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Effect of acidic components (SO_4^{2-} and WO_3) on the surface acidity, redox ability and NH_3 -SCR activity of new CeO_2 - TiO_2 nanoporous aerogel catalysts: A comparative study

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Abstract

Selective catalytic reduction (SCR) of nitrogen oxide (NO) by ammonia (NH_3) was studied in this work over new sulfate (SO_4^{2-}) or tungsta (WO_3) modified CeO_2 - TiO_2 aerogel catalysts. The catalytic systems were elaborated via sol gel method then characterized by: XRD, N_2 -Physisorption at 77 K, DRUV-vis, NH_3 -TPD and H_2 -TPR. It was revealed that the nature of acidic components influences differently the texture, surface oxygen concentration, acidity, reducibility and NH_3 -SCR activity of new Ce-based catalysts. Hence, the incorporation of sulfate modifies the nature of Ce species, improves their dispersion through the Ce- SO_4^{2-} interactions and, particularly, generates new strong acid sites which display superior catalytic performance at high temperature NO reduction (NO conversion into $\text{N}_2 > 90\%$ between 450 and 500 °C over CeO_2 - TiO_2 - SO_4^{2-} catalyst). However, the addition of tungsta affects slightly the surface acidity of CeO_2 - TiO_2 catalyst but it induces the creation of more reactive surface oxygen and new redox sites at its surface (mainly due to the existence of W-Ce interactions) leading to highly active WO_3 - CeO_2 - TiO_2 system for the low temperature NH_3 -SCR reaction with above 90 % NO conversion into N_2 between 320 and 400 °C.

Key words: NO Emissions control, Modified CeO_2 - TiO_2 aerogel catalysts, Acidic components, Surface acidity, Redox ability, NH_3 -SCR activity.

I. Introduction

Diesel engines are considered as one of the largest contributors to the environmental pollution and climate change caused by exhaust emissions containing hydrocarbons (HC), particulate matter (PM) carbon monoxide (CO) and nitrogen oxides (NO_x). NO_x (x = 1 and 2) are constituted by 85-95 % of NO which is an odorless and colorless gas and that is gradually converted, in atmospheric air, into NO₂ (a reddish brown gas with pungent odor and a level of toxicity five times greater than that of NO) [1]. These toxic compounds react chemically with other pollutants to form tropospheric ozone (the primary component of photochemical smog) and contribute to the formation of acid rain, haze, greenhouse gas... [1-4]. In addition, NO_x species are harmful to the human body, causing eye and throat irritation, chest tightness, nausea, headache, lung infections and respiratory allergies like bronchitis and pneumonia [2,5].

In recent years, strict legislations and policies have been imposed worldwide for the purpose of reducing NO_x emissions from vehicles. In Euro V, NO_x emission is limited to <180 mg/km and 60 mg/km for diesel-driven engines and petrol-driven engines, respectively. These values are 55 % lower in Euro VI [2,6]. Besides, in China, the limits of NO_x from light-duty vehicles are fixed at 60 mg/km and 35 mg/km (GB 18352.6-2016) for 2020 and 2023 years, respectively [7]. Consequently, the NO_x removal from flue gases has become an ever more urgent task for environmental protection.

The NO_x control technologies can be classified into three groups: combustion, pre-combustion, and post-combustion. In pre-combustion process, the formation of NO_x is inhibited by the selection of a low-nitrogen fuel. Also, combustion is mainly used to reduce the NO_x emissions by varying the combustion conditions. Nevertheless, using the post combustion methods, the NO_x existing in the flue gas exhaust are converted into essentially

nitrogen (N_2) and other harmless products via physical and chemical transformations which are produced in the denitrification devices installation [8]. Compared with pre-combustion and combustion methods (which help to remove less than 50 % NO_x), the post-combustion technologies are more attractive due to its higher NO_x elimination (> 80 %) [2].

Among several available post-combustion technologies, including selective catalytic reduction (SCR), selective non catalytic reduction (SNCR), electrochemical reduction, catalytic decomposition, non-thermal plasma (NTP), wet scrubbing, adsorption and electron beam [2,8,10] SCR of NO_x with NH_3 , is currently the most popular approach for flue gases denitrification (De NO_x) from stationary and mobile sources [10,11] ; it is based on the reaction between NO_x and NH_3 to produce N_2 and H_2O using a suitable catalyst. V_2O_5 - WO_3/TiO_2 system is the most widely used NH_3 -SCR catalyst to abate NO_x from power plants. It was introduced also on diesel vehicles as the first generation of SCR catalyst [12, 13]. Nevertheless, this system still has some intrinsic drawbacks such as: the narrow and high working temperature window (300-400 °C), low N_2 selectivity at high-temperature and toxicity of vanadium [14, 15]. Accordingly, many research works have been realized to develop vanadium-free catalysts that can be applied to diesel vehicles [4].

It is recognized that the presence of actives acidic and redox sites on the catalyst surface is a key factor for the design of SCR catalysts with a high NO_x removal efficiency [16-19]. Recently, a lot of attention have been devoted to CeO_2 - TiO_2 systems as great candidate to substitute the commercial VO_x - TiO_2 catalysts due to their environmentally friendly and excellent SCR performance. A detailed review about the investigations of CeO_2 - TiO_2 catalysts in the NH_3 -SCR reaction was recently reported by Zheng et al. [16]. The studies demonstrated that CeO_2 - TiO_2 catalysts, prepared via different methods (Impregnation, co-precipitation, homogenous precipitation, spontaneous deposition, sol gel (xerogel form), co-precipitation associated with microwave, supercritical water and dry ball milling in the

presence of an organic ligand), have been proved to be very active in the reduction of NO by NH₃ due to the unique oxygen storage capacity (OSC) of cerium, its excellent redox ability and acid base properties [16,20, 21]. In this framework, Gao et al. [22,23] reported that CeO₂-TiO₂ xerogel catalyst, elaborated via sol-gel method, exhibits much better NH₃-SCR performance than the same catalysts prepared by impregnation and co-precipitation methods, owing to its high surface area, better redox ability, strong interaction between CeO₂ and TiO₂ and well dispersed CeO₂ species. On the other hand, many literature reports have proved that adding acidic components (sulfuric acid [24], phosphoric acid [25]; oxides of: W [26], Mo [27] or Nb [28]) into Ce based catalysts enhances its acidic functions and thereby improves significantly its NO-NO-SCR activity. Yu et al. [29], investigated a series of sulfated catalysts (CuSO₄/TiO₂, Fe₂(SO₄)₃/TiO₂, MnSO₄/TiO₂, Ce(SO₄)₂/TiO₂ and CoSO₄/TiO₂) in the NH₃-SCR reaction and demonstrated that the amount of acid sites was the main factor which affects the catalytic activity of metal sulfate catalysts. Furthermore, in our previous work [26], we showed that WO₃-CeO₂-TiO₂ exhibits higher SCR activity than WO₃-TiO₂ and CeO₂-TiO₂ aerogel catalysts due to the synergetic effect between W and Ce which influences the acidity and reducibility of catalyst. Li et al. [30] reported that a novel CeO₂/TiO₂-MoO₃ catalyst exhibits 100% NO conversion at 200-350 °C. The authors indicated that doping of Mo produces more Brønsted acid and Lewis acid sites, increases the specific surface area and redox ability of catalyst and, consequently, enhances its NH₃-SCR activity. A series of CeO₂-Nb₂O₅/TiO₂ SCR catalysts were investigated by Jiang et al. [28]. Their results revealed that the addition of Nb improves the dispersion of CeO₂, increases the amount of Ce³⁺ and chemisorbed oxygen species on the catalyst surface, which enhances the catalytic activity of CeTi material. The authors attributed the superior SCR activity of CeNbTi to its high redox ability, the enhanced adsorption capacity of NH₃ species and the synergistic action between Ce, Nb and Ti species.

Although CeO₂-TiO₂ catalysts have been extensively studied and demonstrated a high catalytic performance in the NH₃-SCR reaction, the investigation of the aerogel form of CeO₂-TiO₂ in this reaction is still rare and only a few paper deal with this subject. Therefore, in this study we report for the first time a comparative investigation about the effect of acidic components (SO₄²⁻ or WO₃) on the physicochemical properties and NH₃-SCR activity of Ce based aerogel catalysts (CeO₂-TiO₂-SO₄²⁻ and WO₃-CeO₂-TiO₂). These materials were elaborated via sol gel procedure followed by supercritical drying. This method presents several advantages including a simple and low cost technology, low process-temperatures and flexible control of the structure and size of final products using many operating parameters [31]. In addition, it can give aerogel mixed oxides with interesting properties, such as: high purity, nanometer size and developed mesoporous texture..., which make them useful for many applications, especially for catalysis [20, 26, 32].

2. Material and methods

2. 1. Synthesis of Ce based nanoporous aerogel catalysts

The powder aerogels (TiO₂, CeO₂-TiO₂, CeO₂-TiO₂-SO₄²⁻ and WO₃-CeO₂-TiO₂) were prepared via the one step sol gel protocol, then dried under the supercritical drying conditions of solvent (ethanol). The detailed method adopted for the elaboration of samples was described in our previous works [20,26]. Ammonium metatungstate hydrate ((NH₄)₆H₂W₁₂O₂₄.xH₂O, Sigma Aldrich, > 99.9%) and cerium nitrate (Ce(NO₃)₃.6H₂O, Aldrich) were used as W and Ce precursors, respectively. Theoretical loading of WO₃ or CeO₂ were fixed at 10 % wt. For the sulfated catalyst, an appropriate volume of H₂SO₄ solution (Scarlau, 95-97%) giving a molar ratio S/Ti = 0.2 was used. All the aerogel mixed oxides were calcined at 500 °C for 3 h under O₂ flow (30 mL.min⁻¹).

2. 2. Characterization of Ce based nanoporous aerogel catalysts

The structure and crystallites size of aerogels (powder) were determined by X Ray Diffraction (XRD) analysis using a Brüker AXS D8 diffractometer. The XRD patterns were registered, between 2 and 80 ° with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The main reflexion of TiO₂ anatase phase ($\sim 2\theta = 25^\circ$, hkl: 101), was used to determine the crystallites size (D) of solids based on the Scherrer formula ($D = 0.89 (\lambda / \beta \cos\theta)$) [33] 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 101 reflection position.

The textural properties of solids were examined by the N₂ physisorption at 77 K. N₂ adsorption-desorption isotherms, specific surface area (S_{BET}), total pore volume (V_{PT}), pore size distribution and pore size diameter (Φ_{pore}) were determined by means of a Micromeritics ASAP 2020 apparatus. The powder was outgassed in a vacuum during 6 h at 200 °C prior to N₂ adsorption. The residual pressure reached during the degassing step was 10⁻⁵ Torr.

The UV-vis analyses were carried out on a PerkinElmer spectrophotometer type lambda 45 equipped with an integrating sphere type RSA-PE-20. The UV-vis spectra were recorded at room temperature in the 200-900 nm range.

The NH₃ temperature-programmed desorption (NH₃-TPD) experiments were performed using an AUTOCHEM 2920 (Micromeritics) equipped with a TCD detector. For the analysis, 0.05 g of each sample was pretreated in air flow (30 mL min⁻¹) at 500 °C (ramp 10 °C min⁻¹) for 30 min, then cooled to 100 °C in the same stream and subsequently exposed to NH₃ (5 vol% NH₃ in He, flow rate = 30 mL min⁻¹) for 45 min. The physisorbed NH₃ was removed by flushing the catalyst with He (30 mL min⁻¹) for 2 h. Finally, the NH₃-TPD curves

were recorded by heating the samples in He (30 mL min⁻¹) at a heating rate of 10 °C min⁻¹ from 100 to 600 °C.

The H₂ temperature-programmed reduction (H₂-TPR) analyses were done in an AUTOCHEM 2910 (Micromeritics) over 0.05 g of sample. The H₂ consumption was measured by a thermal conductivity detector. First, 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). 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 from 50 to 800 (or 900 °C) at a heating rate of 10 °C min⁻¹.

2. 3. Catalytic activity measurement

The selective Catalytic Reduction (SCR) tests were carried out in a fixed-bed quartz flow reactor, operating at atmospheric pressure. 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 reaction conditions are: 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. During the SCR test, the reactants and products gases were continuously analyzed by an online Pfeiffer Omnistar quadruple mass gas spectrometer equipped with Channeltron and Faraday detectors (0-200 amu).

3. Results and discussion

3. 1. Physico-chemical properties of Ce based nanoporous aerogel catalysts

The XRD patterns of powder aerogels and average crystallites size of TiO₂ carrier are given in Fig. 1 and Table 1, respectively. The peaks, detected 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], in the diffractograms of all the solids are consistent with the characteristic reflections of TiO_2 anatase phase. There are no peaks related to rutile or brookite phases revealing the synthesis of TiO_2 carrier with a high purity of anatase form. Generally, the catalytic activity of SCR catalysts with anatase TiO_2 as carrier was superior to that with rutile or brookite TiO_2 as catalytic support [12, 17]. On the other hand, no typical peaks of tungsten oxide or metal sulfates were observed in the obtained XRD diffraction patterns indicating that tungsten and sulfates species are highly dispersed at TiO_2 surface. This is in agreement with the results already obtained for numerous WO_3 containing catalysts [26,34] such as: xerogel $\text{WO}_3\text{-CeO}_2\text{-TiO}_2$ [35] and supported metal sulfates on Ce-TiO_x SCR catalysts [36]. In the case of unsulfated catalysts, the new peaks of low intensity, located at $2\theta \approx 28.5^\circ$ (hkl: 111) and 32.9° (200), are attributed to a low amount of the crystalline form of cubic ceria (CeO_2) [ICSD 00-034-0394]. These peaks are absent in the diffractogram of $\text{CeO}_2\text{-TiO}_2\text{-SO}_4^{2-}$ catalyst indicating the highly dispersed state of cerium species at the surface of sulfated catalyst. This is mainly due to the existence of strong interactions between Ce and SO_4^{2-} .

From the values listed in table 1, it can be concluded that all the powder aerogels are constituted by nano-sized particles with a size in the range of $\sim 8\text{-}11$ nm. It could be also mentioned that, contrarily to sulfate groups, the presence of W species inhibits the crystallites growth of anatase TiO_2 , since a visible increase of TiO_2 grain is noted for the sulfated sample only. Shan et al. [37] indicated that the Ce species inhibited also the growth of anatase TiO_2 crystallite in the case of $\text{CeO}_2\text{-TiO}_2$ catalyst, prepared via an optimized homogeneous precipitation method.

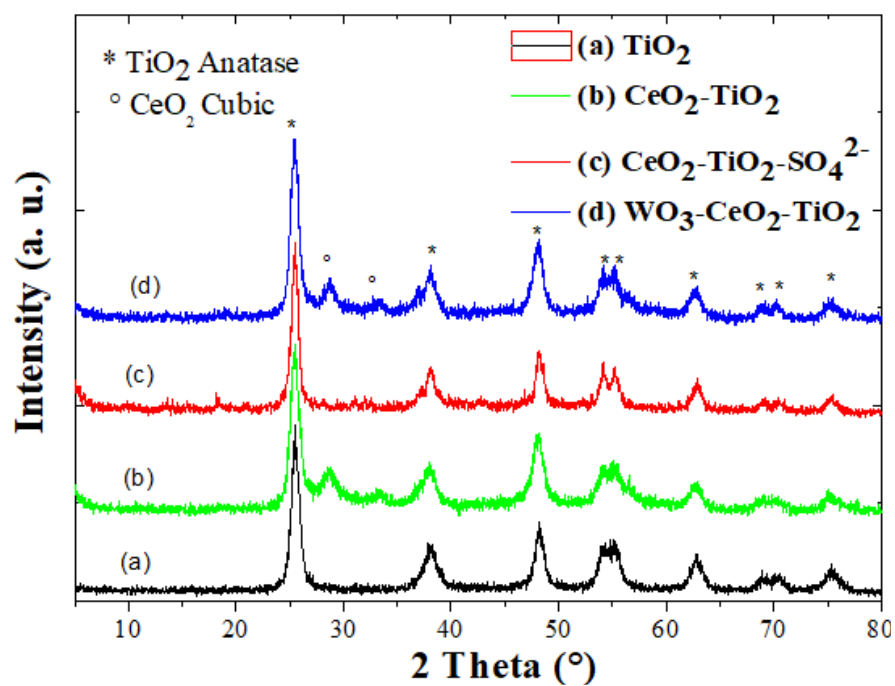


Figure 1. Structure of Ce based nanoporous aerogel catalysts.

Table 1. Crystalline phases and TiO₂ crystallites size of Ce based nanoporous aerogel catalysts.

Sample	XRD phases	FWHM (°)	TiO ₂ crystallites size D (nm)
TiO ₂	Anatase	0.892	8.6
CeO ₂ -TiO ₂	Anatase + Ceria	0.884	8.6
TiO ₂ -CeO ₂ -SO ₄ ²⁻	Anatase	0.689	11.1
WO ₃ -CeO ₂ -TiO ₂	Anatase + Ceria	0.931	8.2

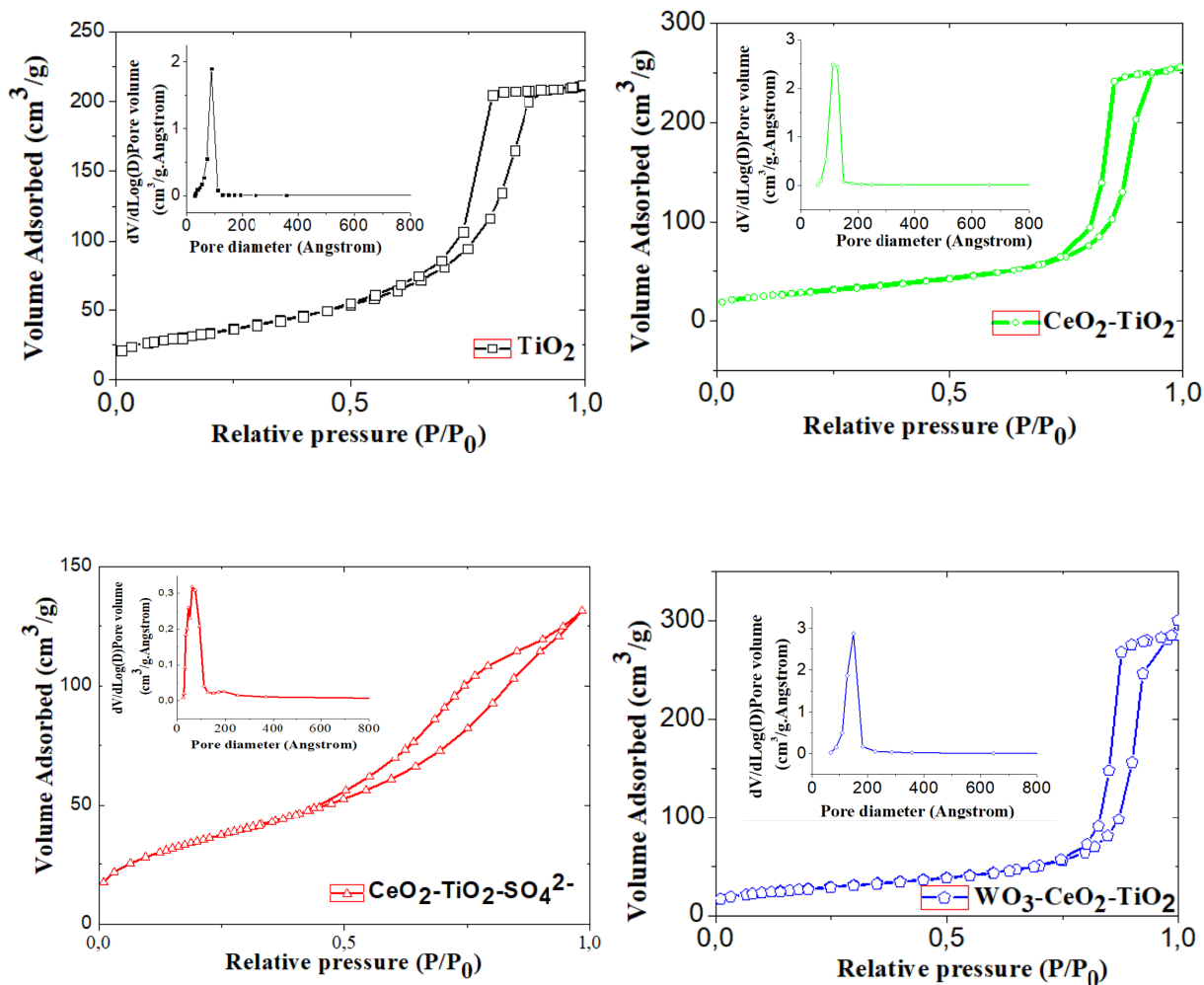


Figure 2. N₂-Isotherms and corresponding pore size distribution curves of Ce based nanoporous aerogel catalysts.

N₂ adsorption-desorption isotherm and corresponding pore size distribution curve of each sample are depicted in Figure 2. As it can be seen, an isotherm belonging to type IV, is obtained for all the aerogels and is indicative, according to the IUPAC classification, of their mesoporous texture [38]. Pure TiO₂ and CeO₂-TiO₂ exhibit a H2 type of hysteresis loops demonstrating the presence of ink-bottle pores in their texture [39]. However, cylindrical mesoporous channels exist in the texture of WO₃-CeO₂-TiO₂ system that is characterized by a H1 type of hysteresis loop [40]. For the sulfated catalyst (CeO₂-TiO₂-SO₄²⁻), the obtained hysteresis loop mostly resembles to H3 type related to mesoporous solids with a broad distribution of the pores size [29,41,42].

As indicated in Table 2, the high values of the specific surface area ($S_{\text{BET}} > 99 \text{ m}^2/\text{g}$) and total pore volume ($V_{\text{PT}} > 0.21 \text{ cm}^3/\text{g}$) obtained in all cases demonstrate that all the investigated catalysts develop a good mesoporous texture which is beneficial for their NO-SCR activity. Nevertheless, it should be mentioned that the slight decrease of the S_{BET} observed in the case of $\text{CeO}_2\text{-TiO}_2$ and $\text{WO}_3\text{-CeO}_2\text{-TiO}_2$ catalysts can be related to the blockage of some pores of TiO_2 by Ce and/or W species [20]. Conversely, the high S_{BET} retained for the sulphated catalyst can be explained by the high dispersion of cerium species at the catalyst surface due to their interactions with sulfate groups. This is consistent with the obtained XRD results.

Table 2. Textural properties of Ce based nanoporous aerogels 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
$\text{CeO}_2\text{-TiO}_2$	106	0.40	117
$\text{TiO}_2\text{-CeO}_2\text{-SO}_4^{2-}$	128	0.21	62
$\text{WO}_3\text{-CeO}_2\text{-TiO}_2$	99	0.46	145

Fig. 3 shows the UV-vis spectra of powder aerogels. It is clearly seen that all the solids display the characteristics bands of TiO_2 anatase phase located in the 200-400 nm range and attributed to $\text{O}^{2-} \rightarrow \text{Ti}^{4+}$ charge transfer transitions [20,43]. Additional bands appeared above 350 nm in the UV spectra of $\text{CeO}_2\text{-TiO}_2$ and $\text{WO}_3\text{-CeO}_2\text{-TiO}_2$ catalysts and could be ascribed, based on the literature reports, to cerium and tungsten species; Ce^{4+} (280-400 nm [20, 26]) and W^{6+} polymeric octahedral species (300-375 nm [26, 34, 44]). Remarkable, the shape of the UV-vis curve of CeO-TiO_2 is strongly changed after sulfate incorporation. In fact, we note the disappearance of bands related to Ce^{4+} species (in the 280-400 nm range [26, 34, 45, 46]), which implies that sulfate groups obviously affect the nature of cerium species (perhaps oxidation state, dispersion and/ or coordination). This suggests, in perfect agreement with our

previous work [20] and in line with the XRD results, the existence of strong interactions between Ce species and sulfate groups which, most probably, contribute to stabilize cerium at its Ce^{3+} form (characterized by $\text{O}^{2-} \rightarrow \text{Ce}^{3+}$ absorption bands in the range of 220-250 nm) [20, 26, 47]. Similar observations demonstrating the modification of the nature of Mn species after sulfate addition have been previously stated for Mn based aerogel catalysts [47].

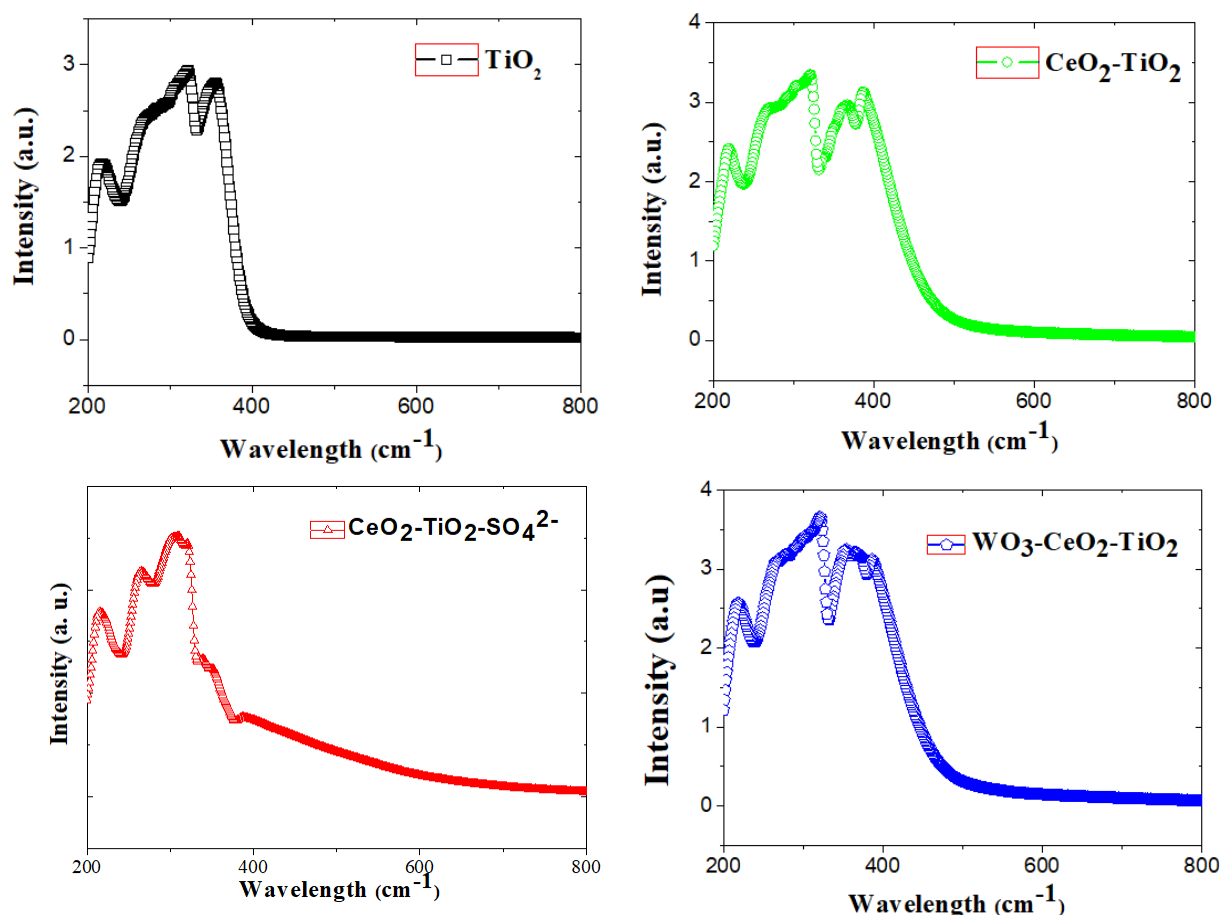


Figure 3. UV-vis spectra of Ce based nanoporous aerogel catalysts.

The NH_3 adsorption on the acidic sites of catalyst is known to be a crucial step for NO-SCR reaction, especially over catalytic systems used under high temperature ($> 300\text{ }^\circ\text{C}$, [48,49]). NH_3 -TPD experiments were performed in order to explore the surface acidity of aerogel catalysts and the results are illustrated in Fig. 4. As observed, all the samples display a broad NH_3 desorption signal from 100 to 400 $^\circ\text{C}$ which could be assigned to ammonia

desorbed from weak and medium acid sites [50]. The shape and intensity of this signal changes as function of the nature of active element added to TiO_2 suggesting the existence of strong and diverse interactions between titania support and supported species (Ce , W , SO_4^{2-}) which affect differently the number and strength of acid sites [44,47]. Remarkably a new high temperature NH_3 desorption peak centered at around 515°C is detected in the NH_3 -TPD profile of sulphated sample only and is ascribed, according to our previous studies [20,41,47] to new strong acid sites generated by sulfate groups. Based on the above results, it can be concluded that adding WO_3 or SO_4^{2-} influences differently the surface acidity of CeO_2 - TiO_2 catalyst and higher total acidity is obtained by adding sulfate groups.

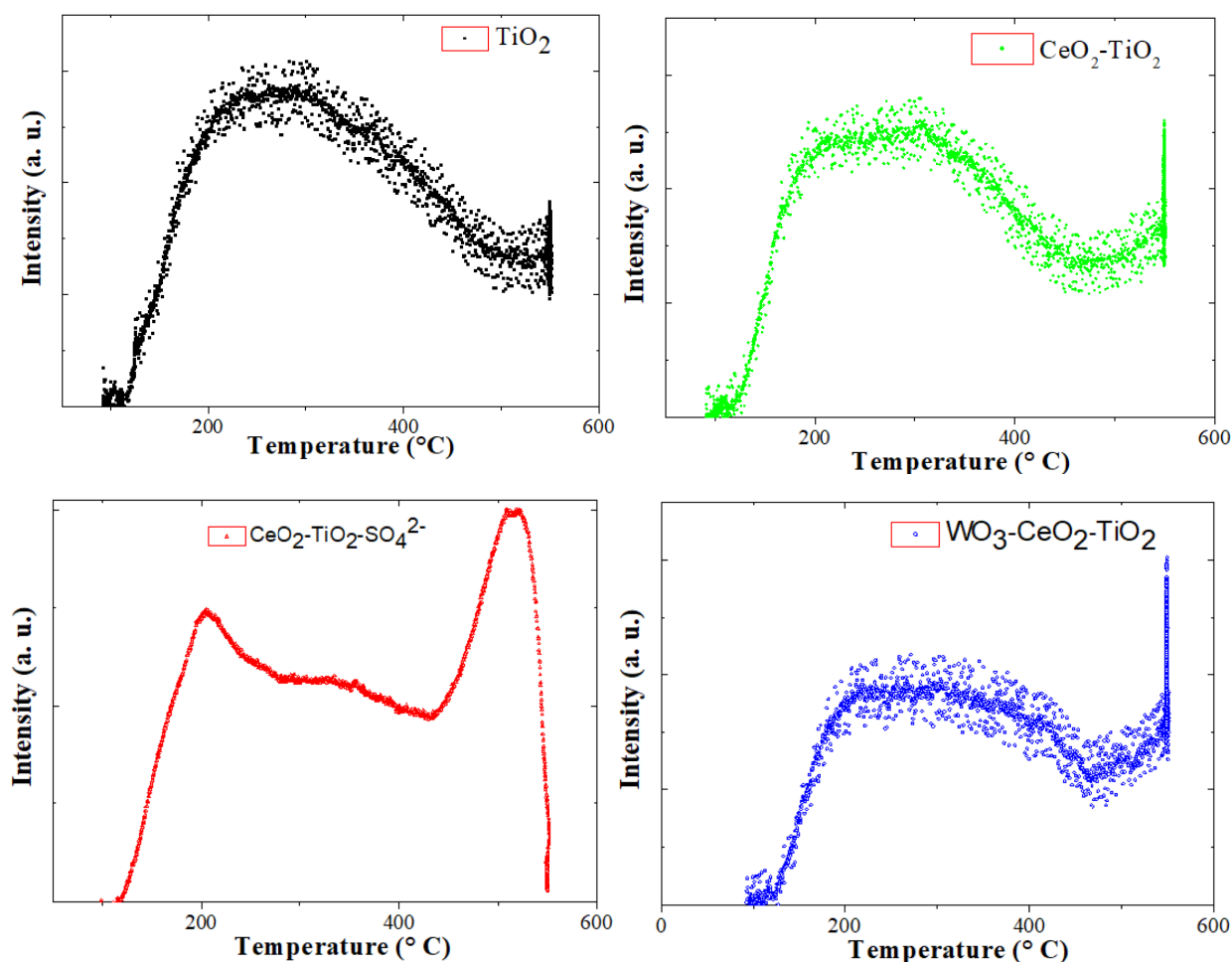


Figure 4. NH_3 -TPD curves of Ce based nanoporous aerogel catalysts.

The redox ability of catalyst plays a key role in the NH_3 -SCR reaction [51]. It was reported that the redox properties have a significant influence on the NH_3 -SCR performance

of CeO₂-TiO₂ catalysts. Usually, a suitable redox property facilitates the activation of NO_x and NH₃ at low temperature and thus increases the low temperature catalytic activity of CeO₂-TiO₂ catalyst. Moreover, it is widely accepted that the adsorption and activation of oxygen and NO_x occur at Ce⁴⁺/Ce³⁺ redox sites [16]. The reducibility of CeO₂-TiO₂ and the effects of adding sulfate and tungsta on the redox behaviour of this aerogel catalyst were examined by means of H₂-TPR technique. The recorded H₂-TPR curves are presented in Fig. 5. As shown, the incorporation of cerium contributes to the creation of redox sites at TiO₂ surface since the CeO₂-TiO₂ sample displays H₂ consumption peaks in the 400 and 600 °C temperature range which can be attributed, according to literature reports, to the reduction of surface oxygen of stoichiometric ceria (Ce⁴⁺-O-Ce⁴⁺) and cerium species (Ce⁴⁺ to Ce³⁺) [26,52]. The addition of acidic components (WO₃ or SO₄²⁻) influences in a different way the nature of redox sites and reducibility of CeO₂-TiO₂ catalyst. Therefore, the WO₃-CeO₂-TiO₂ system demonstrates a broad first peak in the 300-500 °C temperature range corresponding to the reduction of surface oxygen of CeO₂ [26] and a second peak maximized at 570 °C attributed to the reduction of cerium species from Ce⁴⁺ to Ce³⁺ [20,26,52]. The intensities and areas of these peaks are higher compared to these obtained for CeO₂-TiO₂ solid revealing the presence of higher quantities of surface oxygen and Ce redox sites at the WO₃-CeO₂-TiO₂ surface [26]. This is probably due to the existence of Ce-W interactions which enhance the redox ability of WCeTi catalyst. Noting also that WO₃-CeO₂-TiO₂ solid displays a third peak at 860 °C which is ascribed to the reduction of tungsten species [26,44]. The H₂-TPR profile of sulfated catalyst is different from these registered for the other samples; it shows a new high intensive and asymmetrical peak beginning at around 450 °C and centered at ~ 650 °C which is ascribed to the reduction of sulfate groups [20,26,47]. For this sample, the reduction of surface oxygen of CeO₂ and cerium species seems to be overlapped by the former peak.

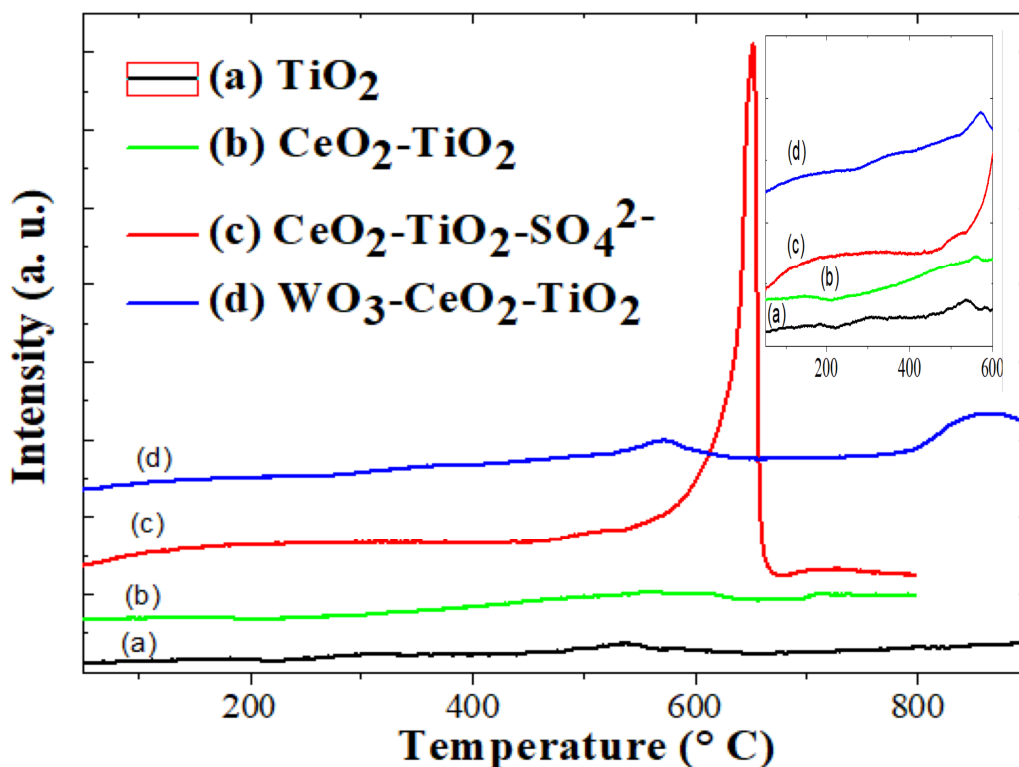


Figure 5. H₂-TPR curves of Ce based nanoporous aerogel catalysts.

It was recognized that the SCR activity is governed by the reducibility of catalyst at low temperatures and by its acidity at high temperatures [53]. The NH₃-SCR activity of Ce based aerogel catalysts was evaluated and the results, in term of NO conversion as function of reaction temperature, are illustrated in Fig 6A. Total conversion and oxidation conversion of NH₃ are also presented (Fig. 6B). As shown in Fig. 6A, the NO conversions are strongly dependent on the nature of active elements and reaction temperature. Therefore, the TiO₂ carrier is inactive at low temperatures (< 300 °C) and exhibits moderate reactivity at higher temperatures with a maximum of 50 % NO conversion into N₂ at 500 °C. The SCR activity is significantly enhanced at low temperatures after adding 10 wt. % CeO₂. This increase in NO conversion is essentially attributed to the reactivity of cerium redox sites created at TiO₂ surface as demonstrated by the H₂-TPR analysis. Noticeably, over this CeO₂-TiO₂ aerogel catalyst, the NO conversion increases from 10 % (at 205 °C) to 90 % (at 330 °C) and remains above 90 % in the 330 - 400 °C interval. This high catalytic activity can be mainly correlated

with the presence of active surface oxygen and redox sites generated by the presence of cerium species at the $\text{CeO}_2\text{-TiO}_2$ surface, as demonstrated by the H_2 -TPR technique. The SCR activity of $\text{WO}_3\text{-CeO}_2\text{-TiO}_2$ system is higher than that of $\text{CeO}_2\text{-TiO}_2$ in the whole temperature range. Hence, the NO conversion increases over the catalyst containing 10 % WO_3 from 10 % (at 197 °C) to 90 % (at 320 °C) and remains above 90 % between 320 and 430 °C. The superior catalytic performance of this sample if compared to that prepared without tungsten can be principally correlated, according to the H_2 -TPR results, with the presence of more reactive surface oxygen and redox sites due to the existence of $\text{W}\leftrightarrow\text{Ce}$ interactions as previously explained [26]. It should be mentioned that the decrease of the NO conversion at high temperature (particularly for $T > 400$ °C) over $\text{CeO}_2\text{-TiO}_2$ and $\text{WO}_3\text{-CeO}_2\text{-TiO}_2$ catalysts is due to the secondary reaction of NH_3 oxidation [41]. In fact, figure 6B clearly shows that for these two samples, NH_3 conversion reaches 100 % at 375 °C and remains at this value up to 500 °C. This means that from around 330 °C, more ammonia is consumed than NO. Therefore, NH_3 conversion due to direct oxidation by O_2 was also reported in Fig 6B. This conversion was inferred from the difference between the total NH_3 conversion and the NH_3 conversion involved in NO reduction. This side reaction starts around 320-330 °C for $\text{CeO}_2\text{-TiO}_2$ and $\text{WO}_3\text{-CeO}_2\text{-TiO}_2$ catalysts and becomes important above 400 °C.

The addition of sulfate groups into $\text{CeO}_2\text{-TiO}_2$ had a different effect than that observed with tungsten species. It induces a visible decrease of the NO conversion at low temperature (< 300 °C) but it increases significantly this conversion into N_2 at high temperatures (> 300 °C). Hence, the sulfated sample was found inactive until 300 °C after which the NO conversion increases with the increase of the reaction temperature up to 500 °C. Above 90 % NO conversions are reached over this sample in the 450-500 °C temperature range. For this catalyst, contrarily to $\text{CeO}_2\text{-TiO}_2$ and $\text{WO}_3\text{-CeO}_2\text{-TiO}_2$ solids, we observe a quite similar conversion of NO and NH_3 (Fig. 6B) since direct NH_3 oxidation by O_2 is insignificant. Based

on this result, it can be confirmed, in line with the UV-vis results, that the presence of sulfate groups modifies the nature of cerium species suppressing the active ones for the low temperature NH_3 -SCR reaction. By contrast, it induces, as shown by NH_3 -TPD analysis, the formation of highly active acid sites for the high temperature NO reduction ($> 450\text{ }^\circ\text{C}$).

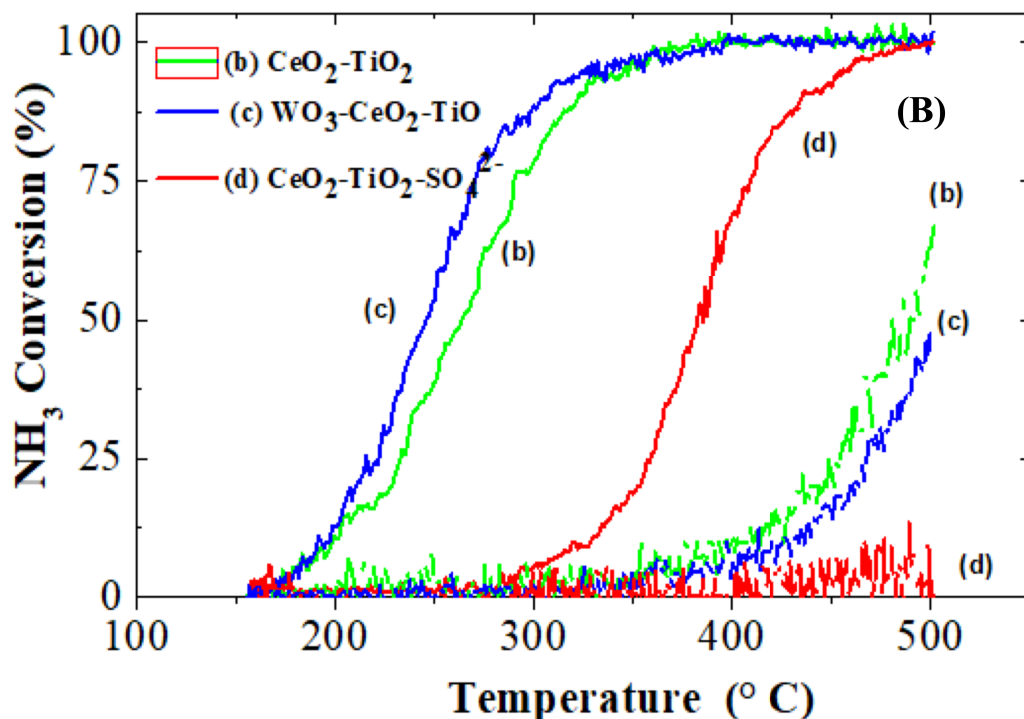
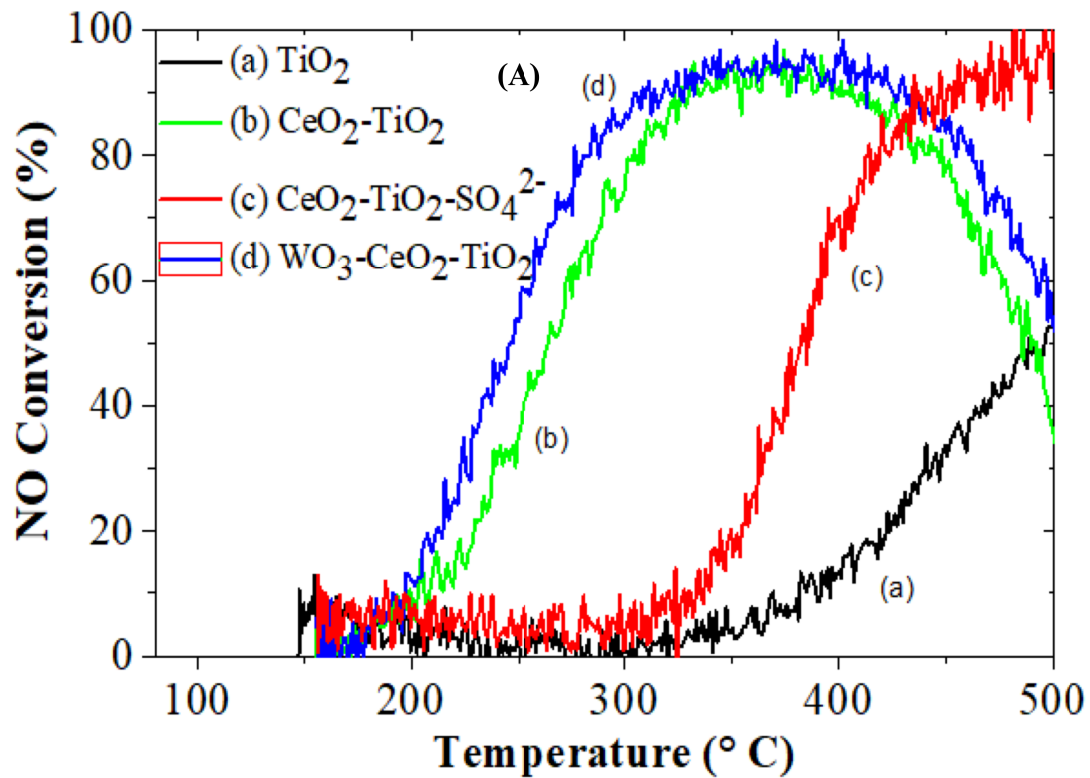


Figure 6. NH₃-SCR performances of Ce based nanoporous aerogel catalysts: **(A)** NO conversion, **(B)** Total conversion (—) and Oxidation conversion (...) of NH₃. Reaction conditions: [NO] = [NH₃] = 0.04 %; [O₂] = 8.00 %; He as balance; (GHSV) = 120 000 h⁻¹.

Conclusion

A comparative investigation about the effect of acidic components (SO₄²⁻ and WO₃) on the physico-chemical properties and NH₃-SCR activity of CeO₂-TiO₂ aerogel catalysts was reported for the first time in this study. The results revealed that the addition of sulfate groups obviously decreases the NO conversion at low temperature (< 300 °C), by changing the nature of Ce species, but it induces the formation of strong acid sites which were found highly active for the NO reduction into N₂ at high temperature (> 450 °C). The incorporation of WO₃ affects slightly the surface acidity of solid and contributes to the creation of more reactive surface oxygen and redox sites leading to more active catalyst at low temperature NH₃-SCR (< 400 °C). The CeO₂-TiO₂-SO₄²⁻aerogel system exhibits, thanks to the high reactivity of acid sites generated by sulfate groups, the best SCR activity at high temperature. However, superior SCR performance was obtained at lower temperature (< 400 °C) over the WO₃-CeO₂-TiO₂ system due to the good reactivity of its redox sites and high concentration of surface oxygen.

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References

- [1] I. A. Resitoglu, K. Altinisik, A. Keskin, The pollutant emissions from diesel-engine vehicles and exhaust aftertreatment systems. *Clean Techn Environ Policy* 17 (2015) 15-27
- [2] F. Gholami, M. Tomas, Z. Gholami, M. Vakili, Technologies for the nitrogen oxides reduction from flue gas: A review. *Sci Total Environ* 714 (2020) 136712
- [3] C. Liu, J. W. Shi, C. Gao, C. Niu, Manganese oxide-based catalysts for low-temperature selective catalytic reduction of NO_x with NH₃: A review. *Appl Catal A: Gen* 522 (2016) 54-69
- [4] W. Shan, Y. Geng, Y. Zhang, Z. Lian, H. He, A CeO₂/ZrO₂-TiO₂ Catalyst for the Selective Catalytic Reduction of NO_x with NH₃. *Catalysts* 8 (2018) 592

- [5] F. Gao, X. Tang, H. Yi, S. Zhao, L. Chen, J. Li, Y. Shi, X. Meng, A Review on Selective Catalytic Reduction of NO_x by NH₃ over Mn-Based Catalysts at Low Temperatures: Catalysts, Mechanisms, Kinetics and DFT Calculations. *Catalysts* 7 (2017) 199
- [6] B. Giechaskiel, R. Suarez-Bertoa, T. Lähde, M. Clairotte, M. Carriero, P. Bonnel, M. Maggiore, Evaluation of NO_x emissions of a retrofitted euro 5 passenger car for the horizon prize “engine retrofit”. *Environ Res* 166 (2018) 298–309
- [7] L. Han, S. Cai, M. Gao, J. Y. Hasegawa, P. Wang, J. Zhang, L. Shi, D. Zhang, Selective Catalytic Reduction of NO_x with NH₃ by Using Novel Catalysts: State of the Art and Future Prospects. *Chem Rev.* 119 (2019) 10916-10976
- [8] C. Chen, Y. Cao, S. Liu, J. Chen, W. Jia, Review on the latest developments in modified vanadium-titanium-based SCR catalysts. *Chinese J. Catal.* 39 (2018) 1347-1365
- [9] H. Wang, B. Huang, C. Yu, M. Lu, H. Huang, Y. Zhou, Research progress, challenges and perspectives on the sulfur and water resistance of catalysts for low temperature selective catalytic reduction of NO_x by NH₃. *Appl. Catal. A Gen:* 588 (2019) 217207
- [10] P. Granger, V. I. Parvulescu, Catalytic NO_x abatement systems for mobile sources: From three-way to lean burn after-treatment technologies. *Chem. Rev.* 111 (2011) 3155-3207
- [11] Y. Peng, J. H. Li, X. Huang, X. Li, W. K. Su, X. Sun, D. Z. Wang, J. Hao Deactivation mechanism of potassium on the V₂O₅/CeO₂ catalysts for SCR reaction: acidity, reducibility and adsorbed-NO_x. *Environ. Sci. Technol.* 48 (2014) 4515–4520
- [12] G. Busca, L. Lietti, G. Ramis, F. Berti Chemical and mechanistic aspects of the selective catalytic reduction of NO_x by ammonia over oxide catalysts: A review. *Appl Catal B* 18 (1998) 1-36
- [13] L. Pang, C. Fan, L. Shao, J. Yi, X. Cai, J. Wang, M. Kang, T. Li, Effect of V₂O₅/WO₃-TiO₂ catalyst preparation method on NO_x removal from diesel exhaust, *Chinese J. Catal.* 35 (2014) 2020–2028

- [14] W. Shan, F. Liu, H. He, X. Shi, C. Zhang, A superior Ce-W-Ti mixed oxide catalyst for the selective catalytic reduction of NO_x with NH₃, *Appl. Catal. B: Environ.* 115-116 (2012) 100-106.
- [15] Z. Song, P. Ning, Q. Zhang, H. Li, J. Zhang, Y. Wang, X. Liu, Z. Huang, Activity and hydrothermal stability of CeO₂-ZrO₂-WO₃ for the selective catalytic reduction of NO_x with NH₃. *J. Environ. Sci.* 42 (2016)168-177.
- [16] Y. Zeng, K. G. Haw, Y. Wang, S. Zhang, Z. Wang, Q. Zhong, S. Kawi, Recent Progress of CeO₂-TiO₂ Based Catalysts for Selective Catalytic Reduction of NO_x by NH₃. *ChemCatalChem* (2020) <http://dx.doi.org/10.1002/cctc.202001307>
- [17] P. Forzatti, Present status and perspectives in de-NO_x SCR catalysis. *Appl. Catal. A Gen:* 222 (2001)221-236
- [18] T. Grzybek, Layered clays as SCR deNO_x catalysts. *Catal. Today*, 119 (2007) 125-132
- [19] W. Shan, Y. Yu, Y. Zhang, G. He, Y. Peng, J. Li, H. He, Theory and practice of metal oxide catalyst design for the selective catalytic reduction of NO_x with NH₃. *Catal. Today* (2020) <https://doi.org/10.1016/j.cattod.2020.05.015>.
- [20] J. Arfaoui, A. Ghorbel, C. Petitto, G. Delahay, Novel V₂O₅-CeO₂-TiO₂-SO₄²⁻ nanostructured aerogel catalyst for the low temperature selective catalytic reduction of NO by NH₃ in excess O₂. *Appl Catal B: Environ* 224 (2018) 264-275
- [21] W. Shan, F. Liu, Y. Yu, H. He, The use of ceria for the selective catalytic reduction of NO_x with NH₃. *Chin J Catal* 35 (2014) 1251-1259
- [22] X. Gao, Y. Jiang, Y. Zhong, Z. Y. Luo, K. F. Cen, The activity and characterization of CeO₂/TiO₂ catalysts prepared by sol gel method for selective catalytic reduction of NO with NH₃. *J. Hazard. Mater.* 2010, 174, 734-739.

- [23] X. Gao, Y. Jiang, Y. C. Fu, Y. Zhong, Z. Y. Luo, K. F. Cen, Preparation and characterization of CeO₂/TiO₂ catalysts for selective catalytic reduction of NO with NH₃, Catal. Commun. 2010, 11, 465-469
- [24] H. Chang, L. Ma, S. Yang, J. Li, L. Chen, W. Wang, J. Hao, Comparison of preparation methods for ceria catalyst and the effect of surface and bulk sulfates on its activity toward NH₃-SCR. J Hazard Mater 262 (2013) 782-788
- [25] F. Li, Y. Zhang, D. Xiao, D. Wang, X. Pan, X. Yang, Hydrothermal method prepared Ce-P-O catalyst for the selective catalytic reduction of NO with NH₃ in a broad temperature range. ChemCatChem 2 (2010) 1416-1419.
- [26] J. Arfaoui, A. Ghorbel, C. Petitto, G. Delahay, New CeO₂-TiO₂, WO₃-TiO₂ and WO₃-CeO₂-TiO₂ mesoporous aerogel catalysts for the low temperature selective catalytic reduction of NO by NH₃. J. Porous. Mater. (2021) <https://doi.org/10.1007/s10934-021-01102-3>
- [27] Y. Jiang, Z. Xing, X. Wang, S. Huang, Q. Liu, J. Yang, MoO₃ modified CeO₂/TiO₂ catalyst prepared by a single step sol-gel method for selective catalytic reduction of NO with NH₃, J Ind Eng Chem 29 (2015) 43-47
- [28] Y. Jiang, C. Bao, S. Liu, G. Liang, M. Lu, C. Lai, W. Shi, S. Ma, Enhanced Activity of Nb-modified CeO₂/TiO₂ Catalyst for the Selective Catalytic Reduction of NO with NH₃. Aerosol Air Qual Res 18 (2018) 2121-2130
- [29] Y. Yu, J. Zhang, C. Chen, M. Ma, C. He, J. Miao, H. Li, J. Chen, Selective catalytic reduction of NO with NH₃ over TiO₂ supported metal sulfate catalysts prepared via a sol-gel protocol. New J Chem 44 (2020) 13598-13605
- [30] L. Li, W. Tan, X. Wei, Z. Fan, A. Liu, K. Guo, K. Ma, S. Yu, C. Ge, C. Tang, L. Dong, Mo doping as an effective strategy to boost low temperature NH₃-SCR performance of CeO₂/TiO₂ catalysts. Catal Comm 114 (2018) 10-14

- [31] H. Jensen, A. Soloviev, Z. Li, E. G. Sogaard, XPS and FTIR investigation of the surface properties of different prepared titania nano-powders, *Appl. Surf. Sci.* 246 (2005)239-249.
- [32] H. Maleki, Recent Advances in Aerogels for Environmental Remediation Applications, *Chem. Eng. J.* 300 (2016) 98-118.
- [33] K. Cheng, J. Liu, T. Zhang, J. Li, Z. Zhao, Y. Wei, G. Jiang, A Duan Effect of Ce doping of TiO₂ support on NH₃-SCR activity over V₂O₅-WO₃/CeO₂-TiO₂ catalyst. *J Environ Sci* 26 (2014) 2106-2113.
- [34] J. Arfaoui, A. Ghorbel, C. Petitto, G. Delahay, Promotional effect of ceria on the catalytic behaviour of V₂O₅-WO₃-TiO₂ aerogel solids for the DeNO_x process. *J. Solid. State Chem.* 300: (2021) 122261
- [35] L. Chen, D. Weng, Z. Si, X. Wu, Synergistic effect between ceria and tungsten oxide on WO₃-CeO₂-TiO₂ catalysts for NH₃-SCR reaction. *Prog Nat Sci* 22 (2012) 265-272.
- [36] X. Du, X. Wang, Y. Chen, X. Gao, L. Zhan, Supported metal sulfates on Ce-TiO_x SCR as catalysts for NH₃-SCR of NO: High resistances to SO₂ and potassium. *J. Ind. Eng. Chem.* 36 (2016) 271-278
- [37] W. Shan, F. Liu, H. He, X. Shi, C. Zhang, An environmentally-benign CeO₂-TiO₂ catalyst for the selective catalytic reduction of NO_x with NH₃ in simulated diesel exhaust. *Catal Today* 184 (2012) 160-165
- [38] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K. S. W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl Chem* 87 (2015) 1051-1069
- [39] G. Imran, R. Maheswari, Mn-incorporated SBA-1 cubic mesoporous silicates: Synthesis and characterization. *Mater Chem Phys* 161(2015) 237-242

- [40] M. A. López-Mendoza, R. Nava, C. Peza-Ledesma, B. Millán-Malo, R. Huirache-Acuña, P. Skewes, E. M. Rivera-Muñoz, Characterization and catalytic performance of Co-Mo-W sulfide catalysts supported on SBA-15 and SBA-16 mechanically mixed. *Catal Today* 271 (2016) 114-126
- [41] Arfaoui J, Ghorbel A, Petitto C, Delahay G, A new V_2O_5 - MoO_3 - TiO_2 - SO_4^{2-} nanostructured aerogel catalyst for Diesel DeNOx technology. *New J. Chem.* 44, (2020) 16119-16134.
- [42] H. Chen, Y. Xia, H. Huang, Y. Gan, X. Tao, C. Liang, J. Luo, R. Fang, J. Zhang, W. Zhang, X. Liu, Highly dispersed surface active species of Mn/Ce/TiW catalysts for high performance at low temperature NH_3 -SCR. *Chem. Eng. J.* 330 (2017) 1195–1202.
- [43] M. A. Larrubia, G. Busca, An ultraviolet-visible-near infrared study of the electronic structure of oxide supported vanadia tungsta and vanadia molybdena. *Mater Chem Phys* 72 (2001) 337–436.
- [44] J. Arfaoui, A. Ghorbel, C. Petitto, G. Delahay, New MoO_3 - CeO_2 - ZrO_2 and WO_3 - CeO_2 - ZrO_2 nanostructured mesoporous aerogel catalysts for the NH_3 -SCR of NO from diesel engine exhaust. *J. Ind. Eng. Chem.* 95 (2021) 182-189
- [45] W. J. Roth, B. Gil, W. Makowski, A. Sławek, A. Korzeniowska, J. Grzybek, M. Siwek, P. Michorczyk, Framework-substituted cerium MCM-22 zeolite and its interlayer expanded derivative MWW-IEZ, *Catal Sci Technol* (2016) <http://dx.doi.org/10.1039/c5cy02074c>
- [46] Y. Shao, L. Wang, J. Zhang, M. Anpo, Synthesis of hydrothermally stable and longrange ordered Ce-MCM-48 and Fe-MCM-48 materials. *J Phys Chem B* 109 (2005) 20835–20841
- [47] J Arfaoui, A Ghorbel, C Petitto, G Delahay New Mn- TiO_2 aerogel catalysts for the low temperature Selective Catalytic Reduction of NOx. *J. Sol-Gel Sci. Technol.* 97 (2021) 302–310

- [48] J. Du, X. Shi, Y. Shan, G. Xu, Y. Sun, Y. Wang, Y. Yu, W. Shan, H. He, Effects of SO₂ on Cu-SSZ-39 catalyst for the selective catalytic reduction of NO_x with NH₃. *Catal Sci Technol* 10 (2020) 1256-1263
- [49] X. Huang, Z. Liu, D. Wang, Y. Peng, J. Li, The effect of additives and intermediates on vanadia-based catalyst for multi-pollutant control. *Catal Sci Technol* 10 (2020) 323- 326
- [50] Z. Song, Y. Xing, T. Zhang, J. Zhao, J. Wang, Y. Mao, B. Zhao, X. Zhang, M. Zhao, Z. Ma, Effectively promoted catalytic activity by adjusting calcination temperature of Ce-Fe-Ox catalyst for NH₃-SCR. *Appl Organometal Chem* e5446 (2019) <https://doi.org/10.1002/aoc.5446>
- [51] Y. Ke, W. Huang, S. Li, Y. Liao, J. Li, Z. Qu, N. Yan, Surface acidity enhancement of CeO₂ catalysts via modification with a heteropoly acid for the selective catalytic reduction of NO with ammonia. *Catal Sci Technol* 9 (2019) 5774-5785
- [52] C. Gannoun, R. Delaigle, P. Eloy, D. P. Debecker, A. Ghorbel, E. M. Gaigneaux, Effect of support on V₂O₅ catalytic activity in chlorobenzene oxidation. *Appl Catal A* 1-6 (2012) 447–448
- [53] L. Lietti, J. L. Alemany, P. Forzatti, G. Busca, G. Ramis, E. Giamello and F. Bregani, Reactivity of V₂O₅–WO₃/TiO₂ catalysts in the selective catalytic reduction of nitric oxide by ammonia, *Catal. Today*, 1996, 29, 143–148