**Table 1.** Textural properties ( $S_{\text{BET}}$ ,  $V_p$ ,  $D_p$ ) and crystallites size ( $D$ ) of catalysts.

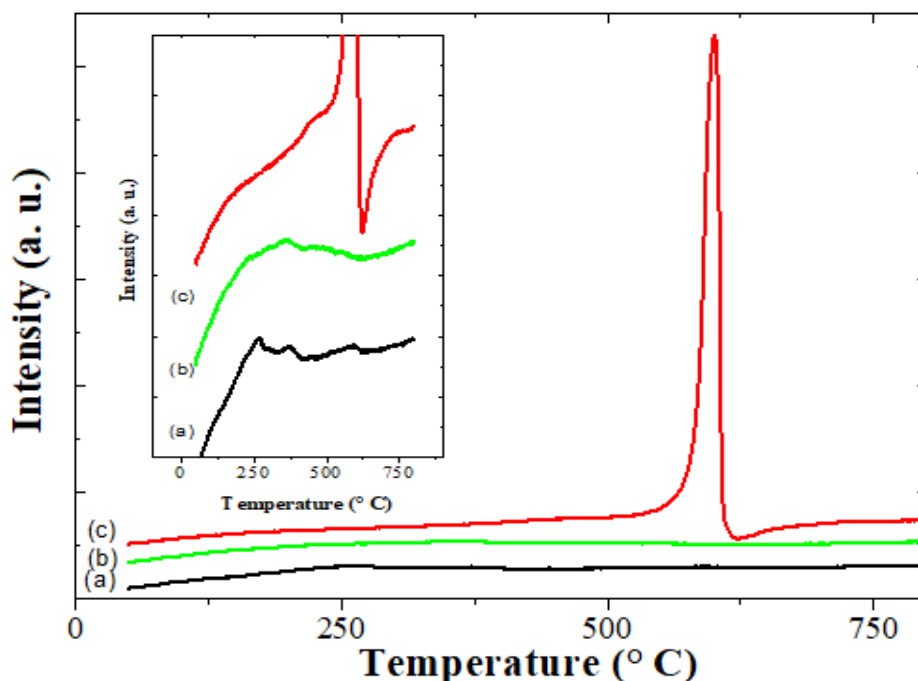
Catalysts	$S_{\text{BET}}$ ( $\text{m}^2\text{g}^{-1}$ )	$V_p$ ( $\text{cm}^3\text{g}^{-1}$ )	$D_p$ ( $\text{\AA}$ )	$D$ (nm)
Mn/ZrO <sub>2</sub>	139	0.244	53	4.2
Mn/CeO <sub>2</sub> -ZrO <sub>2</sub>	130	0.155	37	4.4
Mn/CeO <sub>2</sub> -ZrO <sub>2</sub> -SO <sub>4</sub> <sup>2-</sup>	192	0.096	29	-

The NH<sub>3</sub>-TPD profiles are illustrated in Fig. 2. As shown, the Mn/ZrO<sub>2</sub> displays three signals between 100 and 450 °C with maximums at ~ 200, 347 and 393 °C. This verifies the presence of different type of acid sites (weak, medium and strong) at its surface since it is recognized that the chemisorbed ammonia on weak, medium and strong acid sites gives NH<sub>3</sub>-desorption peaks in the 180-250 °C, 260-330 °C, 340-500 °C temperature range, respectively [28]. The addition of ceria alone led to a slight decrease of the intensity of NH<sub>3</sub>-TPD curves that is mainly due to the interactions between Ce and Mn and/or ZrO<sub>2</sub> which inhibits or changes the surface acidity of catalyst [29,30]. Remarkably, the highest total acidity is detected for Mn/CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup> solid. This is explained by the presence of sulfate groups; in fact, these components, usually, contribute to the creation of strong acid sites at the surface of sulfated catalysts [22,24]. It was proposed that sulfate species interact with adsorbed water to form Brønsted acid sites promoting the adsorption of ammonia and consequently facilitating the NH<sub>3</sub>-SCR reaction [31]. Moreover, X. Guo et al. [32] have claimed that an excellent NO reduction activity was observed since the density of Brønsted acid sites was increased upon sulfation of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> system.



**Figure 2.** NH<sub>3</sub>-TPD profiles of catalysts: (a) Mn/ZrO<sub>2</sub>, (b) Mn/CeO<sub>2</sub>-ZrO<sub>2</sub> and (c) Mn/CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup>.

H<sub>2</sub>-TPR curves are presented in Fig. 3. The peaks located between 200 and 450 in the H<sub>2</sub>-TPR profile of Mn/ZrO<sub>2</sub> catalyst can be ascribed to the reduction of Mn<sup>4+</sup> and Mn<sup>3+</sup> to Mn<sup>2+</sup> [33]. The modification of the shape of these peaks after ceria addition can be explained, in line with the NH<sub>3</sub>-TPD results, by the existence of interactions between Ce and Mn species which affects the redox behaviour of catalysts. Hence, the broad H<sub>2</sub> consumption, registered between 200 and 600 °C for Mn/CeO<sub>2</sub>-ZrO<sub>2</sub> solid, corresponds to the reduction of both Mn and Ce species. It was reported that the reduction of cerium (from Ce<sup>4+</sup> to Ce<sup>3+</sup>) occurs at around 540 °C [34]. The Mn/CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup> catalyst shows a new peak of high intensity at 600 °C that is attributed to the reduction of sulfate groups [22,24,35].

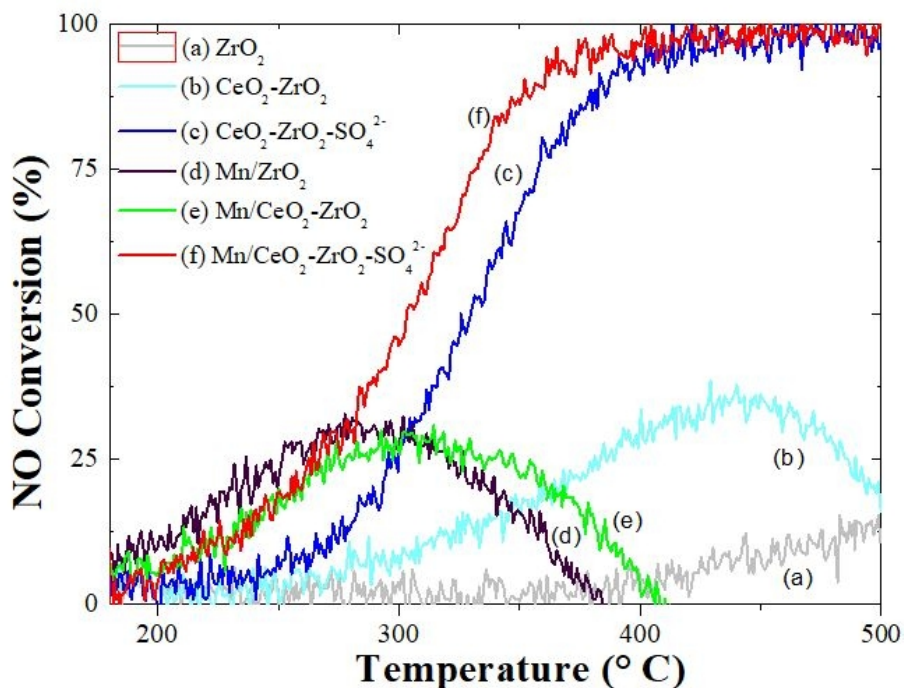


**Figure 3.** H<sub>2</sub>-TPR profiles of catalysts: (a) Mn/ZrO<sub>2</sub>, (b) Mn/CeO<sub>2</sub>-ZrO<sub>2</sub> and (c) Mn/CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup>.

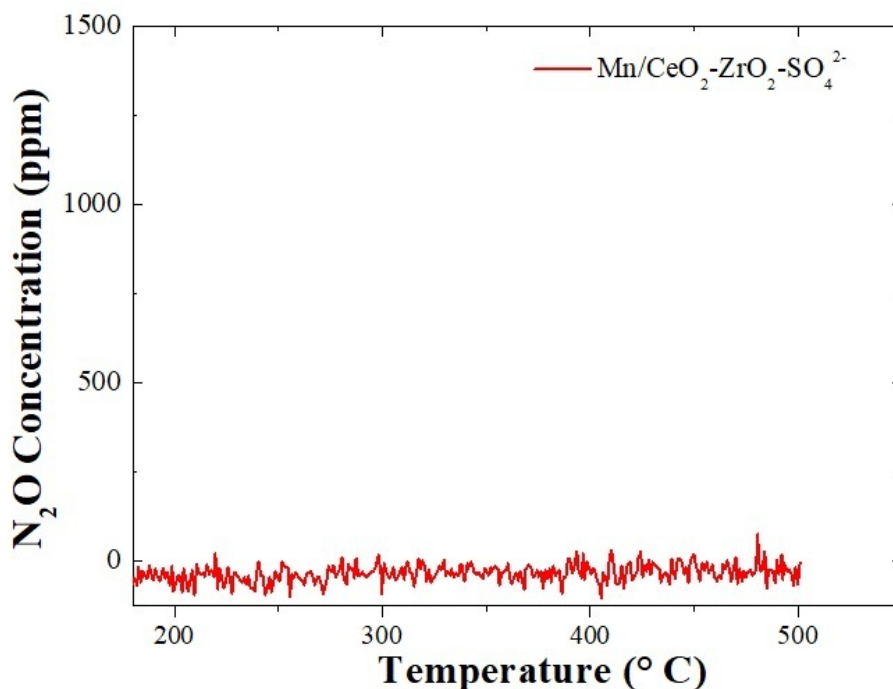
The activity of catalysts is evaluated in NO-SCR by NH<sub>3</sub> process. The results are presented in Fig. 4 (NO conversion as function of reaction temperature), Fig 5 (N<sub>2</sub>O concentration as function of temperature for the best catalyst), and Table 2 (NO conversion and N<sub>2</sub> selectivity for the best catalyst). It is known that the acidity of catalyst plays a key role in the SCR reaction at high temperature however, the SCR activity is controlled by the redox performance of catalyst at low temperature [10]. As it can be seen in Fig. 4, compared to ZrO<sub>2</sub> and CeO<sub>2</sub>-ZrO<sub>2</sub> catalytic supports, which were found inactive in the SCR reaction at low temperature (< 300 °C), Mn/ZrO<sub>2</sub> and Mn/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts display very low activities in this reaction with a maximum of around 30 % NO conversion at 300 °C. This low activity can be explained by the low reactivity of acid and redox sites existing at the surface of unsulfated catalysts. On the other hand, it can be mentioned that adding 10 % wt. CeO<sub>2</sub> improves the SCR activity of ZrO<sub>2</sub>, however, it does not play a role in improving the SCR activity of Mn/ZrO<sub>2</sub> catalyst which suggest that the quantity of CeO<sub>2</sub> need to be optimized in a future investigation. As also shown in Fig 4, the sulfated catalyst is very



active in SCR reaction at high temperature ( $>300\text{ }^{\circ}\text{C}$ ) with 100 % NO conversion into  $\text{N}_2$  above  $400\text{ }^{\circ}\text{C}$  without  $\text{NO}_2$  or  $\text{N}_2\text{O}$  formation (Fig. 5 and Table 2). It can be concluded, in perfect agreement with our previous works, that the presence of sulfate groups generate (as it was shown by  $\text{NH}_3$ -TPD analysis) new strong acid sites which are very reactive and may explain the excellent SCR performance of new  $\text{Mn/CeO}_2\text{-ZrO}_2\text{-SO}_4^{2-}$  catalyst at high temperature [22,24,35]. This conclusion can be confirmed by the much higher reactivity observed over  $\text{CeO}_2\text{-ZrO}_2\text{-SO}_4^{2-}$  sulfated support compared to the corresponding unsulfated one ( $\text{CeO}_2\text{-ZrO}_2$ ). On the other hand, the higher activity obtained at  $T < 400\text{ }^{\circ}\text{C}$  over  $\text{Mn/CeO}_2\text{-ZrO}_2\text{-SO}_4^{2-}$  compared to  $\text{CeO}_2\text{-ZrO}_2\text{-SO}_4^{2-}$  support highlight the role of Mn species in improving the reactivity of catalyst at low temperature.



**Figure 4.** NO conversion for SCR reaction over Mn based catalysts and catalytic supports (used for comparison).



**Figure 5.** N<sub>2</sub>O concentration as a function of SCR reaction temperature over Mn/CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup>.

**Table 2.** Catalytic performances of new Mn/CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup> catalyst in NH<sub>3</sub>-SCR of NO.

Catalyst	Temperature (°C)	NO conversion (%)	Selectivity (%)		
			N <sub>2</sub>	N <sub>2</sub> O	NO <sub>2</sub>
Mn/CeO <sub>2</sub> -ZrO <sub>2</sub> -SO <sub>4</sub> <sup>2-</sup>	200	5	100	0	0
	250	19	100	0	0
	300	45	100	0	0
	350	86	100	0	0
	400	98	100	0	0
	450	100	100	0	0
	500	100	100	0	0

#### 4. Conclusion and perspectives

In summary, the presence of a low quantity of Mn (2 % wt), deposited by the impregnation method, at the surface of simple or mixed aerogel oxides (ZrO<sub>2</sub>; CeO<sub>2</sub>-ZrO<sub>2</sub>) leads to highly structured and mesoporous catalysts containing some acidic and redox sites but exhibiting low activity in NO-SCR reaction. The addition of sulfate affects the structure, leading to a lowly crystalline or even amorphous Mn/CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup> new system but it increases significantly the strong acidity of solid and improves significantly its NO-SCR activity at high temperature.

Compared to VWTi and Mn-Ce based catalysts reported in the literature, our new system (Mn/CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup>) exhibits lower NO conversion at low temperatures (< 400 °C) but it demonstrates higher NO conversion and N<sub>2</sub> selectivity at higher temperatures (400-500 °C).

Further studies are in progress to understand the NH<sub>3</sub>-SCR mechanism over Mn/CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup> system and to extend the windows of temperature for this novel SCR catalyst at low temperatures by optimizing the amounts of Mn and CeO<sub>2</sub>, and by studying the preparation of Mn/CeO<sub>2</sub>-ZrO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup>, with optimized quantities of manganese and cerium, via the one step sol gel method. The analysis of the physicochemical properties of catalysts by more advanced techniques will be also reported.

### Statements and Declarations

- **Competing interests**

The authors have no competing interests to declare that are relevant to the content of this article.

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