

Review

WO₃–V₂O₅ Active Oxides for NO_x SCR by NH₃: Preparation Methods, Catalysts' Composition, and Deactivation Mechanism—A Review

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Abstract: Researchers in the field of the selective catalytic reduction (SCR) of nitrogen oxides (NO_x: NO, NO₂, or N₂O) by NH₃ are still greatly challenging the optimization of low-temperature activity and selectivity, high-temperature stability, resistance to alkali metals and other poisoning agents, such as Hg, As, etc. The present study reviews the research progress, related to the latest 20 years, on WO₃–V₂O₅-based catalysts that are expected to overcome the catalytic performances of the current SCR catalytic devices. In details, the effects of the synthesis methods, chemical composition, type of supports (metal oxides, molecular sieves, and filters), doping elements, or metal oxides added as promoters of WO₃–V₂O₅-based catalysts and, finally, the influence of SO₂ and H₂O in the reaction mixture are addressed. The importance of understanding the deactivation mechanism in the presence of several poisoning agents is also emphasized, which should be taken into consideration for the design of new catalysts.

Keywords: selective catalytic reduction; WO₃–V₂O₅-based catalysts; low-temperature activity and selectivity; deactivation mechanism

1. Introduction

1.1. NO_x Problem, Control Regulations, and Removal Technologies

Agriculture, industries, power generation plants, and transportation are the major sources responsible of air pollution [1]: Ozone depletion, eutrophication, smog, global warming, and acid rain have attracted wide attention from human beings [2,3]. In order to reduce air pollution, new regulations have been introduced in the latest years, such as the Directive 2010/75/EU of the European Parliament and of the Council concerning industrial activities, European standards for vehicles' exhaust gas emissions in Europe, as well as EPA (Environmental Protection Agency) tier regulations in the USA and analogous emission standards developed by the Japanese government.

Naval diesel engines use heavy fuel oil with a high sulfur content, thus most of the pollutants are nitrogen oxides (NO_x), particulate matter (PM), and sulfur oxides (SO_x) [4]. To limit NO_x emissions, strict regulations and legislations have been set up by the international maritime organization (IMO) that came into force on 1 January 2016 (MARPOL Annex VI) and will be tighter in the future [5].

Many techniques have been applied for the abatement of NO_x emissions, such as pre-combustion and combustion modifications [6,7], as well tail-end control equipment [2,8]. Tail-end control devices are the most efficient in the removal of NO_x, including selective noncatalytic reduction

(SNCR) [9,10], selective catalytic reduction (SCR) [11], NO_x storage/reduction (NSR) [12], and electron beam radiation [2]. Among the above-mentioned methods, NO_x-SCR, which was firstly developed in Japan in the 1970s, is applied worldwide today, being regarded as a promising technology [13].

One of the last key reviews addressing the chemical and mechanistic aspects of the selective catalytic reduction of NO_x by ammonia over oxide catalysts was published in 1998 by Busca et al. [14]. The authors reviewed the performances of V₂O₅-WO₃/TiO₂ and V₂O₅-MoO₃ catalysts and compared with catalysts containing Fe₂O₃, CuO, MnO_x, and CrO_x with special attention given to spectroscopic studies, adsorption-desorption measurements, and kinetic experiments. However, the reaction mechanism was not unanimously recognized and some disagreement points were underlined. Since then, the number of articles dealing with NO SCR by NH₃ over WO₃-V₂O₅ basic catalysts has undergone dramatic growth. Moreover, in the last 20 years, new restrictive limits to NO_x emissions have been introduced by world regulations. Therefore, we consider that is worthwhile to summarize here the most recent results on WO₃-V₂O₅ active oxides, paying attention to the chemical effects (preparation methods, catalysts' composition, promoting effects, and deactivation mechanism) that are still a matter of debate in the literature.

1.2. SCR Application for After-Treatment of Fossil Fueled Engines in Transportation

For transportation, NO_x emissions originate from vehicles' and ships' engines. The automotive industry, especially for heavy-duty truck and bus engines, has adopted urea-SCR (Selective Catalytic Reduction) to reach the NO_x limits required by regulations to meet the Euro V (2008) and the JP 2005 NO_x limits. The first commercial diesel truck applications were launched in November 2004 by Nissan Diesel in Japan and in early 2005 by Daimler in Europe [15]. In light-duty vehicles, the SCR was introduced in some US EPA tier 2 vehicles. By 2012 to 2015, most of the tier 2 vehicles with NO_x adsorbers had been converted to urea-SCR. In Europe, the SCR was introduced on certain Euro 5 models, with a much wider application of the technology in Euro 6 vehicles to meet the US Tier 4i/EU Stage IIIB emission standards.

For marine SCR applications, the main challenges are sulfur resistance and activation at low temperatures [16]. The latter is also a challenge for cars, trucks, and non-road applications and may imply that the catalyst remains inactive during start-up and maneuvering [17]. Nowadays, one of the most investigated catalysts for NH₃-SCR is V₂O₅-WO₃ (MoO₃)/TiO₂, which can meet the requirement at temperatures in range ~300–400 °C [18]. At temperatures as low as 100–150 °C, no effective catalytic after-treatment of exhaust gases occurs. For that reason, the SCR catalyst should be placed upstream of the turbocharger, as close to the engine as possible to allow high temperatures for high NO_x conversion and to avoid the formation of ammonium sulfates. In fact, on the one hand, the SCR unit is located downstream of the electrostatic precipitator and desulfurizer to avoid the catalyst deactivation caused by ash and SO₂ poisoning [19,20]. On the other hand, the high pressure increases the catalytic reaction but also enhances the undesired side reactions. Based on the above considerations, an exploitation and investigation of V₂O₅-WO₃-based catalysts with low-temperature activity and high-temperature stability as well as resistance to Hg, alkali metals, is still a great challenge for practical applications.

Over the last 20 years, to overcome the deficiency, many kinds of V₂O₅-WO₃-based catalysts have been prepared with different methods, supports, chemical compositions, and doping agents. Therefore, in this article, we overview the recent progresses in catalytic NO_x SCR by NH₃, especially focusing on V₂O₅-WO₃-based catalysts.

2. WO₃-V₂O₅-Based SCR Catalysts

2.1. Reasons for the Use of WO₃-V₂O₅-Based Catalysts

To date, WO₃-V₂O₅/TiO₂ catalysts are the most effective systems for practical applications and are widely used for NO SCR with NH₃. Therefore, the effect of WO₃ and V₂O₅ on the catalytic performance must be understood for further research in this area.

According to the investigation of Zhang et al. [21], WO_3 play an important role in catalyzing NO SCR with NH_3 , due to the following promotional effects of WO_3 : (i) Increases the amounts of Lewis acidic sites; (ii) inhibits the sintering of anatase TiO_2 ; and (iii) WO_3 can be easily reduced to W^{5+} and the standard reduction potential of W^{6+} to W^{5+} is only -0.03 eV. Thus, the reduced W^{5+} species can be oxidized by oxygen, meanwhile, oxygen may be reduced to superoxide ions. In the case of V_2O_5 , (i) the surface acidity (Brønsted and Lewis) can be improved by adding V_2O_5 ; and (ii) there is a direct correlation between high surface $\text{V}^{3+} + \text{V}^{4+}/\text{V}^{5+}$ and the $\text{V}^{4+}/\text{V}^{5+}$ ratio and the SCR activity. Furthermore, the behavior of the oxygen species bonded to the vanadium and the dispersion of the active species are influenced by the support. Well-dispersed and isolated vanadium oxide species show low activity for the SCR reaction but present a high selectivity towards N_2 .

More importantly, it has been reported that the interaction between WO_3 and V_2O_5 enhances the catalytic performance [22]: (i) V_2O_5 increases Brønsted and Lewis acid sites, while WO_3 promotes Lewis acid sites. Both types of acid sites promote the NO SCR—the Brønsted acidity favors the conversion at low temperatures, up to 300°C , while Lewis acid sites are the active sites above 300°C ; (ii) by increasing the amount of reduced V^{4+} species, the NO conversion also increases. The effects of the supporting WO_3 and V_2O_5 , active oxides, over titania have been also addressed by the authors [21], who investigated $\text{V}_2\text{O}_5/\text{TiO}_2$, $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$, and WO_3/TiO_2 -nanotube model catalysts for NO SCR with NH_3 . The addition of WO_3 between 3 and 6 wt % in the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts increased the reduced V^{4+} species on the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts. However, it has been reported that above 6 wt % of WO_3 , the reduced V^{4+} species remain constant on the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts; and (iii) tetrahedral monovanadate and polymeric surface vanadate also coexist in $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts.

Finally, the effects of SO_2 and H_2O on the catalytic activity of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts were also evaluated by the same authors [22]. They found that the NO conversion is not affected by SO_2 but water inhibits the catalytic activity. The influence of SO_2 and H_2O in the reaction stream, strongly depending on the catalyst composition and reaction conditions, will be addressed in more detail later in the manuscript.

The changes occurring on WO_3 and V_2O_5 after supporting over TiO_2 must be highly evaluated. The relation between tungsten and vanadium oxide species in $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts was widely investigated for two series of catalysts containing 0.5 to 5 wt % V_2O_5 and 0 or 10 wt % WO_3 impregnated onto a high surface-area titania hydrate with an anatase structure [23]. The above-mentioned loadings were chosen in order to keep the theoretical coverages of the transition metal oxides on the surface equal or less than 1. It has been reported that the interaction of TiO_2 with supported V(V) or W(VI) oxide species can strongly affect the structure of the surface oxide phases formed which strongly differ from the corresponding bulk oxides. For instance, isolated surface oxide species having strongly distorted tetrahedral geometry were formed in the case of vanadium at low V oxide coverage, in dehydrated samples. At higher loadings, oligomeric or polymeric metavanadate species forming two-dimensional islands along with V_2O_5 nanoparticles were observed. It is not clear if aggregates or oxide crystals are formed for V_2O_5 contents below the theoretical monolayer, however, it was clearly demonstrated that well-prepared catalysts form two-dimensional surface oxides until the support is completely covered, then the surface oxide species grow into the third dimension. In the case of dehydrated WO_3/TiO_2 catalysts, formation of strongly distorted octahedral surface species $((\text{-O})_5\text{-W}=\text{O})$ occurs up to high tungsten oxide coverage [23].

2.2. Effect of Preparation Method on Activity and Selectivity

According to the literature, impregnation (wet, dry, and incipient wetness) [24–27], co-precipitation [26], deposition–precipitation [28], sol–gel [29], and grafting [30] are the main synthesis methods to prepare $\text{V}_2\text{O}_5\text{-WO}_3$ -based SCR catalysts and all of them are summarized in Table 1.

Table 1. Summary of the synthesis methods of V₂O₅-WO₃-based SCR catalysts.

Catalysts	Syntheses Method (Cal. Tem./°C)	The Key Facts to the Activity	Ref.
V ₂ O ₅ -WO ₃ /TiO ₂	Wet impregnation (450 °C)	Compared with dry-impregnated catalyst, wet-impregnated catalyst increases the intensity of Brønsted acid sites and the oxidation of the ab-NH ₃ .	[24]
V ₂ O ₅ -WO ₃ /TiO ₂	Dry impregnation (450 °C)		
V ₂ O ₅ -WO ₃ /TiO ₂	Wet impregnation (500 °C)	By increasing the precursor solution acidity, more polymeric vanadium species are formed on the catalyst surface; the ratio of V ⁴⁺⁽³⁺⁾ /V ⁵⁺ , surface acidity, and quantity of active sites are increased, whereas the activity of the catalyst is largely improved.	[25]
V ₂ O ₅ -WO ₃ /TiO ₂	Co-precipitation (500 °C)	The enhanced performance of co-precipitated compared to the impregnated catalysts was associated with the co-precipitated V ₂ O ₅ -WO ₃ /TiO ₂ catalysts possess new surface: O = WO ₄ (enhanced the adsorption of NH ₃) and redox surface mono-oxo O = VO ₃ sites, because of the surface defects of the TiO ₂ .	[26]
V ₂ O ₅ -WO ₃ /TiO ₂	Incipient wetness impregnation (500 °C)		
V ₂ O ₅ -WO ₃ /TiO ₂	Oxalic acid leaching and impregnation (600 °C)	Oxalic acid leaching is an effective way to reduce the impurities and increase reducibility of the recovered catalyst.	[27]
Ce-V ₂ O ₅ -WO ₃ /TiO ₂	Deposition-precipitation (500 °C)	The higher NO _x conversion at low temperature has origin from surface Ce species and can be assigned to more active Lewis acid sites, the weakly adsorbed NO ₂ and monodentate nitrate.	[28]
Ce-V ₂ O ₅ -WO ₃ /TiO ₂	Impregnation method (500 °C)		
V ₂ O ₅ -WO ₃ /TiO ₂	Sol-gel method (400–800 °C)	Well dispersed and isolated vanadium oxide species were found to be weakly active for the SCR reaction but with a high selectivity to N ₂ .	[29]
V ₂ O ₅ -WO ₃ /TiO ₂	Grafting (300 °C)	Grafting mode and metal oxides loadings were significantly affecting the strength of interaction of V ₂ O ₅ and WO ₃ .	[30]

As shown in Figure 1, Yu et al. [24] investigated the NH_3 -SCR activities of V_2O_5 - WO_3/TiO_2 catalysts as fresh and poisoned by potassium chloride, prepared by wet and dry impregnation methods. They found that the wet-impregnated sample, VWT(W), shows a slightly higher activity than the impregnated one (D) at around 200 °C and this was ascribed to the formation of agglomerated V species which increases the intensity of Brønsted acid sites and the oxidation of adsorbed NH_3 , while isolated V species were predominant on the dry-impregnated catalyst. After the addition of KCl, both catalysts deactivated due to the decreasing amount of ammonium ions coordinated on the Brønsted acid sites. Isolated vanadia species (DK) appeared to be more reactive with potassium and therefore more severely deactivated.

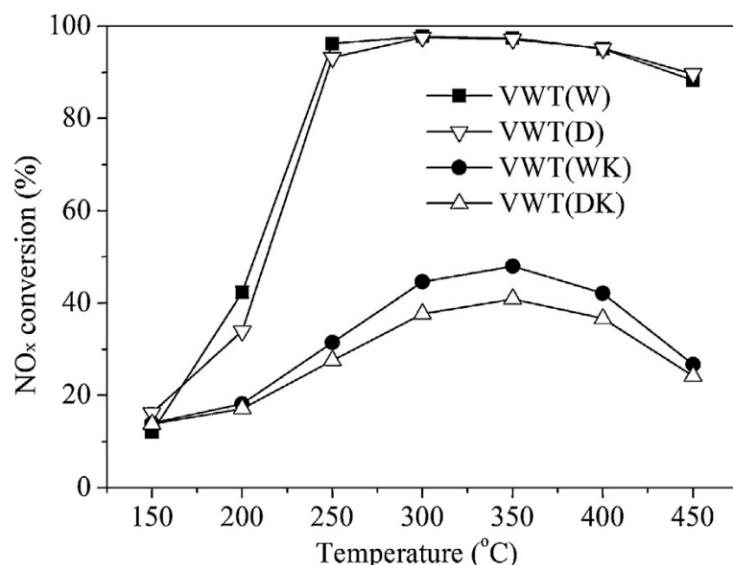


Figure 1. NH_3 -SCR (Selective Catalytic Reduction) activities of the fresh and poisoned (by KCl) V_2O_5 - WO_3/TiO_2 catalysts prepared by wet and dry impregnation methods and denoted as VWT (V_2O_5 - WO_3/TiO_2) (W), VWT (D), VWT (WK), and VWT (DK), respectively. (Reprinted with permission from [24]. Copyright (2013) Elsevier).

Dong et al. [25] optimized the preparation conditions (wet impregnation) by focusing on the effect of the pH value of the vanadium precursor solution on the catalytic performance of V_2O_5 - WO_3/TiO_2 in low temperature NH_3 -SCR of NO_x . According to XPS (X-Ray Photoelectron Spectroscopy), Raman, H_2 -TPR (Temperature Programmed Reduction), NH_3 -TPD (Temperature Programmed Desorption), and NH_3 -DRIFT (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) characterizations, it resulted that the outstanding activity of the catalyst with the decreased pH value could be responsible for the following: More polymeric vanadium species were formed on the catalyst surface; meanwhile, the ratio of $\text{V}^{4+(3+)}/\text{V}^{5+}$, surface acidity, and quantity of active sites were increased. Thus, it should be considered that an enhancement of the precursor solution acidity is an effective way to improve SCR catalysts' activity.

The influence of the catalyst synthesis method on the SCR of NO by NH_3 over V_2O_5 - WO_3/TiO_2 catalysts was also investigated by He et al. [26]. In this article, they prepared the catalysts by two different synthesis methods: Co-precipitation of aqueous vanadium and tungsten oxide precursors with $\text{TiO}(\text{OH})_2$ and incipient wetness impregnation of the aqueous precursors on a crystalline TiO_2 support. The composition difference of the two types of catalysts was confirmed by XRD (X-Ray Diffraction) and HS-LEIS (High Sensitivity-Low Energy Ion Scattering Spectroscopy) and a distinction of their activity was also revealed by in situ Raman and IR (Infrared) spectroscopy. Co-precipitated catalysts contain oligomerized surface mono-oxo $\text{O}=\text{VO}_3$ and $\text{O}=\text{WO}_4$ sites on the TiO_2 support. The enhanced performance of co-precipitated catalysts compared to the impregnated ones was associated with the

formation of new $\text{O} = \text{WO}_4$ species, able to adsorb NH_3 , and to the presence of redox surface mono-oxo $\text{O} = \text{VO}_3$ sites.

Qi et al. [27] reported the synthesis of $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ catalysts from waste commercial SCR catalysts through oxalic acid leaching and impregnation with different V_2O_5 loadings (0.5%, 1.0%, and 1.5 wt %). The NO conversion of the newly synthesized catalyst with 1.0% V_2O_5 almost recovered the activity of the fresh catalyst (91% of the NO conversion at 300 °C) and showed good resistance to SO_2 and H_2O .

Meiqing et al. [28] systematically investigated Ce-modified $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ (V/WTi) catalysts by the deposition–precipitation method (V/Ce/WTi-DP and Ce/WTi-DP) and the conventional impregnation method (V/Ce/WTi-IMP and Ce/WTi-IMP). As shown in Figure 2, the results revealed that the activity was mainly dependent on the status of Ce, which not only possessed more surface Ce species but also presented a higher reducibility of the Ce species. The higher NO_x conversion can be assigned to more active Lewis acid sites, the weakly adsorbed NO_2 , and the monodentate nitrate.

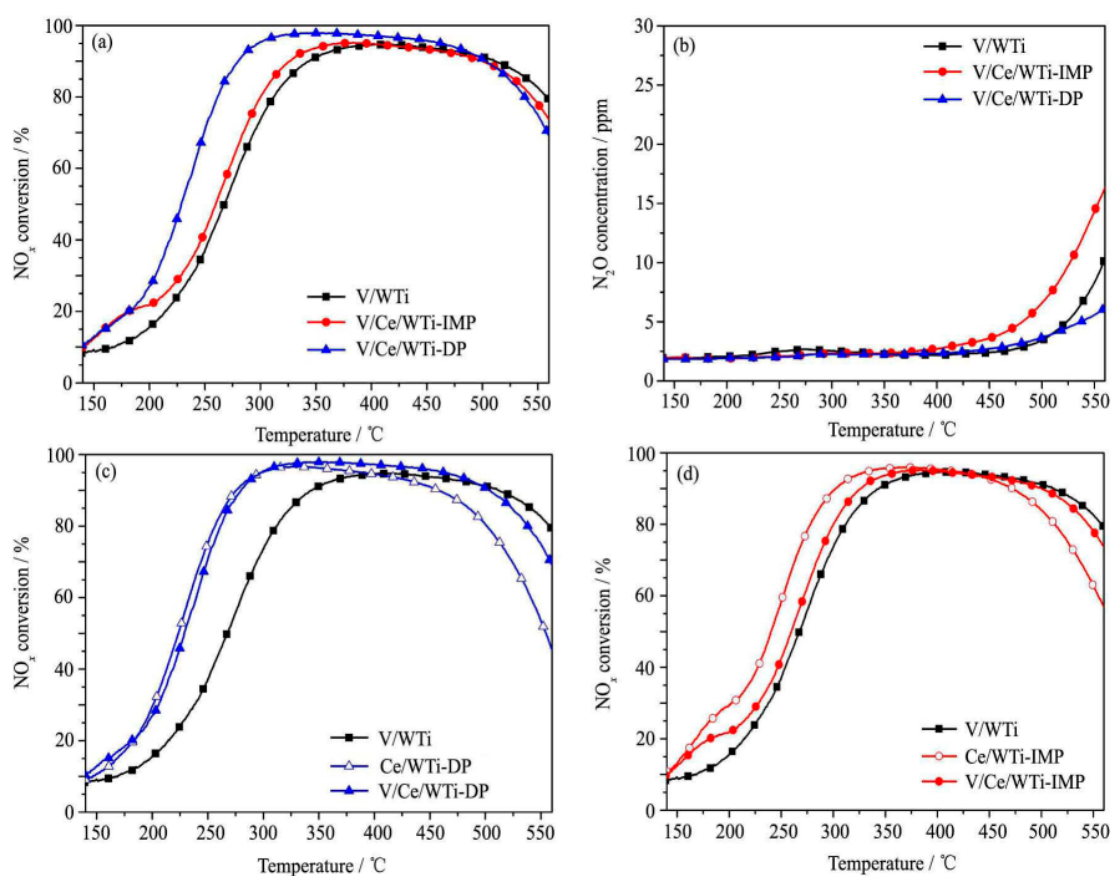


Figure 2. NH_3 -SCR performance over various catalysts as a function of temperature (a), (c), (d) NO_x conversion; (b) N_2O concentration. (Reprinted with permission from [28]. Copyright (2016) Elsevier).

Djerad et al. [29] prepared $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ catalysts by the sol–gel method with different W and V loadings and calcined at different temperatures. The results are shown in Figure 3, in which it is shown that the V_2O_5 content strongly influences the catalytic behavior: Weakly active for the SCR reaction but with a high selectivity to N_2 . Moreover, the NO_x conversion and N_2 selectivity achieved up to 100% in the temperature range of 250 to 325 °C. Meanwhile, 3 wt % V_2O_5 –9 wt % WO_3/TiO_2 was the best catalyst not only for the NO_x conversion, but also for the N_2 selectivity.

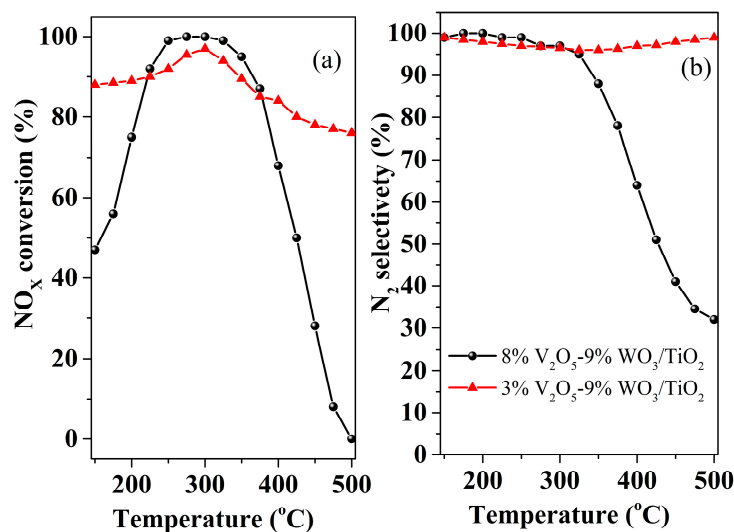


Figure 3. NO_x conversion (a) and N₂ selectivity (b) vs. temperature over 3 wt.% V₂O₅–9 wt.% WO₃/TiO₂ and 8 wt.% V₂O₅–9 wt.% WO₃/TiO₂ catalysts. (Reprinted with permission from [29]. Copyright (2004) Elsevier).

Reiche et al. [30] explored the influence of the grafting sequence and simultaneous grafting of V₂O₅ and WO₃ on the properties of V₂O₅–WO₃/TiO₂ catalysts. DRIFT and XPS indicated that V and W species do not exist independently on the TiO₂ surface. More importantly, V₂O₅–WO₃/TiO₂ catalysts synthesized by sequential grafting do not result in a hierarchical structure. However, changing the grafting mode and metal oxides loadings significantly affected the strength of interaction of V₂O₅ and WO₃.

In Table 1 and from the above-mentioned research, we cannot directly affirm which was the best method to synthesize catalysts with high activity and selectivity in a broad temperature window. New methods able to improve the specific surface area and to increase the active sites of catalysts should be considered in the design of new catalysts. In addition, the activity and selectivity are significantly affected by the active metal oxides loading.

2.3. Effect of the Support on Catalytic Activity

To enhance the stability and the activity, V₂O₅–WO₃-based multiple metal oxides and supported catalysts have been widely studied. They can be classified into two types: Metal oxides and molecular sieves or filters as carriers.

2.3.1. Metal Oxides as Carriers

V₂O₅–WO₃/TiO₂ is a classical commercial catalyst that has been widely investigated for NO SCR. It has been reported that only the TiO₂ anatase phase has no activity for NO SCR with NH₃ [31]. However, it is well known that TiO₂ anatase improves the catalytic activity by dispersing the V₂O₅–WO₃ active phases [32]. At high temperatures, >700 °C, transition from the anatase to rutile phase occurs and such process is strongly influenced by the oxygen vacancies' concentration [21]. As will be discussed in the following Section 2.4, the presence of oxygen vacancies in the support helps the formation of W⁵⁺ species able to active superoxide ions.

Reiche et al. [30,33] prepared V₂O₅–WO₃/TiO₂ by simultaneous grafting of TiO₂ with V₂O₅ and WO₃. According to the DRIFT, XPS, and TOF-SIMS (Time-of-Flight secondary ion mass spectrometry) investigations, indicating V and W species do not exist independently on the titania surface (V–O–W connectivity were present on the V₂O₅–WO₃/TiO₂ catalysts), which results in a higher activity compared to the corresponding titania-supported single oxides. The studies demonstrate that the activity could be enhanced by grafting V₂O₅–WO₃ on TiO₂.

Zhang et al. [34] elucidated the interaction of V, W, and Ti species on the surface of V_2O_5 - WO_3 /TiO₂ catalysts for the improvement of the catalytic activity. XRD, UV-vis, PL spectra, DFT theoretical calculations, and in situ DRIFT showed that WO_3 could interact with TiO₂ to improve the electrons transfer due to the V-O-W species, in agreement with Reiche et al. [30,33]. Moreover, the XPS and EPR observations confirmed the presence V^{4+} species, which are the active sites for the superoxide ion formation. Such species promoted NO oxidation to NO_3^- and improved the decomposition of NO_3^- to NO_2 , facilitating the reaction rate of “fast SCR”.

Kompio et al. [23] highlighted a new point on the relations between tungsten and vanadium, studying two series of V_2O_5 - WO_3 /TiO₂ catalysts with different V_2O_5 contents (0.5–5 wt %) and 0 or 10 wt % WO_3 impregnated over titania hydrate with an anatase structure. The catalysts were investigated by XRD, specific surface area measurements, Raman and EPR (Electron Paramagnetic Resonance) spectroscopy, temperature-programmed reduction (TPR), and SCR. It was concluded that tungsten plays a promotional effect on the neighboring vanadium oxide species, favoring their dispersion.

The positive role of W was confirmed also by Zhang et al. [35] and Wang et al. [36], who found that WO_3 species play an important role in the formation of superoxide ions (O_2^-) over V_2O_5 - WO_3 /TiO₂ catalyst for NH_3 -SCR of NO. This was due to an improved electron transfer between the V-O-W species, which facilitates the formation of reduced V_2O_5 (V^{4+} and V^{3+}). The best activity was registered with a WO_3 loading of 6 wt %. However, it should be noticed that WO_3 was an electron withdrawal, so higher WO_3 loadings might trap electrons to inhibit the formation of superoxide ions.

Zhang et al. [37] investigated the promotional roles of ZrO_2 and WO_3 over V_2O_5 - WO_3 /TiO₂- ZrO_2 SCR catalysts. They found that ZrO_2 improved the thermally stability, while WO_3 increased the Brønsted acid sites of the catalysts. Furthermore, a combination of WO_3 and ZrO_2 enhanced the dispersion of all metal oxides. As shown in Figure 4, the highest NO_x conversion was achieved over V_2O_5 -9wt.% WO_3 /TiO₂- ZrO_2 and this finding partially results from the ZrO_2 doping that considerably increased the BET surface area and favored the dispersion of the active components on the surface. However, the mainly promotional role was to change the pathway of NO_x reduction and the surface acidity of V_2O_5 - WO_3 /TiO₂. There are only Lewis acid sites on the V_2O_5 - WO_3 supported over TiO₂- ZrO_2 , while Brønsted and Lewis acid sites coexisted on V_2O_5 - WO_3 /TiO₂.

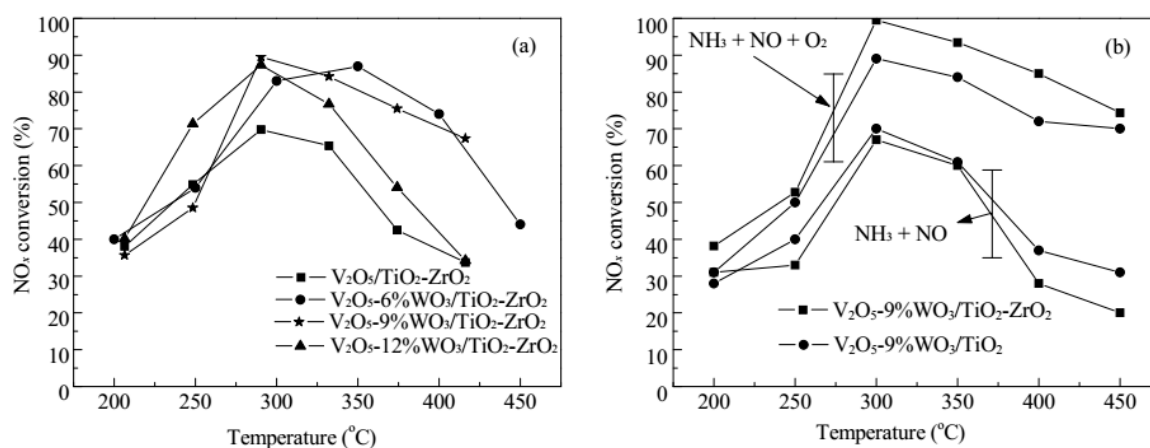


Figure 4. NO_x conversions over different catalysts with (a) and without (b) O_2 . (Reprinted with permission from [37]. Copyright (2016) Elsevier).

Herrmann et al. [38] prepared a V_2O_5 - WO_3 /TiO₂ catalyst by supporting the V_2O_5 - WO_3 over TiO₂ EUROCAT and investigated the electrical properties under different atmospheres, such as pure oxygen, NO, and NH_3 with and without O_2 . In the absence of oxygen, NO has an electron acceptor character (as NO^+) that is able to fill the anionic vacancies, which are mostly present on V_2O_5 . On the other hand, NH_3 had a strong reduction behavior with the formation of ionized vacancies. In the presence of oxygen, the anionic vacancies of the catalysts were filled by oxygen, therefore, the NO did

not exhibit its electron acceptor character anymore, reacting directly with NH_3 , bounded on the acid sites. Under the $\text{NO} + \text{NH}_3$ mixture, without oxygen, an increased electrical conductivity was found, ascribed to the formation of anionic vacancies, especially over vanadia, due to dihydroxylation and dehydration of the surface.

Jung et al. [39] supported $\text{V}_2\text{O}_5\text{--WO}_3$ on $\text{TiO}_2\text{--SO}_4^{2-}$ and characterized the catalysts by BET, XRD, XPS, TPD, and H_2 -TPR analyses. Compared with the $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ catalyst, in the $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2\text{--SO}_4^{2-}$, the sulfate deposited over titania did not affect the physical properties (in terms of the BET surface area and phase transformation). Conversely, in TPD and H_2 -TPR, it was found that the sulfate stability strongly depended on the loaded metal oxides. In addition, the reduction property of V_2O_5 also changed due to the interaction between the V-O-W species. In Figure 5, the SCR activity in terms of the NO conversion over $\text{TiO}_2\text{--SO}_4^{2-}$, $\text{V}_2\text{O}_5/\text{TiO}_2\text{--SO}_4^{2-}$, $\text{WO}_3/\text{TiO}_2\text{--SO}_4^{2-}$, and $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2\text{--SO}_4^{2-}$, is compared.

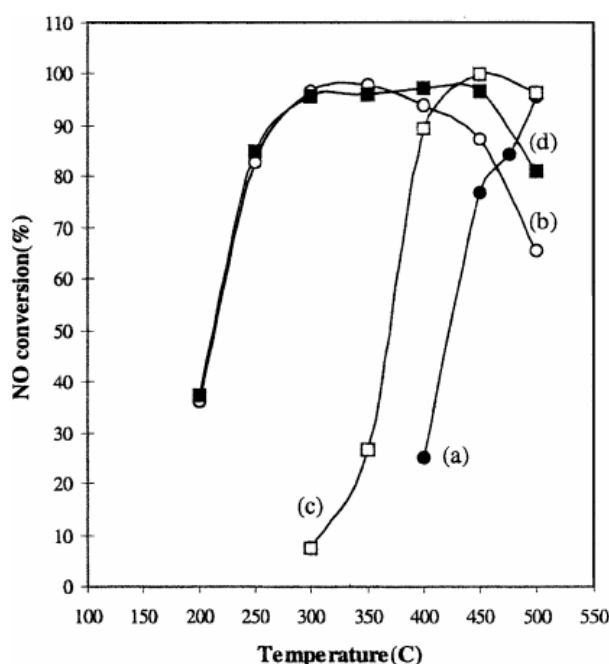


Figure 5. SCR activity: (a) $\text{TiO}_2\text{--SO}_4^{2-}$, (b) $\text{V}_2\text{O}_5/\text{TiO}_2\text{--SO}_4^{2-}$, (c) $\text{WO}_3/\text{TiO}_2\text{--SO}_4^{2-}$, and (d) $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2\text{--SO}_4^{2-}$ (Reprinted with permission from [39]. Copyright (2001) Elsevier).

The similar activity between $\text{V}_2\text{O}_5/\text{TiO}_2\text{--SO}_4^{2-}$ and $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2\text{--SO}_4^{2-}$ at low temperatures was explained by focusing on the dispersion between acid and redox sites. At high temperatures, the redox property modified by the V-O-W species contributed to the high activity.

Sun et al. [40] prepared a $\text{V}_2\text{O}_5\text{--WO}_3/\text{Ti}_{0.5}\text{Sn}_{0.5}\text{O}_2$ (TS) SCR catalyst by supporting $\text{V}_2\text{O}_5\text{--WO}_3$ on $\text{Ti}_{0.5}\text{Sn}_{0.5}\text{O}_2$. The results revealed that the activity of the NH_3 -SCR reaction was closely correlated to the Brønsted acid sites, and they were in direct proportion with the amount of WO_3 up to the highly-dispersed particles formed. Indeed, when the WO_3 exist in a dispersed state, the tungsten atoms are adjacent to the vanadium atoms forming the V-O-W bonds that are responsible for the increased Brønsted acidity. However, further increases of WO_3 (loadings ≥ 1.0 mmol/100 m^2 TS) results in the formation of crystalline WO_3 that covers the active sites, leading to a decrease of the activities.

Camposeco et al. [41] synthesized a series of titanic acid nanotubes (TANs) by the conventional hydrothermal method. Then, $\text{V}_2\text{O}_5/\text{WO}_3$ was added by wet impregnation. The catalytic activity of the V_2O_5 (5 wt %)- WO_3 (3 wt %)/TAN catalysts was strongly improved for the SCR- NH_3 process in a wide range of temperatures in comparison with both samples, V_2O_5 (10 wt %)/TAN and $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ (see Figure 6a). Interestingly, the above mentioned V_2O_5 (5 wt %)- WO_3 (3 wt %)/TAN catalyst showed better NO conversion values than V_2O_5 (10 wt %)/TAN in the presence of water (10 vol %) and SO_2

(50 ppm) (Figure 6b). The reason for the higher activity can be explained by the following factors: (1) The excellent physical properties that TANs possess, such as tubular structure, good thermal stability (460 °C), and high specific surface area (314 m²/g); and (2) the presence of Brønsted and Lewis acid sites that promote NO conversion in a wide range of temperatures.

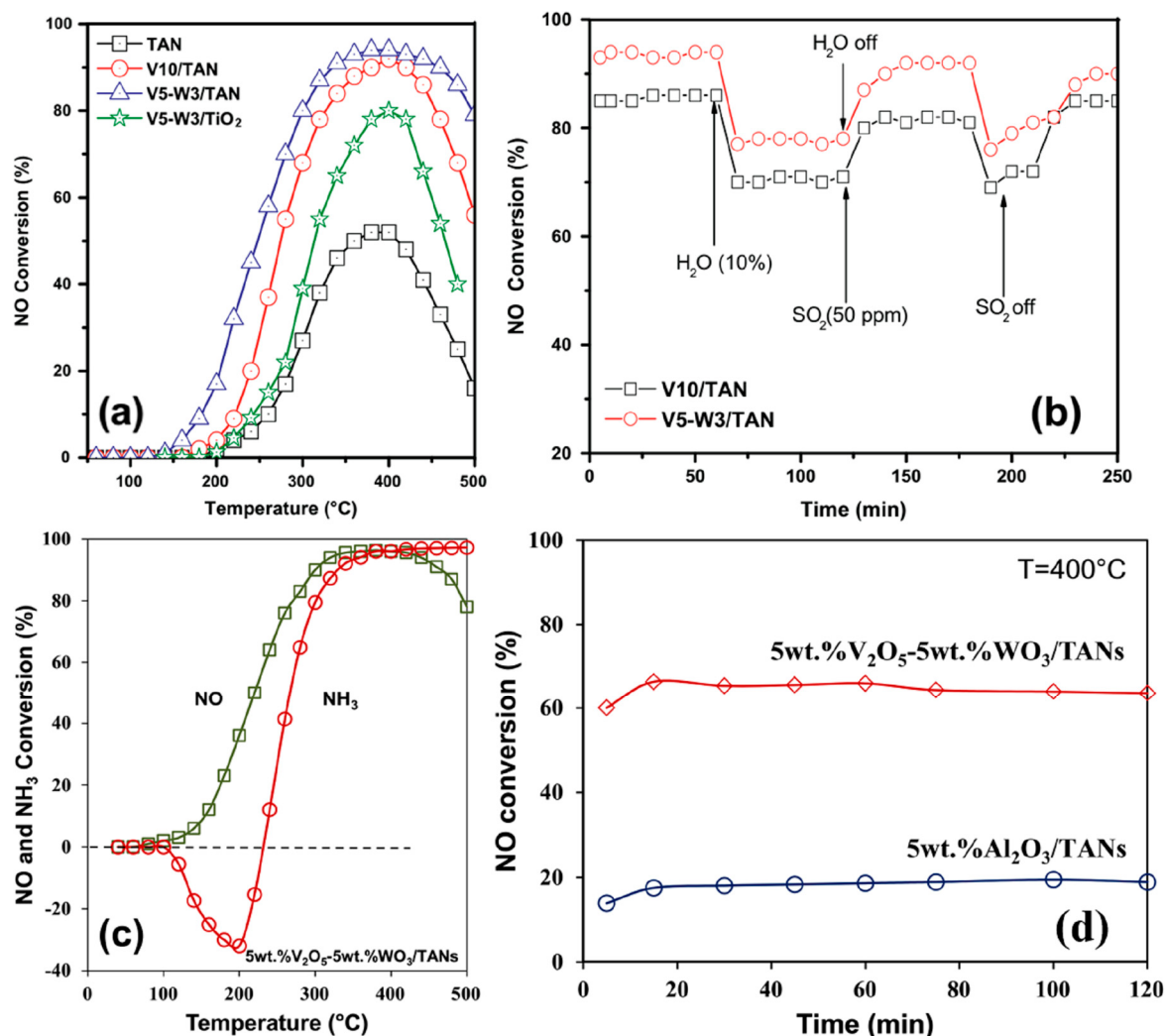


Figure 6. (a) NO conversions over different catalysts; (c) NO and NH₃ conversions over 5 wt %V₂O₅-5 wt %WO₃/TAN catalyst; NO conversions in the presents of H₂O and SO₂ (b,d) over the above mentioned catalysts. (Figure 6a,b reprinted with permission from [41]. Copyright (2014) Elsevier. Figure 6c,d reprinted with permission from [42]. Copyright (2015) Elsevier).

Analogous effects of TANs were reported by Mejía-Centeno et al. [42] (Figure 6c,d). Aguilar-Romero et al. [22] also prepared TANs and employed these as support for V₂O₅-WO₃. They investigated: The effect of WO₃ and V₂O₅ loading on the TiO₂-NT surface acidity, the effect of WO₃ on the V⁴⁺/V⁵⁺ ratio, and its correlation with the catalytic SCR activity. V₂O₅-WO₃/TiO₂-NT displayed a higher NO conversion than WO₃/TiO₂-NT and V₂O₅/TiO₂-NT. In fact, the addition of both V₂O₅ and WO₃ is responsible for the increased surface acidity (Brønsted and Lewis) of the TiO₂-nanotubes. Moreover, they concluded that the morphology of the nanotubes and the metal loading play important roles for the catalyst activity.

Boudali et al. [43] prepared a WO₃-V₂O₅/STi-PILC (Sulfated Titanium Pillared Clay) catalyst for NH₃-SCR. The results showed that the highest NO conversion can reach up to 100% at 300 °C. Vanadia enhanced the NO conversion over STi-PILC, while no significant effect of tungsten was observed for WO₃-V₂O₅/STi-PILC catalyst. When both tungsten and sulfate were simultaneously

present on the surface of vanadia supported STi-PILC, the sulfate species seemed to play a more important role for NO abatement than tungsten.

Najbar et al. [44] synthesized Ti-Sn-rutile for deposition of $\text{WO}_3\text{-V}_2\text{O}_5$. The SCR activity and surface species structure were determined for the freshly prepared catalyst, for the catalyst previously used in NO reduction by ammonia (320 ppm NO, 335 ppm NH_3 , and 2.35 vol % O_2) at 300 °C as well as for the catalyst previously annealed at 300 °C under 2.35 vol % O_2/He . A significant evolution of the active species occurred during the use of the catalyst at 300 °C, especially the increase of the oxidation state of vanadium and the decrease of the tungsten content in the surface layers of the catalyst. Changes in the SCR activity occurring upon the different treatments were discussed in terms of dissociative adsorption of water and the OH group's Brønsted acidity. In detail, the dissociative adsorption of water on $\text{V}^{5+}\text{OW}^{6+}$ sites appeared to be mainly responsible for the activity at 200 °C, while water adsorption on both the $\text{V}^{5+}\text{OW}^{6+}$ and $\text{V}^{4+}\text{OW}^{6+}$ sites determined the activity at 250 °C.

2.3.2. Molecular Sieves or Filters as the Carrier

Li et al. [45] reported an enhanced activity of NO SCR and mechanical stability of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst supported on cordierite after acid pre-treatment of the cordierite substrate and the addition of silica. The acid pre-treatment of cordierite significantly increased the BET surface area and pore volume of the catalysts.

Silica increased the surface acidity of the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst, and the strongest surface acidity was registered at the Si/Ti molar ratio of 5/5. Moreover, by XPS analysis, it was shown that the incorporation of Si shifted the V valence from V^{5+} to V^{4+} , increasing the amount of chemisorbed oxygen, with a positive effect on SCR activity. The optimal catalyst showed a high NO conversion above 90% at 300 to 500 °C, high mechanical stability, and resistance to sulfur and hydrothermal aging.

Kim et al. [46] fabricated three kinds of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ supported-SiC catalytic filters by using the rotational coating method and investigated their NO conversion performances. Three different fabrication routes were used in order to find the effective method for the preparation of the best $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ supported-SiC catalytic filters. Method-III among the three different methods used appeared to be the most effective one. This method deposited the active component, $\text{V}_2\text{O}_5\text{-WO}_3$, by the wet impregnation method over titania, then the powder was dried and calcined at 450 °C for 5 h. The resulting preformed catalyst was ground in wet solution conditions with a ball mill and then used for coating the SiC filter. It was demonstrated that by grinding the catalyst with ball milling, the catalyst particle size was lowered and the particles were dispersed in the coating solution (to produce the high catalytic surface area), which diffused into the pores of the SiC filters, favoring the catalyst dispersion and increasing the exposed active sites. The catalytic filter prepared by method-III (with a 50 nm catalyst particle confirmed with SEM) showed the 99.9% NO conversion with the N_x -slip concentration below 15 ppm in the optimal temperature range from 230 to 350 °C. Figure 7a,b display the NO conversions and N_2O concentration, respectively, over $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ supported-SiC catalysts prepared with the three different methods.

Choi et al. [47] investigated the effect of Pt on the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ supported-SiC catalytic filter ($\text{Pt-V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2/\text{SiC}$). The Pt-added catalytic filter lowered the optimum working temperature from 280 to 330 °C for the non-Pt impregnated catalyst ($\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2/\text{SiC}$) to 180 to 230 °C for the $\text{Pt-V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2/\text{SiC}$. Pt promoted catalytic activity at low temperatures, but increased ammonia oxidation. The Pt promotional effect was believed to result from a high electron transfer achieved on the Pt-catalytic system, as shown in Figure 7c,d.

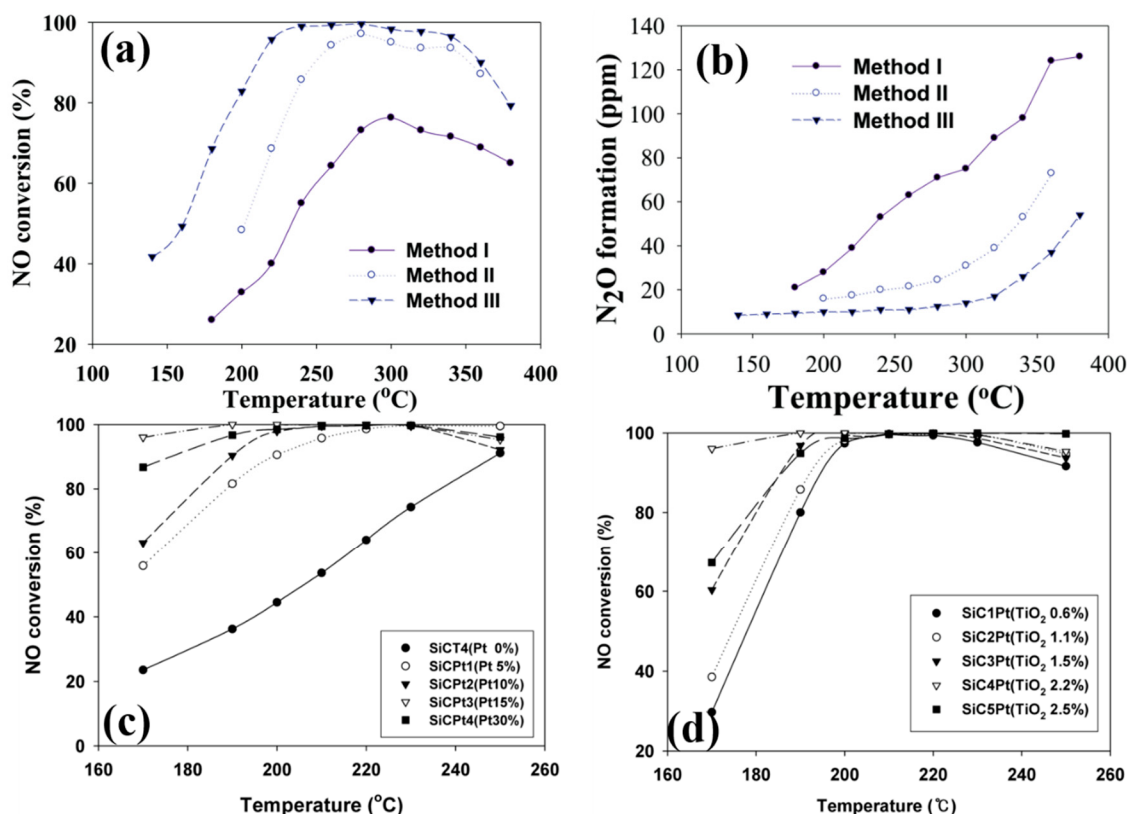


Figure 7. NO conversions (a) and N₂O concentration (b) over V₂O₅–WO₃/TiO₂ supported-SiC catalysts, NO conversion over Pt–V₂O₅–WO₃/TiO₂ supported-SiC catalyst containing different Pt loadings (c) and containing different TiO₂ loadings (d). (Figure 7a,b Reprinted with permission from [46]. Copyright (2018) Elsevier. Figure 7c,d Reprinted with permission from [47]. Copyright (2005) Springer Link).

Najbar et al. [48] focused on the competition between NO reduction and decomposition over V₂O₅–WO₃/Ti(Sn)O₂ catalyst on a Cr–Al steel monolith. Furthermore, they also revealed that the NO conversion was higher than NH₃ over the reduced catalyst. An increase of the pre-reduction temperature was in favor of improving the activity and stability in direct NO decomposition. The reason for the high selectivity of NO decomposition to N₂ was attributed to tungsten nitrosyl complexes via the W–N bond.

Zhao et al. [49] obtained promising catalytic performance over monolithic V₂O₅–WO₃/TiO₂ catalysts by impregnating the active components (V₂O₅, WO₃, and TiO₂) and optimizing the relative amounts and the deposition procedure. The active coating layers were stably deposited over the monolithic substrate as revealed by ultrasonic treatment. XPS analysis confirmed the co-existence of V⁵⁺ and V⁴⁺ species, while the BET surface area was significantly improved after the coating of the monolith due to its porous structure.

According to the data summarized in Table 2, it reveals that SiC or Pt doped SiC filters are the best carriers for promotion, at low-temperatures, of the activity of V₂O₅–WO₃-based catalysts. Indeed, SiC and Pt-doped Si-C filters play an important role in increasing the BET surface area and the dispersion of active components, as well as in the promotion of electron transfer due to Pt introduction. All these factors should be taken into account in the design of new catalysts in the future.

Table 2. Summary of the supports used for the V₂O₅-WO₃-based SCR catalysts.

Catalysts	Carries	NO _x Conversion (Tem./°C)	Surface Active Components	the Key Facts to the Activity	Ref.
V ₂ O ₅ -WO ₃ /TiO ₂	TiO ₂	90–100% (225–375 °C)	V ₂ O ₅ and WO ₃	The well dispersed and isolated vanadium oxide species were found to be weakly active for the SCR reaction but with a high selectivity to N ₂ .	[29]
V ₂ O ₅ -WO ₃ /TiO ₂	TiO ₂	~		V and W species do not exist independently on the titania surface (V-O-W connectivity were present on the V ₂ O ₅ -WO ₃ /TiO ₂ catalysts), which results in a higher activity.	[30]
V ₂ O ₅ -WO ₃ /TiO ₂	TiO ₂	~			[33]
V ₂ O ₅ -WO ₃ /TiO ₂	TiO ₂	90% (>245 °C)			[34]
V ₂ O ₅ -WO ₃ /TiO ₂	TiO ₂	80% (320 °C)		The promotional effect of tungsten may originate from the follows: the influence of the V species or the dispersion of V species ensembles	[23]
V ₂ O ₅ -WO ₃ /TiO ₂	TiO ₂	90–100% (250–360 °C)		WO ₃ species play an important role to form superoxide ions (O ₂ ⁻), which improved the activity.	[35]
V ₂ O ₅ -WO ₃ /TiO ₂ -ZrO ₂	TiO ₂ -ZrO ₂	90–100% (290–370 °C)	V ₂ O ₅ , WO ₃ and ZrO ₂	ZrO ₂ mainly promotional role was to change the path-way of NO _x reduction and surface acidity of catalyst.	[37]
V ₂ O ₅ -WO ₃ /TiO ₂ -SO ₄ ²⁻	TiO ₂ -SO ₄ ²⁻	90–98% (260–480 °C)	V ₂ O ₅ , WO ₃ and SO ₄ ²⁻	Sulfate stability strongly depends on the loaded metal oxides in addition the reduction property of V ₂ O ₅ also changed due to the V-O-W species.	[39]
V ₂ O ₅ -WO ₃ /Ti _{0.5} Sn _{0.5} O ₂	Ti _{0.5} Sn _{0.5} O ₂	90% (>300 °C)	V ₂ O ₅ , WO ₃ and TiSnO ₂	Activity was closely correlated to the amounts of the Brønsted acid sites: they were in direct proportion to highly dispersed WO ₃ . However, too much WO ₃ will cover the active sites and lead to the decrease of the activities; About the reduction temperature, which becomes higher due to the V-O-W species.	[40]
V ₂ O ₅ -WO ₃ /H ₂ Ti ₃ O ₇	H ₂ Ti ₃ O ₇	90–98% (325–450 °C)	V ₂ O ₅ , WO ₃ and H ₂ Ti ₃ O ₇	The higher activity can be explained by the following factors: (1) The excellent physics properties that titanic acid nanotubes possess tubular structure, good thermal stability (460 °C) and high specific surface area (314 m ² /g). (2) TAN as carriers not only significantly increase Brønsted acid sites that light-off conversion at low temperatures, but also increase Lewis acid sites that promote the NO reduction at high temperature.	[41,42]
WO ₃ -V ₂ O ₅ /STi-PILC	STi-PILC	90–100% (250–400 °C)	~	Sulfate species seems to play a more important role for NO removal activity than WO ₃ .	[43]

Table 2. Cont.

WO ₃ -V ₂ O ₅ /Ti-Sn-rutile	Ti-Sn-rutile	90–100% (>230 °C)	~	W species mainly responsible for the oxidation-induced outward vanadium segregation in the vanadia-like species, which was play an important role to improve activity.	[44]
WO ₃ -V ₂ O ₅ /TiO ₂ -NT	TiO ₂ -NT	90–92% (320–380 °C)	V ₂ O ₅ , WO ₃ and H ₂ Ti ₃ O ₇	Morphology of the nanotubes and the metal loading (increased surface Brønsted and Lewis acidity sites) play an important role for the catalyst's activity	[22]
V ₂ O ₅ -WO ₃ -TiO ₂ /cordierite	Cordierite	90–98%(300–500 °C)	V ₂ O ₅ , WO ₃ and SiO ₂	For acid pre-treatment of cordierite, which enlarged the BET surface area and pore volume of the catalysts significantly; SiO ₂ shifted the V valence from V ⁵⁺ to V ⁴⁺ and increased chemisorbed oxygen. All of them enhanced the activity.	[45]
V ₂ O ₅ -WO ₃ -TiO ₂ /SiC	SiC	90–99%(210–360 °C)	V ₂ O ₅ , WO ₃ and TiO ₂	Smaller particle size and better dispersion of catalyst coating solution that is helpful to the catalyst go into the inside of pores of the SiC filters to improve the catalytic activity by increasing the BET surface area and exposing more active sites.	[46]
Pt-V ₂ O ₅ -WO ₃ -TiO ₂ /SiC	SiC	95–100% (170–250 °C)	V ₂ O ₅ , WO ₃ and TiO ₂	Pt promoted catalytic activity at low temperatures but increased ammonia oxidation properties. The promotional effect was believed to result from a high electron transfer of Pt-V ₂ O ₅ -WO ₃ -TiO ₂ /SiC.	[47]
V ₂ O ₅ -WO ₃ -Ti(Sn)O ₂ /monolith	Cr-Al steel monolith	95–100% (150–200 °C)	V ₂ O ₅ , WO ₃ and TiO ₂	Increase the pre-reduction temperature was in favor of improving the activity and stability in direct NO decomposition due to the tungsten cations were substituted by vanadium.	[48]
V ₂ O ₅ -WO ₃ -TiO ₂ /monolith	Monolith	90–92% (420–450 °C)	V ₂ O ₅ , WO ₃ and TiO ₂	It was important to facilitate the NH ₃ -SCR reaction that XPS confirmed the co-existence of V ⁵⁺ and V ⁴⁺ and the BET surface area was significantly improved due to the pore structure.	[49]

2.4. Effect of Chemical Composition on Catalytic Activity

Shen et al. [50] prepared V_2O_5 - WO_3 /TiO₂ and V_2O_5 - WO_3 /TiO₂-SiO₂ SCR catalysts and investigated the resistance toward K and SO₂ poisoning. The calcination temperature of V_2O_5 - WO_3 /TiO₂ catalysts was varied between 400 and 750 °C and played an important role for the activity (Figure 8a). Three different weight ratios of SiO₂/TiO₂ were used, 3 wt %, 6 wt %, and 9 wt %, respectively, and the loading of K poison was fixed as a K/V molar ratio of 0.5. A different catalytic behavior was observed for silica doped and non-doped catalysts: Over K-poisoned V_2O_5 - WO_3 /TiO₂-SiO₂ catalysts, (Figure 8b), the NO conversion values reached up to 90% to 98% (280–410 °C), with a positive effect observed by increasing the silica loading. On the contrary, the K-poisoned catalyst without SiO₂ showed lower activity with a maximum NO conversion of ~70% between 350 and 420 °C. The outstanding performances of V_2O_5 - WO_3 /TiO₂-SiO₂ SCR catalysts were explained by the catalysts' increased acidity due to the silica presence that prevents K poisoning, forming Si-OK scavenger species. As it concerns the SO₂ poisoning, the authors investigated the effect on the catalyst, V_2O_5 - WO_3 /TiO₂, calcined at 750 °C, by adding 1500 ppm to the flue gas. They found that the NO conversion declined sharply by 25% in half an hour, then, by decreasing the SO₂ concentration to 750 ppm over 4 h, the catalyst partially recovered the activity and maintained the 45% NO conversion for the following 3 h.

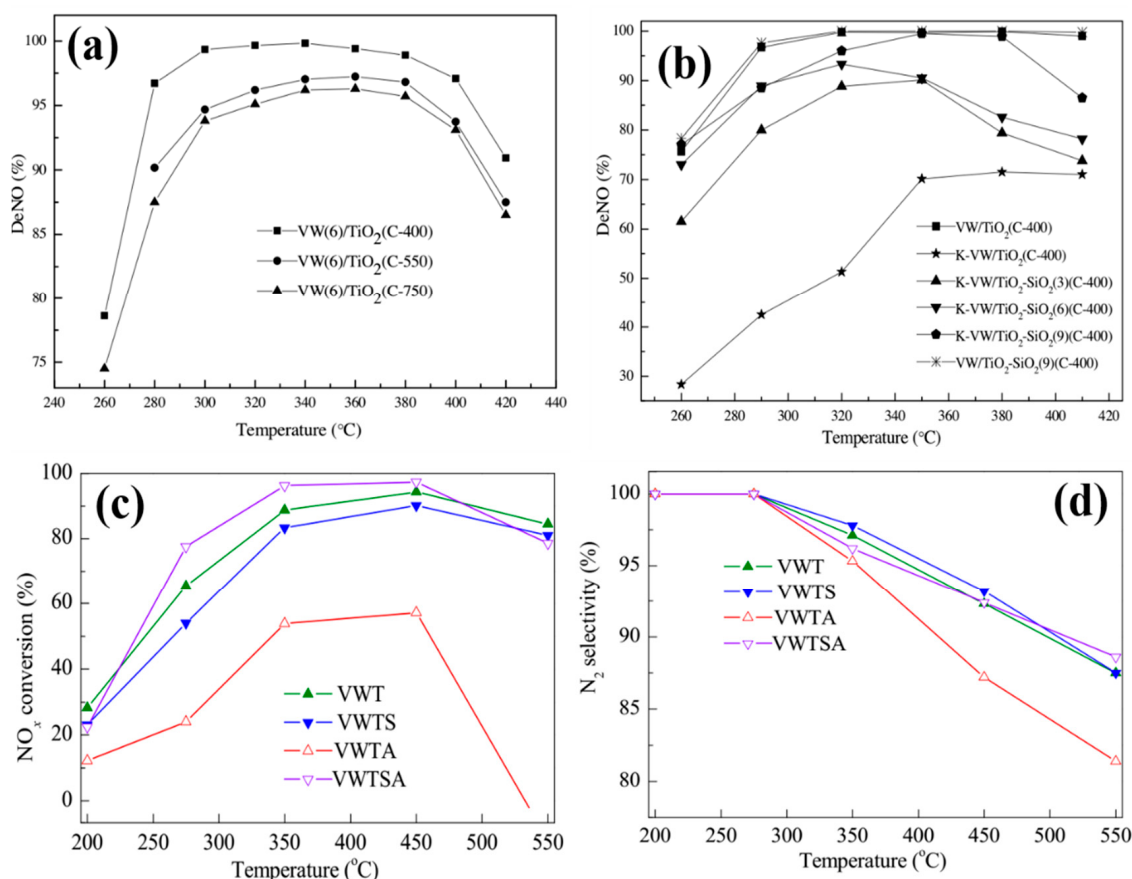


Figure 8. Effects of the TiO₂ gel calcination temperatures on NO conversions over V_2O_5 - WO_3 /TiO₂ catalysts (a) and NO conversions of K poisoned catalysts (b). NO conversion over V_2O_5 - WO_3 /TiO₂ and V_2O_5 - WO_3 /TiO₂-SiO₂ catalyst (c) and corresponding selectivity (d). (Figure 8a,b Reprinted with permission from [50]. Copyright (2018) Elsevier. Figure 8c,d Reprinted with permission from [51]. Copyright (2005) Springer Link).

Liu et al. [51] also studied the effect of SiO₂ additive on the NH₃-SCR activity and thermal stability of V₂O₅-WO₃/TiO₂-SiO₂ catalysts. Compared with V₂O₅-WO₃/TiO₂ catalyst, the SCR activity and selectivity of V₂O₅-WO₃/TiO₂-SiO₂ catalyst was improved after aging at 750 °C in 10 vol % H₂O/air for 24 h (in Figure 8c,d). The different behavior was explained by the addition of SiO₂, which plays different roles: Inhibition of the shrinkage of the catalyst BET surface area due to the phase transition from anatase to rutile and the growth of the TiO₂ size; and maintenance of the highly-dispersed W species.

Dong et al. [52] prepared Mn-Ce/TiO₂ (denoted as M) and Cu-Ce/TiO₂ (denoted as C) by the sol-gel method, then a series of V₂O₅-WO₃/M/cordierite honeycomb ceramics and V₂O₅-WO₃/C/cordierite honeycomb ceramics complex catalysts were obtained by coating V₂O₅-WO₃, M, and C onto cordierite using the impregnation method. The results indicated that the higher activity originated from the high V⁴⁺/V⁵⁺ ratio and the large amount of surface chemisorbed oxygen, as well as the high specific surface area increased by the M and C composites.

Li et al. [53] prepared V₂O₅-WO₃/TiO₂ and CeO₂-WO₃/TiO₂ catalysts by the impregnation method. In comparison with V₂O₅-WO₃/TiO₂ catalyst, the novel CeO₂-WO₃/TiO₂ catalyst exhibited a much better resistance to hydrothermal aging. After aging at 670 °C in 5% H₂O/air for 64 h, the NO conversion was equal to to 80% (238–573 °C) over CeO₂-WO₃/TiO₂ catalyst. Such result was attributed to the well-dispersed CeO₂ and W species, as well as to the formation of a new species, Ce₂(WO₄)₃, due to the interaction of CeO₂ and W. Ce₂(WO₄)₃ prevented the W species' crystallization and TiO₂ phase transition (anatase to rutile) and sintering. Meanwhile, the existence of the Ce⁴⁺-Ce³⁺ couple provided more oxygen vacancies and improved the surface Lewis acid of the catalyst.

Shi et al. [54] added zirconia to V₂O₅-WO₃/TiO₂ catalyst and investigated the performance before and after aging treatment (at 750 °C for 12 h). Compared with V₂O₅-WO₃/TiO₂ catalyst, ZrO₂-V₂O₅-WO₃/TiO₂ catalyst without aging was slightly more active at high temperatures, but less active at low temperatures. After aging treatment, the NH₃-SCR activity of the catalysts was significantly enhanced and exhibited the highest NO conversions and N₂ selectivity (150–550 °C). The following key factors were invoked as being responsible for the improved catalytic behavior: (1) Addition of ZrO₂ improves the thermal stability of ZrO₂-V₂O₅-WO₃/TiO₂ catalysts and preserves the surface area from sintering, resulting in a better dispersion of V sites after aging; (2) ZrO₂ enhances the strength of the surface acidic groups. Regarding the non-aged ZrO₂-V₂O₅-WO₃/TiO₂ catalyst, the decreased activity at low temperatures was attributed to the inhibitions due to ZrO₂, which decrease the amount of Brønsted acid sites and V⁵⁺ = O active sites, inhibiting ammonia absorption.

Tao et al. [55] focused on the relationship between the loadings of V₂O₅ and WO₃ and the catalytic performance of V₂O₅-WO₃/TiO₂ catalysts for the SCR of NO with NH₃. The catalytic activity was enhanced by increasing the V₂O₅ loading less than 2 wt %, in agreement with the presence of TiO₂ as the anatase phase (by XRD) and to the high dispersion on the catalyst surface of all the active species (by XPS). Conversely, when the V₂O₅ loading exceeded 2 wt %, the activity began to decline because the high V₂O₅ loading on TiO₂ favored the phase transition from anatase to rutile. On the other hand, the NO conversion was also improved by moderate WO₃ loadings up to 6 wt %. Exceeding such a percentage, WO₃ inhibited the formation of superoxide ions, decreasing the activity.

As shown in Figure 9, Lietti et al. [56] investigated the NO SCR over commercial and model V₂O₅-WO₃/TiO₂ and V₂O₅-MoO₃/TiO₂ catalysts. The results demonstrated that WO₃ and MoO₃ increased the activity as “structural” and “chemical” promoters for the catalysts, providing better mechanical, structural, and morphological properties. In Figure 9A,B, the NO conversion and N₂ selectivity values are compared for V₂O₅-WO₃/TiO₂ and V₂O₅-MoO₃/TiO₂ catalysts at different V₂O₅ loadings and constant WO₃ or MoO₃ contents, respectively, 9 and 6 wt %. In both cases, the activity was increased by increasing the vanadia loading, so that the “temperature window” of the reaction was widened and shifted towards lower temperatures. However, the V₂O₅(x)-WO₃(9)/TiO₂ samples exhibited higher selectivity in a larger range of temperatures.

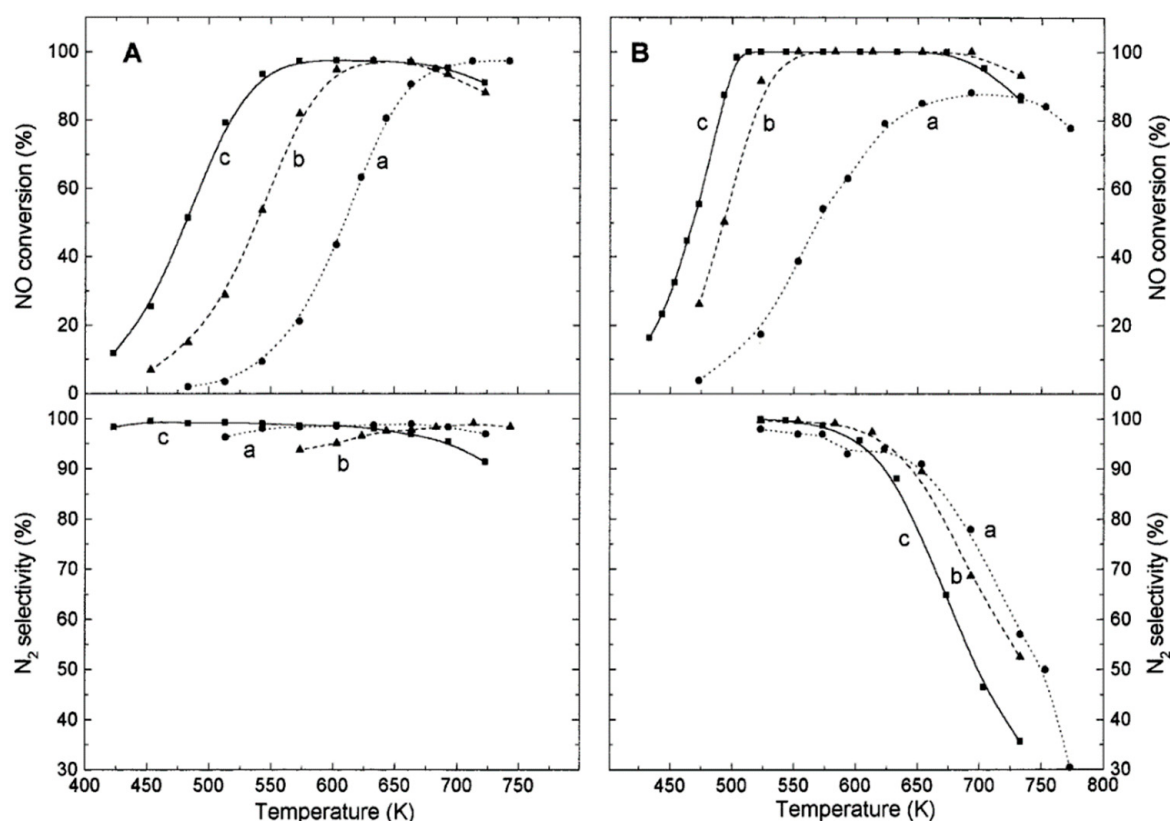


Figure 9. Results of catalytic activity runs in the SCR reaction (NO conversion and N_2 selectivity vs. temperature) performed over: (A) $V_2O_5(x)$ - $WO_3(9)/TiO_2$ samples and (B) $V_2O_5(x)$ - $MoO_3(6)/TiO_2$. (a) V_2O_5 = 0% w/w; (b) V_2O_5 = 0.8% w/w; and (c) V_2O_5 = 1.5% w/w. (Reprinted with permission from [56]. Copyright (2018) Elsevier).

Xu et al. [57] investigated the low-temperature NH_3 -SCR activity of V_2O_5 - Sb_2O_3/TiO_2 and V_2O_5 - WO_3/TiO_2 monolithic catalysts in the presence of SO_2 . V_2O_5 - Sb_2O_3/TiO_2 monolithic catalyst showed a higher NO conversion and broader temperature windows as well as a higher SO_2 and H_2O resistance. The excellent performance was suppressed by the extent of NH_4HSO_4 accumulated on the catalyst surface.

Table 3 summarizes the main results discussed so far on the chemical composition effects of V_2O_5 - WO_3/TiO_2 based catalysts.

Table 3. The relationship between composition and the activity of the V₂O₅-WO₃-based catalysts.

Catalysts	NO _x Conversion (Tem./°C)	the Key Factors for the Activity	Ref.
V ₂ O ₅ -WO ₃ /TiO ₂ -SiO ₂	90–98% (280–410 °C)	The introduction of SiO ₂ significantly increased the catalysts acidity and led to more V and W species exposure on the surface of catalyst by forming Si–OK that was the result of the reaction between enriched K and Si.	[50]
V ₂ O ₅ -WO ₃ /TiO ₂	42–70% (280–410 °C)		
V ₂ O ₅ -WO ₃ /TiO ₂ -SiO ₂	90–98% (500–725 °C)	The addition of SiO ₂ on the one hand, inhibited the shrinkage of catalyst BET surface area due to the phase transition from anatase to rutile and the growth of TiO ₂ size. On the other hand, the W species remained highly dispersion.	[51]
V ₂ O ₅ -WO ₃ /TiO ₂	<58% (500–725 °C)		
V ₂ O ₅ -WO ₃ /TiO ₂	<58% (500–725 °C)	The higher activity origin from high V ⁴⁺ /V ⁵⁺ ratio and large amount of surface chemisorbed oxygen as well as BET surface area caused by the M and C composites.	[52]
V ₂ O ₅ -WO ₃ /C/ ceramics	52–99% (200–50 °C)		
V ₂ O ₅ -WO ₃ /C/M/ ceramics	78–99% (200–550 °C)		
V ₂ O ₅ -WO ₃ / ceramics	10–65% (200–550 °C)		
CeO ₂ -WO ₃ /TiO ₂	90–99% (250–550 °C)	The higher activity of CeO ₂ -WO ₃ /TiO ₂ is responsible for the well dispersion of CeO ₂ and W species; Ce ₂ (WO ₄) ₃ prevent the W species crystallization and TiO ₂ sintering and phase transition; The existence of Ce ⁴⁺ -Ce ³⁺ couple that provide more oxygen vacancies and improve the surface Lewis acid of catalyst.	[53]
V ₂ O ₅ -WO ₃ /TiO ₂	90–95% (275–350 °C)		
1.5%V ₂ O ₅ -1%WO ₃ /TiO ₂	96–100% (100–550 °C)	Catalytic activities could improve by increasing V ₂ O ₅ loading less than 2 wt%. However, when V ₂ O ₅ loading exceeds 2 wt%, the activity begins to decline because high V ₂ O ₅ loading on TiO ₂ speeds up the phase transition from anatase to rutile. On other hands, NO conversion also can be significantly improved with the increase of moderate WO ₃ loadings; however, too much WO ₃ will inhibit the formation of superoxide ions.	[55]
1.5%V ₂ O ₅ -6%WO ₃ /TiO ₂	70–100% (100–550 °C)		
0.5%V ₂ O ₅ -1%WO ₃ /TiO ₂	70–100% (100–550 °C)		
0.5%V ₂ O ₅ -6%WO ₃ /TiO ₂	70–100% (100–550 °C)		
V ₂ O ₅ -WO ₃ /TiO ₂	90–98% (550–725 °C)	WO ₃ and MoO ₃ could promote the activity not only due to the special structural, but also to the unique chemical property; Compared with the commercial V ₂ O ₅ -WO ₃ /TiO ₂ catalyst, V ₂ O ₅ -MoO ₃ /TiO ₂ catalyst was more active, but less selective.	[56]
V ₂ O ₅ -MoO ₃ /TiO ₂	90–100% (500–725 °C)		
V ₂ O ₅ -Sb ₂ O ₃ /TiO ₂	90–100% (225–380 °C)	Sb ₂ O ₃ -based catalyst showed a higher NO conversion and broader temperature windows as well as higher SO ₂ and H ₂ O resistance. The excellent performance was suppressed by the extent of NH ₄ HSO ₄ accumulated on the catalyst surface	[57]
V ₂ O ₅ -WO ₃ /TiO ₂	90–94% (275–350 °C)		

2.5. Positive/Negative Effects of Different Doping Agents on Catalytic Activity and Selectivity

Addition or doping with other metal oxides or elements, such as F [21,58], Nb, Sb [59], Cu, Mn, and Ce [60–62] is the main way to improve catalyst activity, whereas alkaline and alkaline earth metals (Na, K, Ca, and Mg) [63] deactivate catalysts.

Zhang et al. [21] found that NO conversion was improved by F doping. As shown in Figure 10, V_2O_5 - WO_3 /TiO₂-F_{1.35} (the ratio of Ti/F was 1.35) exhibited the highest NO removal efficiency (82.8% at 210 °C), owing to the improved interaction of WO_3 with TiO₂ forming oxygen vacancies and increasing the number of reduced W species (W^{5+}), which play an important role for superoxide ion formation. To further investigate the mechanism, molecular modeling was employed using density functional theory (DFT) and first principles molecular dynamics simulations [58].

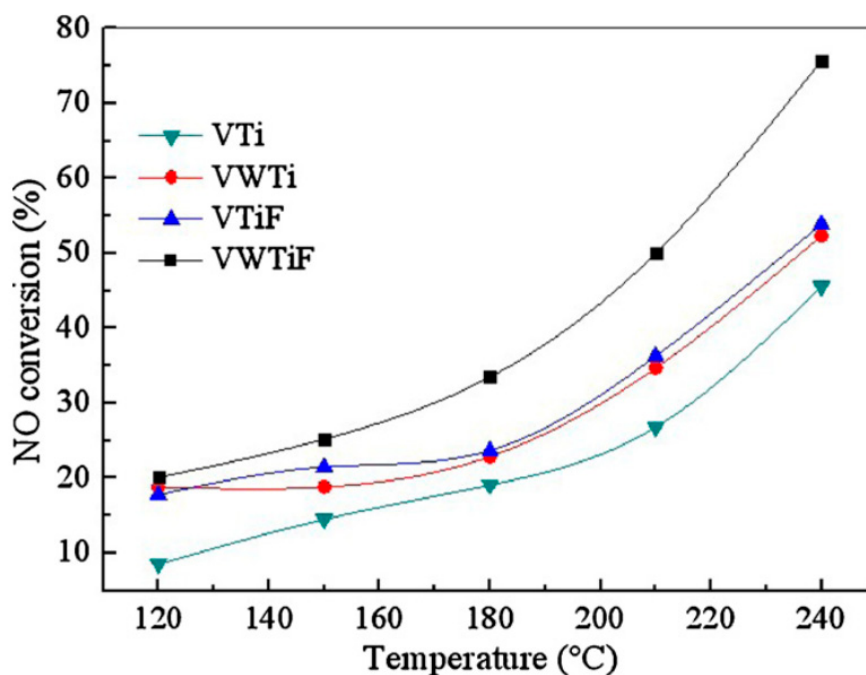


Figure 10. NO conversion vs. temperature performed over V_2O_5 - WO_3 /TiO₂-F_{1.35} and a series of catalysts. (Reprinted with permission from [21]. Copyright (2012) Elsevier).

Ye et al. [59] investigated the enhanced activity of Nb and Sb doped V_2O_5 - WO_3 /TiO₂ SCR catalysts (V_2O_5 - WO_3 -Nb₂O₅/TiO₂ and V_2O_5 - WO_3 -Sb₂O₅/TiO₂) that was assigned to the increase of reactive electrophilic oxygen species on the surface of V_2O_5 - WO_3 -Nb₂O₅/TiO₂ and V_2O_5 - WO_3 -Sb₂O₅/TiO₂. Moreover, the catalysts' deactivation by SO₂ and H₂O was inhibited through the addition of Nb₂O₅ and Sb₂O₅.

Tian et al. [60] prepared Cu, Mn, and Ce doped V_2O_5 - WO_3 /TiO₂ catalysts and studied their performances. The activity was improved because Cu, Mn, and Ce can make the surface of the catalyst moderately acidic, increasing the V^{4+}/V^{5+} ratio and enhancing the redox performance of the catalyst.

Chen et al. [61] also investigated Ce doped V_2O_5 - WO_3 /TiO₂ catalysts with low vanadium loadings in the NH₃-SCR of the NO_x, and the optimized catalyst showed an above 90% NO_x conversion from 200 to 450 °C. Additionally, the selectivity could be significantly increased at high temperatures, even at a high GHSV (Gas Hourly Space Velocity) of 113,000 h⁻¹, and NO_x conversion nearly reached 100% in the temperature range of 250 to 350 °C. According to XPS, analysis cerium was present as Ce³⁺, causing a charge imbalance and therefore oxygen vacancies' formation. Such defects increased the amount of chemisorbed oxygen, indicating that more NO can be oxidized to NO₂.

The effect of Ce doping of TiO_2 support on NH_3 -SCR activity over V_2O_5 - WO_3 /CeO₂- TiO_2 catalyst was investigated by Cheng et al. [62]. The catalytic activity of V_2O_5 - WO_3 / TiO_2 was greatly enhanced by Ce doping, the best NO conversion being achieved at the molar ratio of Ce/Ti = 1/10 (see Figure 11). The crystalline structure also played an important role on the activity; indeed, the catalysts showing predominantly anatase TiO_2 showed better catalytic performance than the catalysts with predominantly a fluorite CeO₂ structure. Moreover, the Ce additive enhanced the amount of oxygen adsorbed on the surface with beneficial effects on the SCR reaction.

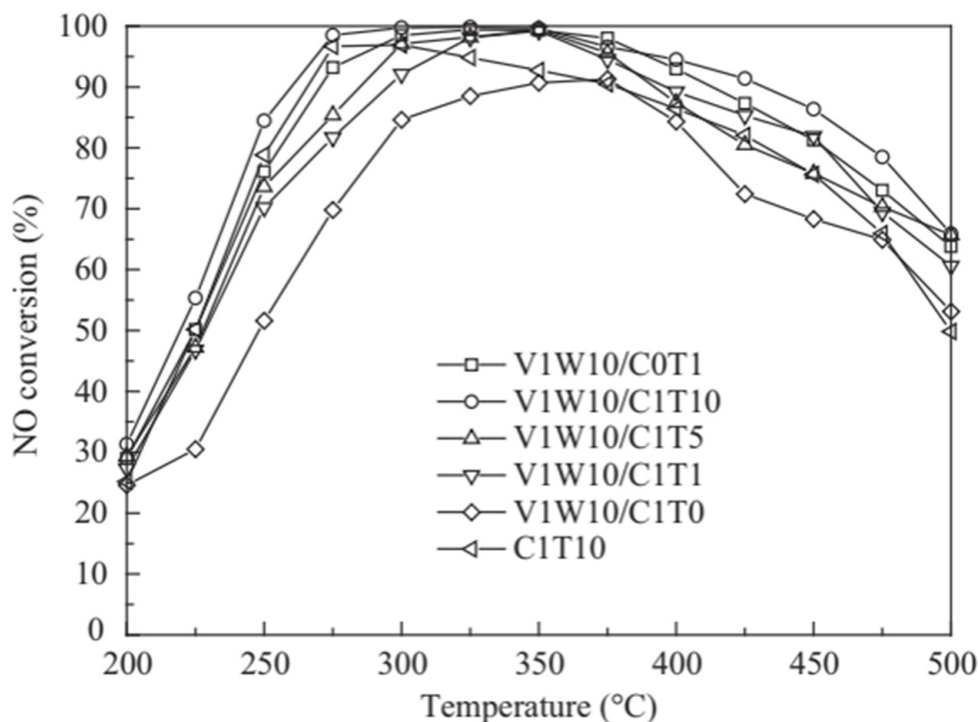


Figure 11. NO_x conversion over Ce doped V_2O_5 - WO_3 / TiO_2 catalysts with various Ce loadings (Reprinted with permission from [62]. Copyright (2014) Elsevier).

The activity of alkaline and alkaline earth metals (Na, K, Ca, and Mg) doped V_2O_5 - WO_3 / TiO_2 catalysts was investigated by Chen et al. [63]. The activity downward trend is: $\text{K} > \text{Na} > \text{Ca} > \text{Mg}$. Several effects must be taken into account in order to explain these findings: (1) Na and K decrease the quantity and stability of the Brønsted acid sites more than Mg and Ca; (2) the surface chemisorbed oxygen decreased in the same order; (3) the reducibility of vanadium species on the Na and K doped catalysts is lower than that on the Ca and Mg doped catalysts with the same alkali metal oxides loadings; (4) Na and K ions also affect the reduction degree of tungsten species, while no effect was experienced by Ca and Mg; and (5) the poisoning by alkali metals of vanadium species appears to be the main factors for V_2O_5 - WO_3 / TiO_2 catalysts' deactivation.

In Table 4, the NH_3 -SCR performances of V_2O_5 - WO_3 / TiO_2 catalysts doped by various elements (F, Nb, Sb, Na, K, Ca, Mg, Cu, Mn, Ce), as discussed above, are summarized. Based on such results, simultaneous doping with F and Ce could be the most effective way to optimize the performance of new V_2O_5 - WO_3 / TiO_2 based catalysts due to the positive roles played individually by F and Ce in enhancing the NO_x conversion and selectivity.

Table 4. NH₃-SCR performances of V₂O₅-WO₃/TiO₂ catalysts doped by different agents: positive or negative effects.

Doping-Agents	C ₀ /C _d (C _c)	Reaction Conditions	Deactivated/Recovered Activity (concentration of H ₂ O and SO ₂)	Key Factors for Enhancing SCR Efficiency	Ref.
F	52%/82.8% (+57%)	[NO] = [NH ₃] = 500 ppm, [O ₂] = 5 Vol % and N ₂ in balance, GHSV = 43,000 h ⁻¹ at 240 °C	62%/99% ([H ₂ O] = [SO ₂] = 300)	Improve the interaction of WO ₃ with TiO ₂ by oxygen vacancies; Increase the number of the reduced W species (W ⁵⁺).	[21,58]
Na	100%/20% (−80%)	[NO] = [NH ₃] = 500 ppm, [O ₂] = 3 Vol % and N ₂ in balance, GHSV = 70,000 h ⁻¹ at 450 °C	~	Decrease the quantity and stability of the Brønsted acid sites;	[63]
K	100%/30% (−70%)			Reduced catalysts surface chemisorbed oxygen;	
Ca	100%/53% (−47%)			Decrease the reducibility of vanadium and tungsten species.	
Mg	100%/95% (−5%)			Form moderate acidity and improve the V ⁴⁺ /V ⁵⁺ ratio on the catalyst surface;	
Cu	72%/98% (+36.1%)	exhaust gas and [NO] = 1200 ppm [O ₂] = 2 Vol % and N ₂ in balance, GHSV = 10,800 h ⁻¹ at 550 °C	~	Increase the redox performance of the catalyst.	[60]
Mn	72%/97% (+34.7%)				
Ce	52%/95% (+82.6%)	[NO] = [NH ₃] = 500 ppm, [O ₂] = 3 Vol % and N ₂ in balance, GHSV = 28,000 h ⁻¹ at 200 °C	95%/100% (100 ppm SO ₂ and 10% H ₂ O)	Increase chemisorbed oxygen; Provide stronger and more active Brønsted acid centers	[60–62]

*Note: 1. C₀ and C_d represent the original and doped-catalyst's maximum NO conversion. 2. C_c reflect the gradient of NO conversion and it was calculated by the formula: $C_c = \frac{C_d - C_0}{C_0} \times 100\%$.

3. Deactivation or Poisoning Mechanism

In practical applications of NO-SCR by NH_3 , the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts can be poisoned by several species, such as impurities of biodiesel (K, Na, P), urea solution (K, Na, Ca, Mg), and abrasion of the engine (Cr, Cu). As introduced in Section 2.5, alkaline and alkaline earth metals have a negative effect. Following the study of Chen et al. [63], further investigations on alkali ions as well as on other poisoning species have drawn great attention: Hg [64–66], alkali metals [66–70], P [69], Cr [69], Cu [69], Mg [69], Ca [69,71], and As [72]. The main poisoning elements and corresponding reasons for catalysts' deactivation are listed in Table 5.

Table 5. Mainly deactivating species and corresponding key factors over $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts.

Deactivating Species	Key Factors	Ref.
HgCl_2	Reduce the Brønsted acid sites (V-OH) but produce new NH_3 adsorption sites (Cl-V-O-H).	[64]
Hg	Transform V^{5+} species to V^{4+} species and consumed the lattice oxygen.	[65]
KCl	KCl could react with V-OH, leading the active sites for NH_3 absorption inactive.	[66]
Hg	The gaseous Hg adsorbed on the vanadia sites reduce the active sites.	
KCl and Hg	There is the competition for active sites that are partially reduced by gaseous Hg, while others can be increased by delaying the deactivation caused by KCl.	[66]
KCl	Lowering the acidity at different extent by different forms of V species; NH_3 adsorption temperature allows to evaluate the acid sites.	[67]
Alkali metal	Decrease the ability of NH_3 adsorption but increase in the NH_3 desorption rate.	[68]
P, Cr and Cu	Moderate poisoning of the catalysts due to competition between increase the N_2O production and lowering the number of acid sites.	[69]
K, Na, Mg and Ca	Reduced capacity of ab- NH_3 .	[69,70]
Ca	Can passivate surface acid sites of fresh and bulk W species.	[71]
As	As_2O_5 dense layers derived from the ab- As_2O_3 oxidized of by chemisorption oxygen on catalyst surface prevent NH_3 adsorption and active sites recovery.	[72]

Kong et al. [64] investigated the HgCl_2 deactivation mechanism over $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ SCR catalysts. The results showed that HgCl_2 caused an agglomeration of active components, the BET surface area decreased significantly, and the reaction of HgCl_2 with Brønsted acid sites (V-OH) occurred. From NH_3 -TPD, NH_3 chemisorption, FTIR, and XPS characterization data, it was found that V-OH and V = O bonds were affected by HgCl_2 . NH_3 was adsorbed on new sites (Cl-V-O-H) that were not active for NO SCR, and HgCl_2 existed in a stable form bonded to the bridge sites.

Yang et al. [65] evaluated the activity of mercury exposed catalysts by XPS and found that mercury oxidation led to the transformation of the V^{5+} to V^{4+} species and consumed the lattice oxygen of catalyst, thus decreasing the activity. In another article, Kong et al. [66] introduced KCl by impregnation of the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts and added Hg by the dry-gas adsorption method. The catalysts modified with KCl were deactivated due to the reaction of KCl with V-OH acidic groups forming -V-O-K and Cl-V-O-K inactive sites. Hg had a weaker negative effect, and it did not cause catalyst agglomeration and increased the amount of chemisorbed NH_3 , thus delaying the deactivation caused by KCl. However, Hg reacted with Cl (from KCl), forming HgCl or HgCl_2 . Then, inactive species, such as -V-O~Hg or -V-O-Hg-Cl, were formed that were able to adsorb NH_3 in competition with the active sites.

The deactivation of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst induced by KCl was investigated systematically via three methods (wet impregnation, solid diffusion, and vapor deposition) by Lei et al. [67]. The deactivation rate occurred in the following order: Vapor deposition >> solid diffusion > wet impregnation, and was mainly attributed to the presence of different forms of V species that reduced the acidity to different extents as previously found by Yu et al. [24].

When KCl was added by wet impregnation, the activity of V_2O_3 species was only slightly reduced, possibly due to the intimate interaction between K and oxygen in vanadium oxides. On the contrary, by the solid diffusion method, the formation of V_2O_5 - $K_2S_2O_7$ eutectic occurred, leading to a very small surface area and a too strong oxidation ability, which were the main reasons for the catalyst deactivation.

Xie et al. [68] assessed the deactivation mechanism by investigating a commercial V_2O_5 - WO_3 /TiO₂ catalyst through exposure to the flue gas of a coal-fired power plant by a transient kinetic analysis that focused on the distinction between the deactivation behaviors of adsorption sites and redox sites. The results showed that the alkali element preferentially poisons the active sites associated with vanadium (V^{5+} -OH and/or $V^{5+} = O$) rather than the sites associated with Ti and W. Thus, it was concluded that the poisoning of vanadium-linked species caused decreased NH_3 adsorption and increased NH_3 desorption, negatively affecting the SCR reaction.

The deactivation mechanism of V_2O_5 - WO_3 /TiO₂ ceramic honeycomb catalysts induced by P, K, Na, Mg, Ca, Cr, and Cu was assayed by Klimczak et al. [69]. The catalysts were poisoned by two different methods: (i) wet impregnation of dilute aqueous solution of the corresponding nitrate or ammonium salts; (ii) deposition of the inorganic aerosol particles. The second approach is more realistic as it uses reaction conditions close to the mobile application and it seems to be more harmful. Both impregnated and aerosol deactivated catalysts showed a strong poisoning effect of alkaline metals due to a reduced capacity of absorbed NH_3 . P, Cr, and Cu moderately poisoned the catalysts because there was competition between the increased N_2O production and reduced acid sites. In Figure 12, the NO_x conversion curves over V_2O_5 - WO_3 /TiO₂ (400 cpsi monoliths) are compared [69]. Figure 12a shows fresh, hydrothermal aged and K, Na and Ca poisoned samples; Figure 12b displays fresh, hydrothermal aged and Cr and Cu poisoned catalysts. In both cases, a molar throughput of 3 mmol of poisoning was used and added by aerosol.

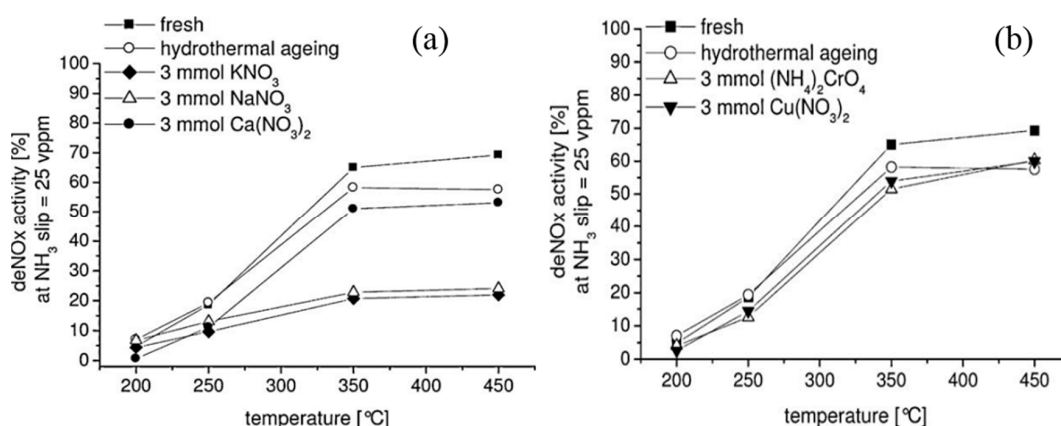


Figure 12. NO_x conversion over V_2O_5 - WO_3 /TiO₂ (400 cpsi monoliths) as (a) fresh, hydrothermal aged and K, Na and Ca poisoned samples; (b) fresh, hydrothermal aged and Cr and Cu poisoned catalysts. Conditions: 1000 vppm NO, 1000 vppm CO, 5 vol.% CO₂, 8 vol.% O₂, 5 vol.% H₂O and balance N₂ at NH_3 slip of 25 vppm and 50,000 h⁻¹. (Reprinted with permission from [69]. Copyright (2010) Elsevier).

Deng et al. [70] studied alkali metals' deactivation process of V_2O_5 - WO_3 /TiO₂ SCR catalyst by using an entrained-flow combustion system. The conclusions can be described as follows, and the activity of the catalyst sample was affected by the fly ash. The order of the poisoning effects of different alkali salts on the activity was $Na_2CO_3 < K_2CO_3 < Na_2SO_4 < K_2SO_4 < NaCl < KCl$. Both the decrease of the specific surface area and the masking of V_2O_5 caused the activity reduction, which can be attributed to mechanical deactivation. More importantly, the deposited particles of alkali salts can both coordinate to the -OH on the surface and interact with the lattice oxygen in the V species, which can be assigned to chemical deactivation. All of them can be ascribed to the reduction of the capacity of ab- NH_3 .

Li et al. [71] studied the activity of Ca poisoning V_2O_5 - WO_3 /TiO₂ catalysts based on the modification of activity, structure, reducibility, acidity, and reaction properties. The results revealed

that the bulk W species and surface acid sites could be passivated with high contents of CaO, leading to CaWO_4 formation. Additionally, the reducibility and surface oxygen species were also inhibited by CaO species.

Kong et al. [72] studied the poisoning of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts by arsenic (As). In Figure 13a,b, the NO_x conversion curves over fresh and poisoned catalysts and the deactivation mechanism are displayed. The main reason for catalytic deactivation originates from the following: As_2O_3 would be adsorbed on the surface of catalyst, then oxidized into As_2O_5 by surface chemisorption oxygen. The As_2O_5 dense layers deposited on the catalyst surface prevent NH_3 adsorption and the active sites' recovery.

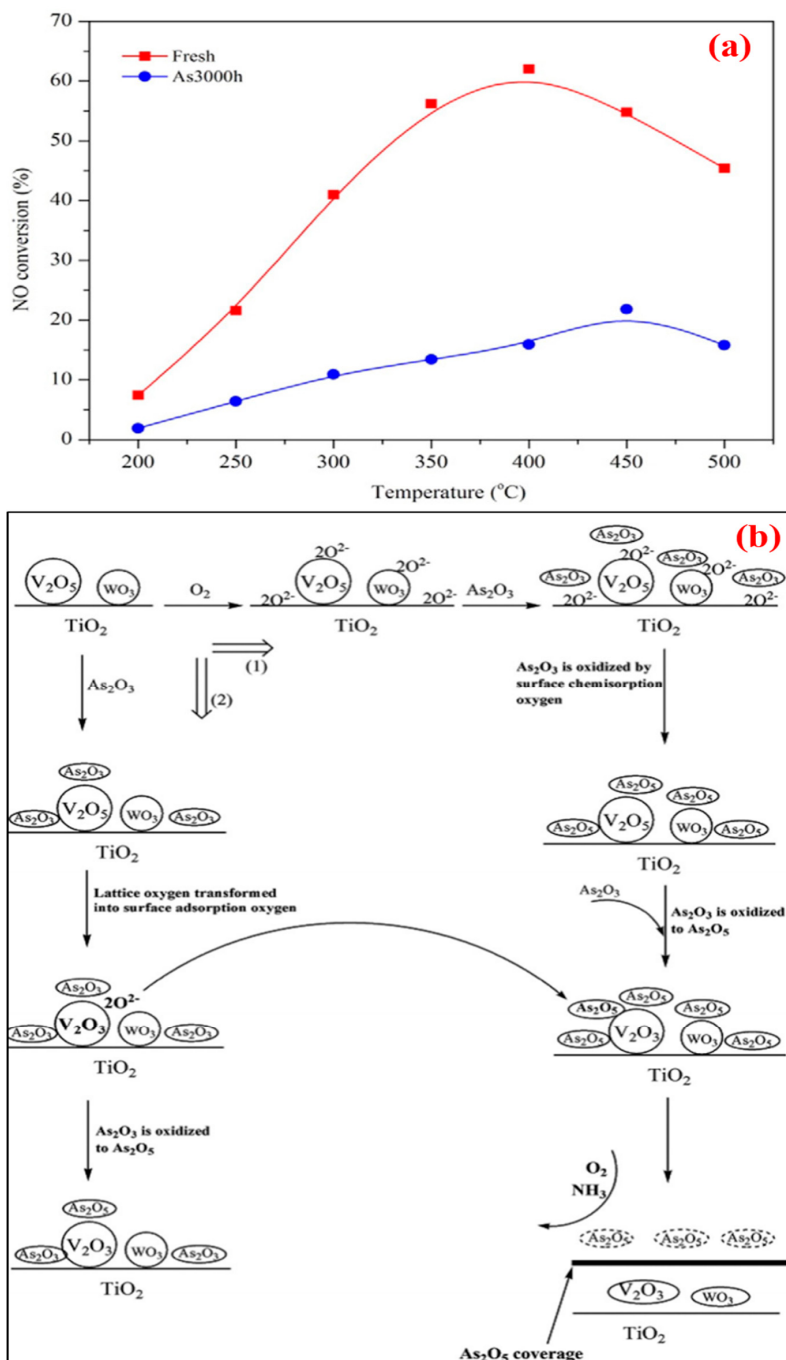


Figure 13. NO_x conversion over fresh and poisoned $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts (a); picture for deactivation mechanism (b). (Reprinted with permission from [72]. Copyright (2015) Elsevier).

4. SO₂ and H₂O Effects

A discussion about deactivation and poisoning effects on V₂O₅-WO₃-based catalysts cannot exclude the influence of SO₂ and/or H₂O for realistic applications. Indeed, flue gas emissions from power plants always contain SO₂ (200–1500 ppm) that can be further oxidized to SO₃ by the supported V₂O₅-WO₃/TiO₂ catalysts. Moreover, SO₃ is corrosive to stainless steel SCR reactor components and readily reacts with ammonia to form ammonium sulfate/bisulfate that deposit on the catalysts, causing deactivation, and on the walls of heat exchangers to reduce their efficiency. Regarding the effects of water, it must be pointed out that significant amounts of moisture, 10% to 30%, are present in the flue gas exiting from industrial combustion processes. Moreover, moisture interacts with the surface of the catalysts and modifies the surface's active sites and the distribution of Lewis and Brønsted acid sites. However, the role of water has not been extensively investigated, so it deserves further attention.

In the 1990s, preliminary investigations about SO₂ effects were reported by Chen et al. [73], who found that SO₂ promotes the activity by increasing the Brønsted acidity, in accordance with the assumption that Brønsted acid sites are the active sites for the reaction. A few years later, the same authors [74] investigated SO₄^{2−}/TiO₂ superacid for NO SCR with NH₃. Since SO₄^{2−}/TiO₂ is formed on TiO₂ under SCR reaction conditions when SO₂ is present, the results elucidated the role of TiO₂ support (and SO₂) in the SCR reaction. XPS and chemisorption measurements along with SCR kinetic results indicated that the reaction takes place by an Eley–Rideal mechanism, on Brønsted acid sites on SO₄^{2−}/TiO₂ surface. The catalytic results showed NO conversion is in the range of 96% to 100% at temperatures between 400 and 425 °C and the good performances were explained considering that at 400 °C, about 70% of the SO₄^{2−} ions are occupied by ammonia that is active for reactions with NO.

The promoting effect of the sulphate content on the catalytic activity of titania was also reported by Ciambelli et al. [75], who found an enhanced NO conversion without decreased selectivity to N₂, which was attributed to the enhanced chemisorption of ammonia.

The coupled effect of SO₂ and H₂O was investigated by Amiridis et al. [76] at 350 °C over V₂O₅/TiO₂ catalysts with variable vanadia loadings. Independently on the vanadia surface coverage, the addition of H₂O to the reaction mixture resulted in a decrease of the SCR turnover frequency of approximately 40% to 50% due to a competitive adsorption of H₂O on the active vanadia sites. The presence of SO₂ in the gas phase resulted in a significant increase of the turnover frequency at low vanadia surface coverage due to the formation of surface sulfate species that in the presence of H₂O, act as strong Brønsted acid sites. However, an excess of water had a negative effect in the SCR by slowing the reoxidation of vanadia.

The reported results on the effect of SO₂ and water thus far were confirmed by Magnusson et al. [16], who investigated how SO₂ affects the NO_x activity of a V₂O₅-WO₃/TiO₂ urea-SCR catalyst for marine applications. Surprisingly, the authors found that the addition of SO₂ in the absence of H₂O promoted NO_x reduction at 350 °C, while only H₂O gave rise to a decrease in the NO_x abatement and also an inhibition of the N₂O formation. No promotional effect by SO₂ was observed at temperatures below 230 °C. Further, long term effects of SO₂ and H₂O were investigated and the NO_x reduction remained stable, also after long term exposure of SO₂. Finally, it was concluded that in the presence of both H₂O and SO₂, the catalyst did not show any deactivation at temperatures above 300 °C and fairly low space velocities (below 12,200 h^{−1}). However, at lower temperatures (250 °C) and/or higher space velocities, the catalytic performance for NO_x reduction decreased with time. Therefore, for V₂O₅-WO₃-based catalysts used at low temperatures, the effects of water and sulfur dioxide must be carefully addressed.

A recent detailed investigation about H₂O and SO₂ effects has been carried out by Lai and Wachs [77]. This is a perspective study addressing the current fundamental understanding and advances on V₂O₅-WO₃/TiO₂ catalysts taking into consideration the main parameters affecting the activity, such as the catalyst synthesis, molecular structures of titania supported vanadium and tungsten oxide species, surface acidity, catalytic active sites, surface reaction intermediates, reaction mechanism, rate determining-step, and reaction kinetics.

As remarked in [77] and as well in the references therein, water inhibits the SCR reaction rate at low (~1%) but does not affect the SCR reaction at high concentrations (>5%). Such an effect arises from (1) competitive adsorption with the reactants (NO or NH₃) and/or (2) inhibition of the reaction between NO and adsorbed NH₃. H₂O increased the concentration of surface NH₄⁺ species on Brønsted acid sites and such surface NH₄⁺ intermediates arise from the reaction of NH₃* species with moisture.

Regarding the effect of SO_x, the effects of SO₂ and SO₃ on TiO₂ and supported V₂O₅/TiO₂ has received much attention, while less investigation has focused on tungsten catalysts. For V₂O₅-WO₃/TiO₂, both surface vanadia and tungsten oxide sites contribute equally to the overall SO₂ oxidation reaction to SO₃.

5. Conclusions and Perspectives

In summary, a fundamental understanding and recent advances on the respective role of V₂O₅-WO₃/TiO₂ catalysts were reviewed in detail, with special concern to the literature published in the last 20 years. It is generally accepted that WO₃ increases the Lewis acidity and inhibits the initial sintering of TiO₂ as well as helping to form superoxide ions. Concerning V₂O₅, it increases the surface Brønsted and Lewis acidity and enhances N₂ selectivity. The importance of interaction between V₂O₅ and WO₃ was also revealed. In addition, the relationships between the catalytic activity and synthesis methods, supports, composition, and doping agents were discussed as well. It can be pointed out that alkaline and alkaline earth metals (K, Na, Ca, Mg) as well other elements, such as Cr, As, and Hg, deactivate the V₂O₅-WO₃-based catalysts. Especially, alkali metals decrease the ability of NH₃ adsorption, which is a disadvantage for low-temperature activity and selectivity.

The specific surface area of titania plays an important role for the dispersion and interaction of V₂O₅ and WO₃ active oxides. In addition, the support composition influences the activity. For example, the addition of SiO₂ inhibits the shrinkage of the catalyst's specific surface area, avoiding the phase transition from anatase to rutile and growth of the TiO₂ size.

A Pt doped SiC filter is a promising carrier that not only improves the surface acid sites, but also significantly enlarges the BET surface area, the pore volume of the catalysts, and favors high electron transfer, enhancing the absorption of NH₃ and lighting-off NO conversion at low temperatures.

The presence of SO₂ and/or H₂O on the flue gases must be carefully addressed for practical applications, paying special attention to the experimental conditions that can affect positively or negatively the catalytic performances of V₂O₅-WO₃ based catalysts.

Considering that V₂O₅-WO₃ based catalysts are inactive during the engine cold-start, the enhancement of NO SCR at low temperatures (<200 °C), maintaining high selectivity to N₂, is still challenging for a successful application of such systems for automotive and naval usage. Such improvement could be achieved by doping V₂O₅-WO₃ based catalysts with new oxides. According with recent data, MnEuO_x, MnSmO_x, MnGdO_x, MnCeO_x represent promising co-catalysts.

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