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Review

The Deactivation of Industrial SCR Catalysts—A Short Review

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Abstract: One of the most harmful compounds are nitrogen oxides. Currently, the common industrial method of nitrogen oxides emission control is selective catalytic reduction with ammonia (NH_3-SCR). Among all of the recognized measures, NH_3-SCR is the most effective and reaches even up to 90% of NOx conversion. The presence of the catalyst provides the surface for the reaction to proceed and lowers the activation energy. The optimum temperature of the process is in the range of 150–450 °C and the majority of the commercial installations utilize vanadium oxide (V_2O_5) supported on titanium oxide (TiO_2) in a form of anatase, wash coated on a honeycomb monolith or deposited on a plate-like structures. In order to improve the mechanical stability and chemical resistance, the system is usually promoted with tungsten oxide (WO_3) or molybdenum oxide (MoO3). The efficiency of the commercial V_2O_5-WO_3-TiO_2 catalyst of NH_3-SCR, can be gradually decreased with time of its utilization. Apart from the physical deactivation, such as high temperature sintering, attrition and loss of the active elements by volatilization, the system can suffer from chemical poisoning. All of the presented deactivating agents pass for the most severe poisons of V_2O_5-WO_3-TiO_2. In order to minimize the harmful influence of H_2O, SO_2, alkali metals, heavy metals and halogens, a number of methods has been developed. Some of them improve the resistance to poisons and some are focused on recovery of the catalytic system. Nevertheless, since the amount of highly contaminated fuels combusted in power plants and industry gradually increases, more effective poisoning-preventing and regeneration measures are still in high demand.

Keywords: SCR-NH_3; $DeNO_x$; water; sulphur compounds (SO_x); alkali metals; heavy metals; halogens

1. Introduction

The issue of air pollution caused by the increasing industrialization of the society still remains an unsolved environmental problem. One of the most harmful compounds are nitrogen oxides (NO_x) [1–4], mainly due to their strongly climate-changing character that contributes to acid rain and photochemical smog formation or ozone layer depletion [5–9]. Over last decades, the public awareness of the environmental subjects greatly increased, resulting in the implementation of political regulations about the emission limits. In order to meet the restrictions imposed by governments, a number of methods of NO_x abatement were developed [8,10,11]. Currently, the common industrial method of nitrogen oxides emission control is selective catalytic reduction with ammonia (NH_3-SCR) [12–14]. Among all of the recognized measures, NH_3-SCR is the most effective and reaches even up to 90% of NO_x conversion [8,15–18]. NH_3-SCR assumes the reaction between NO and NH_3 (the reducing agent) that yields molecular nitrogen and water vapor as the desired products [12]. The presence of the catalyst provides the surface for the reaction to proceed and lowers the activation energy of the process [19,20]. The optimum temperature of NH_3-SCR is in the range of 150–450 °C and the majority of the commercial installations utilize vanadium oxide (V_2O_5) supported on titanium oxide (TiO_2) in a form of anatase, wash coated on a honeycomb monolith or deposited on a plate-like structures [3,21–23]. In order to improve the mechanical stability and chemical resistance, the system is usually promoted with tungsten oxide (WO_3) or molybdenum oxide (MoO_3) [24–26].

Although the catalyst is highly active, there are some considerable operating problems that limit its efficient application. One of the most important is the narrow temperature window (300–450 °C). Thus, it is required to place the SCR unit in so-called "high-dust" configuration in order to avoid re-heating of the exhausts and in consequence, cut down the costs of $DeNO_x$ installation [27–29]. However, despite the high temperature of the flue gas, the position before the desulphurization installation (FGD) and electrostatic precipitator (ESP) can cause severe poisoning by harmful components of the fumes, such as SO_2 and fly ash, especially when the contaminated fuel is burned [30–33]. The fly ash of coal-fired power plants contains significant amounts of alkali metals or alkaline earth metal compounds, including K, Na, Mg or Ca [3,34–36]. Another adverse compounds that can be deposited on the catalyst's surface are non-metallic compounds, such as arsenic or lead [37–40]. Additionally, under the influence of elevated temperature and moisture, with the passing of time the material can undergo thermal or hydrothermal aging [41–43]. Under typical conditions of NH_3-SCR, the catalyst can also be affected mechanically by sintering, surface masking, fouling or losing of active components and the specific surface area [44]. All of these aspects can lead to irreversible deterioration of the catalytic performance. Since the lifetime of the commercial catalysts is a crucial issue in the economics of industrial processes, the assurance of the stability and resistance is indispensable. It undoubtedly helps to avoid downtimes and maintain the continuous and efficient work of the purification installation. Additionally, in many cases it is possible to regenerate the poisoned material and restore the activity to some extent. Therefore, the development of the new recovery methods is highly required.

In the following research, we presented the studies on the most adverse compounds that can affect the catalytic performance of the commercial vanadium-titanium-based NH_3-SCR system. We analyzed and described the mechanisms proposed in the literature concerning the typical degradations. In order to provide the most reliable description of each mechanism of deactivation, we focused mostly on the findings published in the last 10 years. Our research offers a clear explanation of the interactions of contaminations with the active sites of commercial type of selective catalytic reduction (SCR) catalyst V_2O_5-TiO_2. Additionally, in each paragraph we presented concise and precise description of the origin of each type of poisoning agent in the flue gas.

2. Methodology of the Literature Review

The following paper is focused on the deactivation of the commercial vanadium-based catalyst of NH_3-SCR process. The study was concentrated on the effect of the contaminations commonly present in the exhaust gas that affect the proper work of the NH_3-SCR catalyst. The considerations included the interactions of water vapor, sulphur dioxide, alkali metals, heavy metal oxides and halogens with promoted or non-promoted V_2O_5-TiO_2. Additionally, the deactivation mechanisms of each poison have been briefly discussed.

The review article was divided into sections that were preceded by the short introduction to the problem of nitrogen oxides emission and their negative influence on the quality of the environment, description of the basis of selective catalytic reduction with ammonia as the most effective method of NO_x abatement, typical composition and features of the commercial vanadium-based catalyst of the process and problem of the placement of SCR installation in the gas purification system in stationary sources of emission. Furthermore, the reader was introduced to the main topic of the paper by the short presentation of the pollution present in the flue gas. Finally, the effects of each poison on the catalyst were extensively described. The summary includes critical findings essential for our research, conclusions that can be drawn on its basis and brief description of the future perspective of the study.

3. Effect of Water Vapor

The presence of water vapor in the flue gas under industrial conditions of NH_3-SCR reaction is inevitable. Typically, the exhausts contain 10–30 vol.% of H_2O and even if the process takes place in dry conditions, as the product of the reaction, H_2O molecules can cover the active sites of the catalyst. Physically, water can impair the fine structure or lead to the cracking of the catalyst as a result of vaporization and swelling. Moreover, in the presence of alkali metals it can form soluble salts that poison the acid sites of the material [45]. In general, the chemical deactivation by H_2O can occur according to two routes. The first and reversible interaction of water with the catalyst surface assumes its adsorption on the active sites that can be inhibited after removal of H_2O from the gas stream [15,46]. Zhu et al. [47] analyzed the effect of the presence of 5 vol.% of water in the exhausts on the catalytic performance of 3 wt.% V_2O_5-MoO_3-WO_3-TiO_2. The authors observed that at 200 °C the conversion of NO declined from 83.4% in dry conditions to 63.9% in wet conditions. However, the hampering effect was recovered after switching off the feed of H_2O. The second and irreversible deactivation occurs when the molecules of H_2O undergo chemisorption on the surface and form hydroxyls of very high decomposition temperature [48]. The major reason of the decreased activity is competitive adsorption of NH_3 or NO and H_2O on the active sites of the catalyst. Additionally the primary studies in that field confirmed that effect is independent of the vanadium loading [49,50].

The moisture influences significantly the form of V_2O_5, due to its reconstruction under the in situ conditions of NH_3-SCR [50]. Jehng et al. [51] analyzed the impact of moisture on the molecular structure of vanadia using in situ Raman spectroscopy in the temperature range of 120–450 °C. The behavior of the commercial system: 1, 5 or 7 wt.% V_2O_5-TiO_2 was investigated in the presence of oxygen under dry conditions and with 8 vol.% of H_2O in the gas stream. It was observed that in the absence of moisture, V_2O_5 existed in a form of isolated and polymeric species. When water was introduced into the feed above 230 °C, the surface vanadium moieties formed hydrogen bonds with H_2O. The effect of water adsorption at elevated temperature proves that it can interact competitively with NH_3 during NH_3-SCR by the formation of coordinative bonds with surface vanadia species. Additionally, below 230 °C only the monomeric VO_x species were observed to become extensively solvated by the moisture. As a result, the hydrated surface vanadate structures, such as decavanadates were formed. Additionally, the oxygen-18 isotopic labeling experiments confirmed that terminal V=O, bridging V–O–V and V–O–support bonds form the hydrogen bonds with H_2O. Therefore, consumption of active O from the catalyst surface can considerably decrease NO conversion in SCR process.

Furthermore, water vapor has a substantial impact on the ratio of Brönsted/Lewis acid sites [38]. Zhu et al. [47] examined the distribution and reactivity of ammonia species on the acid sites of V_2O_5-WO_3-TiO_2 in the presence of moisture in the feed gas using time-resolved in situ Fourier transform-infrared (FT-IR). The results of the studies suggested that exposition of the catalyst to the flue gas containing water (8 vol.%) increased the amount of surface NH_4^+ species and decreased the density of coordinatively bounded ammonia, especially at 250 °C. It is known that both Brönsted and Lewis acid sites participate in the adsorption of ammonia during NH_3-SCR [52–54]. However, according to the turnover frequency (TOF) calculations, the specific activity of surface V^{5+} sites of Lewis acidity is higher than that of Brönsted acidity, due to their better thermostability [55]. Therefore, it was suggested that the domination of less active Brönsted acid sites can be an alternative reason of the diminished catalytic activity of NH_3-SCR in the wet conditions.

In summary, due to the unclear assumptions concerning the mechanism of NH_3-SCR, it is rather difficult to draw unambiguous conclusions about the influence of H_2O in the catalytic performance. On the basis of the suggestions of Topsøe et al. [50], Brönsted acid sites are the only active centers of the vanadium-based catalyst. The participation of V-OH Brönsted acid sites as the main centers of the process was also confirmed by Janssen et al. [56]. Therefore, hydration of the active centers by moisture should elevate the catalytic activity. Nevertheless, due to the fact that the studies were performed a few years ago, the outcomes of the analysis may not be fully reliable. According to the more recent postulations of Marberger et al. [57] and Zhu et al. [55], Lewis acid sites are the most active and significant in NH_3-SCR. Thus, while Brönsted acid sites are produced in the presence of H_2O, the catalytic activity is significantly diminished. Hence, due to the convoluted mechanism of the process, dependent on many external factors, it is rather complicated to determine the role of water in the catalytic system and the issue definitely deserves further attention.

4. Effect of SO_x

In the practical applications of NH_3-SCR, the catalyst is under high risk of being deactivated by sulphur compounds (SO_x). Sulphur appears in the combustion zone due to its presence in fuel and the largest amount of SO_2 is generated in the first stage of incineration. The poisoning effect is observed mainly in the low-temperature range of SCR (below 300 °C). Since vanadium catalysts are commonly used for sulphur dioxide oxidation in the technology of sulphuric acid production, the active phase of commercial NH_3-SCR system is capable to oxidize SO_2 to SO_3 [46,58]. The main problem of the exposition of the catalyst to SO_x is the formation of ammonium bisulphates (NH_4HSO_4) and ammonium sulphates ($(NH_4)_2SO_4$) on its surface [59]. The extent of deactivation with SO_x is determined by the operating conditions of NH_3-SCR. The prime analysis of the presence of SO_2 in the flue gas was performed by Svachula et al. [60] and Dunn et al. [61] who analyzed the influence of O_2, H_2O, NO_x and NH_3 concentration on the oxidation of SO_2 to SO_3 over honeycomb V_2O_5-TiO_2. It was found that the oxidation of SO_2 is almost independent of the partial pressure of O_2 in the flue gas if its concentration is approximately 2% v/v (representative operating conditions of SCR). On the contrary, with the increasing concentration of H_2O or NH_3, the tendency of the catalyst to convert SO_2 was significantly diminished, due to the competitive adsorption of H_2O and SO_2 on the acid sites of the material. Furthermore, the presence of NO_x in the flue gas slightly facilitates the conversion of SO_2. However, it is meaningful only in the low-temperature range of SCR, when the concentration of NO_x is high. The results of more recent studies in the topic of SO_2 presence in the exhausts suggest that SO_2 oxidation depends linearly on the catalyst's wall thickness and increases with the increasing temperature of the reaction [30,62]. The produced SO_3 can react with the steam in the rotary air heater and form corrosive sulphuric acid (H_2SO_4) in the temperature range of 204–426 °C [63].

In general, V_2O_5-WO_3-TiO_2 can be deactivated by sulphur compounds according to two routes. The first one, already mentioned, involves the reaction between SO_3 with gaseous NH_3 and H_2O to generate NH_4HSO_4 and $(NH_4)_2SO_4$. These compounds tend to form deposits in the cold equipment downstream of the SCR reactor and lead to the corrosion of the equipment. Moreover, the accumulation of ammonium sulphates and bisulphates in air-preheater results in the pressure drop and its clogging [64]. The second route involves the reaction of SO_2 with the active sites of the catalyst and of thermally stable metal sulphites/sulphates that affect redox properties of the material and block the active centers for the adsorption of reactants. The formation of metal sulphites and sulphates can be explained by the difference in the desorption temperature of NH_3 (150–400 °C) and SO_2 (>400 °C). Since the decomposition of $(NH_4)_2SO_4$ occurs at 150–400 °C, the residual SO_4^{2-} species combine easily with the free metal sites left by the desorbed NH_3 and form metal sulphites and sulphates. Due to the fact that the adsorption of SO_2 on TiO_2 is extremely favorable, V_2O_5-TiO_2 can be easily sulphated according to two routes—direct reaction of SO_2 with the anatase surface or its oxidation by VO_x to SO_3 that is subsequently adsorbed on the catalyst's support [59,64]. In summary, the phenomena partly clarify the poisonous influence of SO_2 in the low temperature range of NH_3-SCR [64]. Furthermore, the inhibited adsorption of NO (according to Langmuir-Hinshelwood mechanism) by the metal sulphites and sulphates causes the suppression of its oxidation to NO_2, lowers NH_3-SCR activity and irreversible deactivation of the catalyst [32,65]. The poisoning influence of SO_2 on V_2O_5-TiO_2 is depicted in Figure 1.

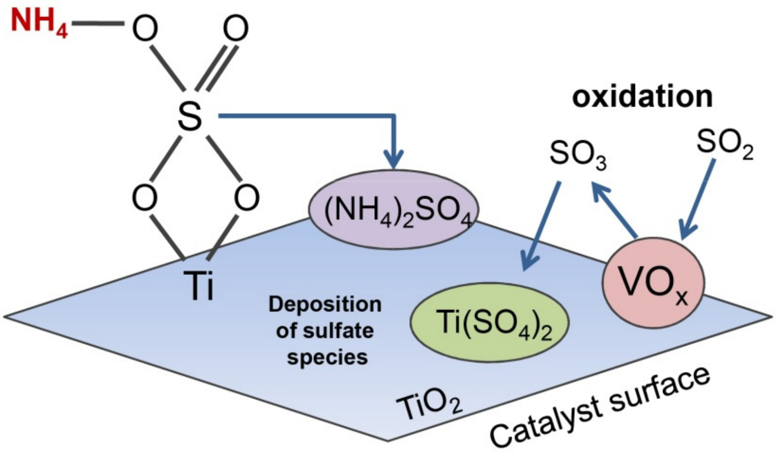

Figure 1. Mechanism of V_2O_5-TiO_2 deactivation by SO_2 (based on References [53,59]).

Xu et al. [62] investigated the effect of *in-situ* poisoning with SO_2 and H_2O on V_2O_5-WO_3-TiO_2 by simulating the conditions of flue gas in stationary sources. The reference catalyst reflecting commercial material was prepared by the impregnation method using ammonium vanadate and ammonium tungstate hydrate as the precursors of V and W, respectively. The amounts of the precursors of active phase and the promoter were calculated to obtain 1 wt.% and 5 wt.%, respectively. The catalyst was poisoned for 24 h in a fixed bed quartz reactor, using the inlet gas composed of 500 ppm of NH_3, 500 ppm of SO_2, 5% of H_2O, 5% of O_2 and N_2 as balance. The results of the catalytic tests over the poisoned catalyst indicated that the conversion of NO decreased significantly due to the contact with SO_2, especially below 300 °C. However, the results of low-temperature N_2 sorption measurement indicated only a weak influence of the SO_2 on S_{BET} of the materials. Therefore, lower catalytic activity of SO_2-poisoned catalysts is not determined by the loss of the specific surface area, which was also confirmed by earlier research in that field [66]. According to the outcomes of thermogravimetric analysis (TGA), a significant amount of NH_4HSO_4 was formed on the surface of the catalyst, which was suggested to have the major influence on the catalytic performance. Ma et al. [64] prepared the series of V_2O_5-TiO_2 catalysts with the vanadium content of 1 wt.% and 3 wt.% and doped the materials with W and/or Ce. The authors performed temperature programmed surface reaction (TPSR) and temperature programmed decomposition (TPDC) studies in order to investigate the mechanism of ammonium and metal sulphates formation. On the basis of the obtained results, the highest amount of ammonium sulphates (587.6 $\mu mol \cdot g_{cat}{}^{-1}$) was generated for the non-promoted V_2O_5-TiO_2, while for the W- and Ce-promoted samples the formation of $(NH_4)_2SO_4$ was considerably inhibited (to 45.5 $\mu mol \cdot g_{cat}{}^{-1}$ and 16.7 $\mu mol \cdot g_{cat}{}^{-1}$, respectively). However, according to the outcomes, the Ce-doped catalyst had high tendency to generate metal sulfates, in contrast to V_2O_5-WO_3-TiO_2. The effect was explained by the high temperature of $Ce(SO_3)_2$, $Ce(S_2O_7)_2$, $CeOSO_4$ and $Ce_2(SO_4)_3$ decomposition detected by TPDC analysis. In contrast, the addition of WO_x species hindered the formation of $Ti(SO_4)_2$. The probable reason is the basic nature of ceria and its ability to donate oxygen for SO_2, sulphation of the catalyst's surface and higher conversion of sulphur dioxide.

Undoubtedly, the formation of ammonium and metal sulphates and sulphites severely affects the catalytic activity of V_2O_5- TiO_2. The early studies on the interaction between SO_x and the catalyst's surface were carried out by Orsenigo et al. [67]. The researchers suggested that the sulphation occurs firstly on vanadia sites and later on tungsten and titania sites. On the contrary, Amiridis et al. [49] and Choo et al. [68] found that TiO_2 is sulphated first. Nevertheless, the studies were not confirmed by the full surface analysis [67] or the sulphate species were introduced artificially by impregnation [49]. Guo et al. [69] performed the in situ experimental investigation of the interaction between SO_2 and vanadia-titania catalyst and monitored the reaction by *operando* FT-IR spectroscopy. The results of the research evidenced that the surface sulphate species were formed rather upon the interaction with titania than with vanadia. Interestingly, the results of NH_3-SCR catalytic tests indicated that the sulphated 1 wt.% V_2O_5-TiO_2 exhibited 200% higher intrinsic rate than non-sulphated sample. It was concluded that the formation of S–OH groups attached to the support introduced new Brönsted acid sites which accelerated NO conversion.

There is a general agreement that the oxidation of SO_2 to SO_3 over V_2O_5-WO_3-TiO_2 is promoted by the increasing loading of V_2O_5 and thus higher aggregation degree of vanadium on the catalyst surface [24]. When vanadium content on the catalyst is high, the predominant species are polymeric vanadyls (–V(=O)–O–O–V(=O)–) that tend to form aggregates on the catalyst surface. Kamata et al. [66] investigated the relationship between the amount and structure of vanadium oxide and the catalytic activity in SO_2 oxidation. The outcomes of the studies indicated that the oxidation rate increased from 0.002 $\mu mol \cdot m^{-1} \cdot s^{-1}$ to 0.008 $\mu mol \cdot m^{-1} \cdot s^{-1}$ while the loading of V_2O_5 was increased from 1.5 wt.% to 5 wt.%, respectively. The infrared analysis (DRIFT) carried out over the catalysts suggested that both V=O and V–O–V species are involved in the adsorption of SO_2 and desorption of SO_3. On the other hand, on the basis of the reaction turnover frequency (TOF) measurement, Dunn et al. [61] reported that both the bridging V–O–V and terminal V=O do not play a crucial role in the oxidation of SO_2. The authors assumed that only vanadium species attached to the support (V–O–Ti) are active towards SO_2 oxidation. It is in agreement with the conclusion that sulphur species have significantly higher affinity to the species containing TiO_2. A few years later, the availability of more advanced techniques opened up new possibilities to analyze the mechanism of the SO_2 oxidation over V_2O_5-TiO_2. Du et al. [59] confirmed that polymeric vanadate species very active in SO_2 oxidation and for that reason, the commercial SCR catalyst should contain small amount of V_2O_5 (below 2.5%). According to the density functional theory (DFT) calculations performed by the authors, the energy barrier of SO_2 adsorption and oxidation to SO_3 is almost equal for both vanadium monomers and dimers. Three possible routes of SO_2 adsorption and oxidation on the SCR catalyst were considered. The first one involves the adsorption on TiO_2 uncovered by the active phase. The results of the calculations based on the projected model catalyst indicated that sulphur dioxide can interact with Ti–O–Ti sites due to the escape of bridge oxygen from the structure and its strong bonding with sulphur atom to form Ti(SO_3)Ti– configurations. However, the high energy barrier of SO_3 desorption needs to be overcome to break the structure of the complex (~100 kcal mol^{-1}). Thus, the formation of harmful SO_3 and subsequent deactivation can hardly happen due to the low reducibility of Ti^{4+} species. The study confirmed the earlier assumptions of Dunn et al. [61] that the coexistence of Ti–OH and vanadia monomer species facilitate capturing of SO_2. Nonetheless, DFT calculations indicated that in this case, the most favorable is the formation of stable Ti–OSOOH intermediates and the exchange of Ti–OH Brönsted acidic sites with S–OH sites. The second path that was appraised, involved the interaction of SO_2 with a vanadia monomer. In this case, sulphur dioxide can be oxidized by bridge oxygen of V–O–Ti or terminal oxygen of V=O. According to the authors, the direct release of SO_3 from this site is hampered by the high energy needed for desorption and $Ti(SO_4)_4$ deposits that are formed. In contrast, it was also found that for the terminal oxygen of V=O the oxidation process passes via sulphation of the vanadia site and not by direct oxidation. The phenomenon was explained by the reduction of energy barrier, while SO_2 reacts with active sites of the catalyst surface first. This results in the close interaction of SO_2 with the catalyst-detached oxygen. Herein, tetrahedral –V(SO_4)– species are formed and SO_3 can be simply released. Additionally, the analysis revealed that for the vanadia dimer, the energy barrier for SO_2 oxidation is slightly higher (about 4–5 kcal mol^{-1}) than for vanadia monomer. The assumptions presented by Du et al. [59] on the influence of vanadium content on the activity in SO_2 oxidation were in agreement with those postulated by Ma et al. [64]. The latter authors found that the formation of polymeric vanadium species resulted in higher reducibility of the catalyst and facilitated activity towards SO_2 oxidation. However, the increased loading with vanadium inhibited the formation of $(NH_4)_2SO_4$ deposits, probably due to the higher catalytic activity and increased consumption of NH_3 provided by the abundance of polyvanadates. Thus, the main role in the mechanism of SO_2 oxidation is played not only by the loading of vanadium on the catalyst surface but also by the nature of oxygen in the vanadium species. Additionally, due to the acidic character of V_2O_5, the SO_2 adsorption capacity is poor and vanadia sites oxidize SO_2 to SO_3 by the sulphation of the catalyst's surface.

In summary, both previous and more recent studies on the presence of SO_2 in the flue gas and its influence on the catalytic performance of SCR reaction confirm that the oxidation to SO_3 and poisoning by the sulfate and sulfite compounds is influenced by the composition of the flue gas, geometry of the catalyst and temperature of NO reduction process. There is a general agreement that on two routes of deactivation of the catalyst by the sulfur compounds confirmed by primary and most recent studies on that topic. However, the explanation of the mechanism of poisoning evaluated significantly among the last few years. Most of the original studies carried out in 90s of XX century and at the beginning of XXI century confirm that the main role in the sulphation of the catalyst is played by TiO_2. Indeed, more recent studies postulate that the stable Ti-OSOOH intermediates are formed with the participation of Ti-OH Brönsted sites. Nonetheless, in general the energy barrier of SO_3 desorption from this configuration is too high to overcome and instead the presence of both mono- and polyvanadate species is the main reason for SO_2 oxidation and formation of $(NH_4)_2SO_4$ and NH_4HSO_4 by the reaction with NH_3, which leads to the formation of deposits. The summary of the most important findings about the deactivation of V_2O_5-TiO_2 with sulphur compounds discussed in the section is presented in Table 1.

Table 1. The most important findings on the interaction of SO_2 with V_2O_5-TiO_2.

No.	Important Assumption	Reference
1	SO_2 oxidation is independent of the concentration of O_2 (below O_2 level of 2 vol.%) and decreases linearly with increasing concentration of NH_3 and H_2O	[58,59]
2	Ce and W applied as promoters inhibit the formation of $(NH_4)_2SO_4$ but can lead to the formation of metal sulphates/sulphites	[62]
3	Surface sulphate/sulphite species are formed mainly upon the reaction of SO_2 with TiO_2	[47,66,67]
4	Tendency of V_2O_5-TiO_2 to oxidize SO_2 to SO_3 increases linearly with the increasing concentration of vanadia sites on the catalyst surface; polymeric vanadate species are more active in SO_2 oxidation than monomeric species	[23,64]
5	Polymeric vanadate species inhibit the formation of $(NH_4)_2SO_4$	[62]

Interestingly, according to a number of studies, the exposition of the catalyst to SO_2 results in the formation of additional acid sites provided by the generation of SO_4^{2-}. Therefore, the commercial SCR catalyst contains about 0.5–1.0 wt.% of sulphur, mainly in the form of surface sulphate, in order to promote adsorption of NH_3 and NO reduction [70]. The role of sulphate groups in the catalytic activity in NH_3-SCR was widely discussed by the scientists in recent times [70–73]. According to some studies, surface sulphate groups can act as the reservoir for the adsorbed NH_3 [70]. Nevertheless, the issue of the beneficial effect of sulphation of V_2O_5-TiO_2 is still unclear and remains under intensive investigation.

5. Effect of Alkali Metals

Alkali metals and alkaline-earth metal oxides are one of the strongest poisons of NH_3-SCR catalyst. The large amount of alkaline metals in the fly ash of coal-fired power plants results in their deposition on the catalyst surface, especially while it is placed in the "high dust" configuration. Additionally, the strict legislations regarding air pollution control popularized the renewable energy sources, such as biomass [74,75]. In fact, the utilization of biomass as an energy source can reduce the combustion of fossil fuel but biomass contains a large amount of alkali metal compounds and the fly ash produced during its combustion can severely contaminate $DeNO_x$ catalyst [76,77].

The main reason of the strongly poisoning impact of these compounds on the catalyst is their basic character. Therefore, when adsorbed on the acidic sites of the active phase, they reduce NH_3 adsorption capacity and decrease the catalytic activity. Most of the studies performed so far assumed that the poisoning by the elements of basic character is caused by the formation of alkali—vanadium compounds (such as $NaVO_3$, KVO_3, $RbVO_3$) upon acid-base reactions that change the properties of the catalyst's surface. These formations tend to block the pores of the catalyst and adsorb as deposits causing strong deactivation of the active phase [31,78]. The schematic representation of the chemical poisoning of V_2O_5-TiO_2 by alkali metals is presented in Figure 2.

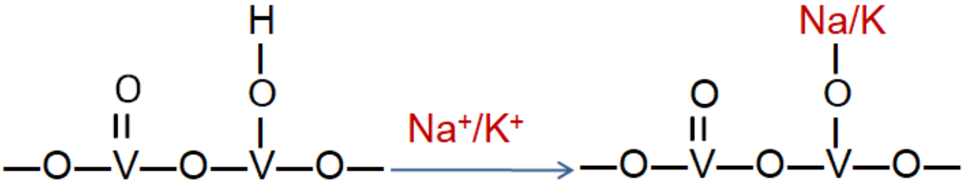

Figure 2. The mechanism of V_2O_5-TiO_2catalyst deactivation by alkali metals (based on Reference [45]).

Evaporation of the alkali metal compounds during combustion and further condensation when the temperature decreases results in the formation of submicron solid particles that are hard to remove from the exhausts [75]. Most of the studies concluded that the alkalis of IA group (Na and K) are stronger poisons than those belonging to IIA group (Ca and Mg) [72].

The deactivation of V_2O_5-TiO_2 by alkali metal compounds was extensively investigated both on a pilot-scale and in lab experiments at the beginning of XXI century [75,79–82]. The primary study in that field was carried out in 1990 by Chen et al. [83]. It was suggested that the strength of the poison follows the order of basicity—$Cs_2O > Rb_2O > K_2O > Na_2O > Li_2O$. The authors also analyzed the influence of atomic ratios of the alkali metal-vanadium species on the poisoning degree and it was found that one atom of Cs deactivates ca. 14 atoms of V. Furthermore, the poisoning effect of CaO was found to be considerably weaker in comparison to the alkali metal oxides of IA group, which is consistent with the scale of basicity of the metal oxides. The poisoning effect of alkali metals and their compounds on the SCR catalyst was extensively studied in further times. Zheng et al. [75] suggested that both chemical and physical deactivation of the catalyst is caused by the interaction of alkali metals with active sites but the former is more severe and more difficult to reverse. Moradi et al. [82] analyzed the behavior of the vanadium catalyst contaminated with various alkali metal-aerosol particles. It was observed that the deactivating effect was accelerated when the temperature of the process was elevated. Generally, according to most of the studies, the poisoning by alkali metals is caused by their interaction with the active phase-V_2O_5 via blocking the Brönsted active sites (V–OH). Besides, the latest investigations confirmed that the decreased catalytic activity may be correlated with the lowered reducibility of vanadium and tungsten species under the influence of alkaline compounds [84]. Chang et al. [34] analyzed the influence of different alkali metal cations (Na^+, K^+ and Ca^{2+}) in the form of bromides on the deactivation of a commercial SCR catalyst. In comparison to the fresh material, the samples treated with alkali metals exhibited lower NO conversion above 350 °C and slightly diminished selectivity to N_2 in the temperature range of 150–450 °C. The most noticeable decrease in catalytic activity (24% of NO conversion at 450 °C) was observed for the material poisoned with potassium. Moreover, the shift of NH_3 desorption temperature to lower value for all of the considered materials indicated that the strength of acidic sites was affected by alkali metals. CO_2-TPD analysis confirmed the formation of new basic sites, especially after addition of potassium. Doping with alkali metals had only negligible effect on the specific surface area. Therefore, it can be concluded that the poisoning effect is correlated only with the changes in the chemical properties of the catalysts.

Most of the studies focused on the influence of alkaline metals on the catalytic performance of V_2O_5-TiO_2 in NH_3-SCR concentrated on the surface acidity of the active material. However, the key step of the reaction is the oxidative dehydrogenation of ammonia (following Eley-Rideal mechanism of SCR) by vanadia species, which was suggested in the most original studies of the mechanism of SCR reaction with ammonia over vanadium-based catalyst [85,86] and confirmed by the updated research [87,88]. The phenomenon is strongly correlated with the reducibility of the active phase on the anatase support, which can be affected by alkali metals. Tang et al. [89] prepared 3.87 wt.% V_2O_5-TiO_2 using impregnation method and poisoned the catalyst with Na^+ and Ca^{2+} cations. The results of H_2-TPR experiments carried out over the poisoned materials indicated that the presence of sodium or calcium cations shifts the reduction temperature peak from 535 °C to about 560 °C, especially when alkali metal/vanadium ratio is higher than 0.05. In UV-vis DR spectra it was observed that the deposition of sodium caused the decrease in the position of absorption band from 518 nm to 515 and 507 nm, suggesting that Na^+ lowers the polymerization degree of vanadia species which results in lower catalytic activity in NH_3-SCR. On the contrary, no significant changes were observed in the spectra obtained for Ca^{2+}-poisoned samples, regardless its content. The results of the catalytic tests confirmed that Na^+ species exhibit significantly stronger poisoning effect in comparison to Ca^{2+}.

Thus the poisoning effect of alkali metals is diversified and depends on many number of factors. Nevertheless, both primary and recent studies over the deactivation by alkali metal-containing deposits are in agreement and confirm that the poisoning influence is strictly correlated with the consumption of acid sites and inhibition of the adsorption of NH_3. Nevertheless, it is worth to emphasize that among K, Na and Ca, every particular compound undergoes various interactions with the catalyst surface. Hence, in the next subchapters special attention is paid to the influence of specific alkali metal on the catalytic performance of promoted or non-promoted V_2O_5-TiO_2. In order to present various points of view and evolution of the studies and the understanding of the interactions, chronological review over the poisoning with alkali metals was presented.

5.1. The Effect of Potassium

Potassium, belonging to the IA group, was confirmed to react actively with the Brönsted acid sites of the catalyst and thus inhibit the adsorption of ammonia during NH_3-SCR. The element occurs in the oxide form (K_2O) or inorganic salts (KCl or K_2SO_4), mainly in the exhaust gas produced by the combustion of biomass [90] and, according to the studies carried out by Zheng, Jensen and Johnsson in 2004, the average amount of potassium in straw oscillates between 0.2 to 1.9 wt.% [74]. The authors also found that in the presence of potassium, the Brönsted center is affected by K^+ and the amount of adsorbed NH_3 decreases with the increasing content of alkali metal. Moreover, the authors suggested that raising the operation temperature cannot inhibit deactivating effect of potassium. Thus, the most probable consequence of deactivation with potassium is the interruption in the SCR mechanism involving Brönsted acid sites.

Kong et al. [76] suggested that the vanadium content can play a key role in the level of deactivation by potassium, which is in disagreement with the conclusions drawn on the basis of earlier studies [74]. The former authors investigated KNO_3-poisoned V_2O_5-WO_3-TiO_2 with various loadings of vanadium and potassium (1, 3, 5 wt.% and 0.8, 0.45 and 2.4 wt.%, respectively). NH_3-SCR catalytic tests over the poisoned samples showed that the material containing 3 wt.% of V_2O_5 exhibited the highest activity and resistance to K-poisoning. When the vanadium loading was increased to 5 wt.%, significant deactivation of the catalyst was observed, especially above 450 °C. The effect was explained by the combined oxidation of NH_3 at elevated temperature and adsorption of K^+ on V–OH polymeric active sites generated due to high content of vanadium. The mechanism of deactivation with potassium and the influence of vanadium content was explained basing on three factors—(1) decreased amount and strength of the acid sites (2) lower reducibility of vanadium species as a result of KVO_3 formation and (3) intensified formation of polymeric forms of V–OH sites with the increasing vanadium content and competitive adsorption of K^+ and NH_3 on the Brönsted centers. On the basis of the obtained results, it can be assumed that an appropriate content of vanadium can reduce harmful influence of potassium on the active sites and thus, result in maintaining, to some extent, satisfactory catalytic activity.

It is known that potassium can be released as a gas phase, aerosols or in the form of condensed compounds [75]. Additionally, the influence of K was found to depend on the quantity of the poison and its precursor, as well as on the introduction pathway. Due to that, Lei et al. [84] compared the deactivating effect of KCl introduced onto V_2O_5-TiO_2 by vapor deposition, solid diffusion and wet impregnation, in order to reflect the three major routes of deactivation by potassium in the industrial conditions. The results of the inductively coupled plasma analysis (ICP) over the poisoned samples showed that vapor deposition resulted in the lowest concentration of potassium on the catalysts' surface, while comparable contents were obtained for the samples treated by solid diffusion and wet impregnation. NH_3-SCR catalytic tests showed that the deactivation followed the order—wet impregnation < solid diffusion ≤ vapor deposition. Basing on the outcomes of the X-ray photoelectron spectroscopy analysis (XPS), the reason for the highest deactivation after poisoning of the catalyst by vapor deposition was concluded to be the formation of eutectic V_2O_5-$K_2S_2O_7$ that significantly decreased the specific surface area of the catalyst. Additionally, H_2-TPR experiment showed that the temperature of V^{5+} reduction was shifted to the higher values for the impregnated materials. The effect was explained by the deeper penetration of the catalyst's channels with KCl and stronger interaction with vanadium species. For all of the analyzed materials vanadium was present in a form of V^{5+}, V^{4+} and V^{3+} species. Thus, all of the procedures of K^+ deposition negatively influenced the redox properties of the catalysts and interrupted the catalytic cycle of SCR. Despite the fact that the K-diffused samples adsorbed more NH_3 than the impregnated one, it exhibited lower catalytic activity. Thus, it was concluded that not NH_3 adsorption capacity but rather the interaction of potassium with vanadium species is the main factor in terms of NO conversion.

The formation of V_2O_5-$K_2S_2O_7$ eutectic as the major reason of deactivation of the catalyst by potassium was confirmed also by Li et al. [91]. The authors poisoned V_2O_5-TiO_2 with KCl by impregnation and obtained 0.02, 0.1, 0.3 molar ratios of K/V. In order to reflect the real conditions of NH_3-SCR, the catalytic tests were carried out in the presence of SO_2 with a long running time of 140 h. It was observed that the precursor of potassium determined the level of chemical deactivation. The results of XPS analysis indicated the formation of V_2O_5-$K_2S_2O_7$ eutectic at K/V ratio of 0.1 and 0.02 and K_2SO_4 for K/V ratio of 0.3. NH_3-TPD and NH_3-TPO experiments confirmed that the presence of V_2O_5-$K_2S_2O_7$ results in lower catalytic activity due to the decreased Brönsted acidity and oxidation ability.

Kong et al. [92] analyzed the effect of different potassium species on the deactivation of V_2O_5-WO_3-TiO_2. In order to elucidate the influence of different precursors on the catalytic behavior, a fresh catalyst containing 1 wt.% or 5 wt.% of V_2O_5 was poisoned with the solutions of K_2SO_4, KCl and KNO_3 (as K_2O precursor) by wet impregnation procedure. The results of the studies indicated that the deactivation rate is determined strongly by the precursor of potassium—the introduction of $SO_4{}^{2-}$ anions was beneficial for the adsorption of NH_3 and behaved as a weak Brönsted acid site. In contrast, despite acidic character of Cl^- it was recognized as inactive in NO conversion. Additionally, when the catalyst was poisoned with KCl the vanadium species reached the highest temperature of reduction and the lowest activity in NH_3-SCR. Deposition of K_2O resulted in the substitution of hydrogen from V–OH species for K^+ and blocking the Brönsted active sites.

The most important assumptions regarding the deactivating effect of potassium on the catalytic properties of V_2O_5-TiO_2 in NH_3-SCR are presented in Table 2.

Table 2. The most important findings on the interaction of potassium with V_2O_5-TiO_2.

No.	Important Assumption	Reference
1	Potassium species adsorb on Brönsted acid sites and block the active centers for NH_3 adsorption	[72]
2	The level of deactivation with potassium species increases linearly with the content of V_2O_5 on the catalyst surface	[74]
3	The presence of potassium species decreases reducibility of V^{5+} species	[82]
4	V_2O_5-$K_2S_2O_7$ is one of the most poisoning K-containing compound for V_2O_5-TiO_2	[89]
5	The level of deactivation of V_2O_5-TiO_2 with potassium depends on K precursor	[90]

5.2. The Effect of Sodium

According to most studies, Na is placed in the second position in terms of harmful influence on the catalyst between potassium and calcium [34,93]. In coal, sodium occurs in the highest amounts in a form of sodium oxide (Na_2O), sodium hydroxide (NaOH), sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) [93] and exhibits a tendency to adsorb competitively with NH_3 on the acid centers of the catalyst. Moreover, it influences the reducibility of the vanadium species and hinders surface dehydrogenation of ammonia which is a key step of NH_3-SCR [89,94].

Du et al. [93] investigated the influence of sodium on V_2O_5-WO_3-TiO_2 by its impregnation with the solutions of NaCl, NaOH and Na_2SO_4. It was found that NaOH is the most severe agent, since less than 15% of NO conversion was obtained for sodium hydroxide-poisoned catalyst in the whole temperature range. It was assigned to the high alkalinity of the poison that removed the majority of acidic sites of the catalyst. On the other hand, NaCl caused negligible deactivation, while the catalytic performance of Na_2SO_4-doped material exhibited the highest catalytic activity. Therefore, not only the alkali metal cation but also the coexistent anion determines the level of the catalyst's deactivation.

Hu et al. [94] investigated the resistance of V_2O_5-WO_3-TiO_2 to poisoning with Na deposited as NaCl and Na_2O. It was found that the level of deactivation depended on the alkali metal loading. When the ratio of Na/V was below 1, the conversion of NO decreased only slightly, while for Na/V above 1 it was significantly lowered. Additionally, the poisoning effect of NaCl was smaller than Na_2O in the temperature range of 200–500 °C. The main reason was assigned to the formation of strongly basic NaOH on the catalyst's surface in the presence of water of the flue gas. Additionally, despite adverse influence of Cl^- on the vanadium catalyst, its coexistence with Na^+ can neutralize the basic character of sodium cations. As a consequence, the total amount of acidic sites detected for NaCl-doped samples was higher than that for Na_2O-poisoned ones. The authors suggested two main reasons for the deactivation with sodium. Firstly, in the presence of sodium, the $O_\alpha/(O_\alpha + O_\beta)$ ratio (where O_α—surface chemisorbed oxygen; O_β— lattice oxygen) significantly decreased, inhibiting the effective oxidation of ammonia in the NH_3-SCR cycle. Secondly, sodium tends to lower the stability and the amount of acidic sites, especially Brönsted centers. It was proposed that the addition of ceria can hinder the negative effect of sodium on V_2O_5-WO_3-TiO_2, due to its capacity to store and release oxygen and form of new Brönsted acid sites. Similar experiments concerning poisoning of the vanadium catalyst with Na_2O were performed by Gao et al. [45]. According to the authors, sodium changes the environment of vanadium species and blocks V–OH acid sites by the formation of V–ONa deposits. Additionally, the results of XPS measurement of the amount of surface active oxygen species were in agreement with that carried out by Hu et al. [94]. Interestingly, in comparison to the K_2O-doped sample, the one with Na_2O exhibited significantly worse catalytic performance, which contradicted the generally established regularity of alkali metal poisoning impact [34,95]. The summary of the most important assumptions about deactivation of V_2O_5-TiO_2 with sodium are presented in Table 3.

Table 3. The most important findings on the interaction of sodium with V_2O_5-TiO_2.

No.	Important Assumption	Reference
1	Sodium species adsorb on Brönsted acid sites and block the active centers for NH_3 adsorption	[91]
2	The level of deactivation of V_2O_5-TiO_2 with sodium depends on Na precursor	[91,92]
3	The presence of sodium decreases NO conversion over V_2O_5-TiO_2 due to the consumption of surface chemisorbed oxygen	[43,92]

5.3. The Effect of Calcium

Calcium is one of the alkali metals commonly present in the low-rank fuels, such as lignite or subbituminous coals used for the generation of electricity in power plants [96,97]. Some studies on the impact of alkali metals on the catalytic performance of V_2O_5-TiO_2 in NH_3-SCR proved that the poisoning effect of calcium is much lower than that of potassium or sodium [62]. The primary studies carried out in 1994 on the influence of calcium oxide on the efficiency of the work of commercial SCR catalyst confirmed that CaO narrows the operating temperature window of V_2O_5-TiO_2 and inhibits the effective conversion of nitrogen oxides [98]. Additionally, the coexistence of Ca and other compounds present in flue gases, such as CO_2, H_2O or SO_2 results in the formation of CaO, $CaSO_4$ or $CaCO_3$ that are hard to remove and tend to accumulate on the catalyst's surface. A few years later, Benson et al. [99] suggested that the main reason of the deactivation of the catalyst with calcium is the blocking of pores of the catalyst and hindering of the diffusion of NO and NH_3 to the active sites. A number of the most recent studies in that field have confirmed that ammonia can be adsorbed on the surface of CaO and dissociate to the–NH_2 intermediates that react with surface oxygen and produce secondary NO [96].

Li et al. [97] investigated the deactivating effect of Ca on the commercial vanadium-based catalyst. The honeycomb V_2O_5-WO_3-TiO_2 was shredded and poisoned with calcium by ultrasonic-assisted equivalent-volume impregnation with $Ca(NO_3)_2$ to obtain the 10 wt.% of calcium loading. According to the results of NH_3-SCR catalytic tests, the activity of the poisoned material decreased to less than 50% in the whole temperature range. Despite the fact that SEM and EDX analysis confirmed the presence of Ca-containing sediments on the catalyst's surface, the lowered catalytic activity was not attributed to the structural or textural changes that occurred. NH_3-TPD experiments demonstrated that the major reason of deactivation was the interaction of CaO with weak and strong acid sites and competitive adsorption of calcium oxide and ammonia. Additionally, the lack of the V=O bond on the FT-IR spectrum of the poisoned sample suggested that the presence of Ca caused transformation of these groups into V–OH species and increase of Brönsted active sites. Hence, considering the mechanism of NH_3-SCR, the presence of calcium can cause disruptions in both acid-basic and redox reactions involved in the catalytic cycle of NH_3-SCR [57,90,100].

For the application of $DeNO_x$ installations on an industrial scale, the influence of calcium-containing compounds, such as CaO, $CaSO_4$ and $CaCO_3$ must be taken into account, especially in coal-fired power plants that emit large amounts of SO_2 and CO_2. Li et al. [96] deactivated the V_2O_5-WO_3-TiO_2 with 2 wt.% of calcium oxide, calcium carbonate and calcium sulfate. The results of NH_3-SCR catalytic tests showed that $CaCO_3$ had the most severe influence on the activity in NO conversion and the declined formation of N_2O. The effect was probably caused by its agglomeration and plugging of the catalyst's pores and channels. On the other hand, the poisoning effect of $CaSO_4$ on the catalytic performance was minor, which was explained by the formation of additional Brönsted acid sites in the catalyst's surface by SO_4^{2-}. The outcomes of the structural analysis suggested that for all of the materials the specific surface area decreased after doping with Ca-containing compounds. Moreover, according to XPS and X-ray diffraction (XRD) results, the surface tungsten species of the catalyst react with calcium and form $CaWO_4$ that leads to poorer dispersion of the promoter and diminishes the activity of the catalyst. Apart from the interaction with the active species of the catalyst, the studies on the surface acidity indicated that the strength and amount of acid sites were the determining factors in the declined catalytic activity. Brönsted as well as Lewis, acid sites were significantly influenced by CaO and $CaCO_3$. According to in situ DRIFTS experiments, for CaO- and $CaCO_3$-doped samples only the remaining Lewis acid sites exhibited activity in the adsorption of NH_3, while for $CaSO_4$-doped sample both the coordinated and protonated ammonia took part in the NH_3-SCR cycle.

The formation of $CaWO_4$ and bulk tungsten species was acknowledged to be one of the main reasons of V_2O_5-WO_3-TiO_2 deactivation with Ca. Li et al. [101] poisoned V_2O_5-WO_3-TiO_2 with $Ca(OH)_2$ in order to obtain 4 wt.% of CaO and obtained the maximum conversion of NO below 25% at 450 °C. XRD and Raman spectroscopy analysis of the poisoned material showed that a significant amount of $CaWO_4$ and aggregated CaO species were formed on the catalyst's surface. On the basis of H_2-TPR studies, it was concluded that these deposits were the main reason of the increased temperature of reduction of V^{5+} to V^{4+} and W^{6+} to W^{4+}. Due to that, the completion of catalytic cycle of SCR was suppressed. Additionally, it was suggested that the addition of CaO leads to the irreversible changes in the interaction between vanadium and tungsten and in the ratio of W=O/V=O. As the latter one is crucial for the effective adsorption and activation of NH_3 in the initial step of NH_3-SCR, the changes lead to disruption of the catalytic cycle.

More detailed understanding of the deactivating effect of calcium-containing deposits on V_2O_5-TiO_2 can be provided by the analysis of the interaction between CaO with ammonia and nitrogen oxide. As it was already emphasized, one of the key steps of NH_3-SCR cycle is the abstraction of hydrogen from NH_4^+ ions or coordinated NH_3 molecules attached to the acidic sites, so called "activation of ammonia." Yang et al. [102] found that calcium oxide activates ammonia to the–NH surface species, while calcium sulfate promotes the formation of–NH_2 form. Additionally, the presence of SO_4^{2-} was confirmed to increase the amount of surface chemisorbed oxygen, resulting in the formation of NO and N_2O due to the oxidation of ammonia. Correlating the findings with the mechanism of NH_3-SCR, it can be assumed that even though SO_4^{2-} supplies the catalyst with the additional Brönsted sites, its presence can lead to undesired reactions, formation of side-products and consumption of the reducing agent for NO abatement. The essential findings on the interaction of calcium with the surface of V_2O_5-TiO_2 during NH_3-SCR reaction are summarized in Table 4.

Table 4. The most important findings on the interaction of calcium with V_2O_5-TiO_2.

No.	Important Assumption	Reference
1	CaO narrows the operating temperature window of V_2O_5-TiO_2	[96]
2	NH_3 tends to adsorb on CaO which accelerates its oxidation to NO	[94]
3	The presence of $CaCO_3$ declines the strength and amount of acid active sites of V_2O_5-TiO_2	[94]
4	The presence of Ca^{2+} species decreases reducibility of V^{5+} species	[99]
	The presence of Ca species leads to the consumption of tungsten species due to the formation of agglomerated bulk $CaWO_4$	[99]

6. The Effect of Heavy Metals and Heavy Metal Oxides

6.1. The Effect of Lead Oxide

The presence of lead (Pb) is more common in the outgases emitted by municipal solid waste incinerators than those produced by the combustion of fossil fuel [71]. The average concentration of lead in the particulate matter from the majority of waste incinerators is up to 30 mg g^{-1}, while before the electrostatic precipitator it reaches about 6–40 $mg \cdot g^{-3}$ [103]. Therefore, the amount of lead can vary and is strictly dependent on the place in the combustion installation, the conditions and the form of the catalyst. The speciation of the form of lead present on the poisoned catalysts depends on many factors, including the temperature, amount of moisture in the combustion chamber or the level of alkali metals in fly ash. It was suggested that the combined low content of Na and H_2O and low temperature of the flue gases promote the interaction of Pb and Cl and result in the formation of $PbCl_2$ deposits [103].

In 1990, Chen et al. [83] reported that the deactivating effect of lead oxide on V_2O_5-WO_3-TiO_2 can be compared to that caused by K_2O or Na_2O but it is considerably weaker than in case of Rb_2O and Cs_2O. Further studies on the poisoning with lead confirmed that the type of lead-containing deposits on the catalyst's surface is determined by the temperature of the process and parameters of the incinerator or furnace [104]. A year later, Khodayari et al. [105] continued the research into Pb poisoning of the catalyst. The crushed and monolithic vanadium SCR catalyst was covered with 0.19 wt.% of Pb and the authors analyzed its efficiency in NO conversion. It was observed that the catalytic activity decreased by 12% for the crushed samples and only by 1% for the monolithic material at 340 °C. Thus, the form of the catalyst definitely determines its interaction with lead-containing deposits. The main reason of deactivation with lead is the chemical poisoning that diminishes the strength and quantity of the acidic sites caused by the competitive adsorption of the reactants of NH_3-SCR and Pb.

The up to date research confirmed that the particles of Pb are likely to accumulate on the surface of SCR catalysts and decrease the NH_3 adsorption capacity of the material [106]. Moreover, the formation of PbO changes the redox properties of the active phase and disturbs the catalytic reaction [39,107].

Additionally, the particles of PbO tend to block the catalyst's channels and inhibit the free diffusion of the gas molecules throughout the porous structure of the material [107]. Therefore, the deactivating effect of Pb can be explained by the creation of the barrier between the active sites and the gas phase, in both chemical and physical sense.

The most detailed investigation over the mechanism of V_2O_5-TiO_2 deactivation by lead was carried out by Gao et al. [106]. The authors combined density functional theory studies (DFT) and laboratory experiments in order to elucidate the exact influence of PbO on the catalytic properties and performance in NH_3-SCR. The 1 wt.% V_2O_5-TiO_2 was prepared using impregnation method and doped with Pb by aqueous acetate solution with the same procedure, in order to reach Pb/V molar ratio of 0.5. The outcomes of DFT calculations showed that the introduction of Pb significantly influenced the electronic surface properties (ESP) of the material. The negatively charged zone near the terminal oxygen that plays an important role in the formation of Brönsted acid sites was diminished, indicating lower tendency of the site to be protonated [50]. The calculations were in agreement with the results of NH_3-TPD studies that showed considerable decrease in the surface acidity of the contaminated materials. Basing on the Raman spectroscopy measurements, the phenomenon was explained by the chemical interaction between Pb and V=O acid site. The spectrum of the poisoned sample revealed, that the introduction of lead resulted in the shift of the band of V=O species from 1023 cm^{-1} to 973 cm^{-1}, which indicates the weakening of the bonding. Additionally, the NH_3 desorption curve of the poisoned samples was shifted to lower temperature, confirming that PbO species interacted chemically with the active sites of the catalyst. However, deposition of PbO had no visible impact on the formation of by—products during the catalytic reaction. Therefore, Pb does not catalyze the side reactions, such as NH_3 oxidation.

Jiang et al. [103] investigated the changes that occurred in V_2O_5-TiO_2 under the influence of lead chloride and observed that $PbCl_2$ had a remarkable impact on the acidity and reducibility of the catalyst. The analyzed 1 wt.% V_2O_5-TiO_2 was poisoned with the solutions of $PbCl_2$ of different concentrations, in order to reach the molar ratio of Pb to V of 0.01, 0.05, 0.1 and 1, respectively. The results of NH_3-SCR catalytic tests showed that the activity of the $PbCl_2$-doped samples decreased with the increasing Pb loading only below 350 °C, while no dependency was observed up to 400 °C. The results of XPS analysis showed that the materials doped with $PbCl_2$ exhibited lowered level of vanadium in comparison to the fresh catalyst. The effect was explained by the coverage of the active sites with Pb-containing deposits and making them undetectable by that spectroscopic technique. Furthermore, the molar ratio of V^{4+}/V^{5+} was elevated upon poisoning, pointing to the fact that lead changes the oxidation state of vanadium and decreases reducibility of the catalyst. The impact on the redox features is a key factor that diminishes the catalytic activity, since the adsorbed ammonia was not able to undergo the oxidative dehydrogenation on the V^{5+} site during NH_3-SCR [108]. Additionally, the intensities of O 1s peaks detected for the contaminated samples showed that the electronic beam values were moved to the lower range. It pointed to the strong interaction between Pb and the lattice oxygen of VO_x and blocking of the Brönsted acid sites, similarly as in the case of the interaction of oxygen with potassium [76]. NH_3-TPD results indicated that the increasing amount of $PbCl_2$ introduced onto the catalyst resulted in the minimized NH_3 adsorption capacity, especially in terms of Brönsted acid sites. On the basis of the presented analysis, it can be assumed that the proposed overall poisoning mechanism of V–OH species involves the elimination of the protons from the hydroxyl groups and creation of the bond between the active oxygen and Pb. Therefore, as presented in Figure 3, one atom of lead is capable to poison two active sites of the vanadium catalyst.

Analyzing the evolution of the studies over the influence of lead-containing compounds on V_2O_5-TiO_2 with lead-containing compounds, it can be concluded that the main reason of poisoning is chemical deactivation. Nevertheless, the recent findings provide the extend explanation of the mechanism of Pb-deposits formation and profound analysis of their formation. Nonetheless, due to the fact that it was postulated that lead interacts mainly with Brönsted acid sites that are confirmed to be less active in NH_3-SCR, further analysis of the interaction of Pb-deposits with more stable and active Lewis acid sites are in high demand. Table 5 summarizes the most important findings regarding the influence of lead species on the catalytic performance of V_2O_5-TiO_2 in NH_3-SCR.

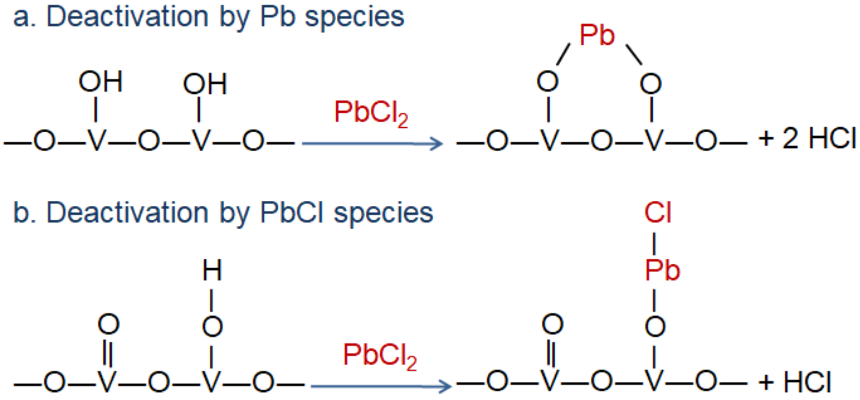

Figure 3. Deactivation mechanism of V-OH species by $PbCl_2$ (based on [103]).

Table 5. The most important findings on the interaction of lead with V_2O_5-TiO_2.

No.	Important Assumption	Reference
1	The presence of Pb species decreases NH_3 adsorption capacity of V_2O_5-TiO_2	[104]
2	Accumulation of PbO particles in the pores hinders free diffusion of the gas mixture through the catalyst channels	[105]
3	The presence of PbO on the catalyst decreases both surface acidity and reducibility of V^{5+} species	[48,101,104]

6.2. The Effect of Arsenic Oxide

Arsenic (As) is one of the most common harmful trace elements that is emitted in a form of vapor-phase as a result of coal combustion. The approximate amount of arsenic compounds in the gas phase of power plants is between 1 $\mu g \cdot m^{-3}$ and 10 $mg \cdot m^{-3}$ and it is usually present in a form of As_2O_3 or a dimer-As_2O_6 [37,38]. The influence of As is not as severe as that of alkali metals and it is less abundant in coal in comparison to them. However, since Na or K are highly mobile and soluble in water as metal salts, applying washing or electrophoresis is usually sufficient to remove them. On the other hand, arsenic compounds can permanently adsorb on the active sites of the catalyst and its regeneration without degradation of the catalytic activity is very difficult. SCR catalyst can be seriously affected by As but the issue of deactivation mechanism is still unsolved. The two most probable suggested reasons are blocking of the active sites by gaseous As_2O_3 (or As_4O_6) or the reaction between As^{5+} and vanadium oxide [109]. It was reported that As_2O_3 molecules are smaller than the pores of the catalyst and can diffuse into the inner surface of the material. The adsorption of these species occurs in the standard SCR temperature (200–370 °C), therefore the deactivation during the catalytic reaction takes place very easily.

The mechanism of arsenic poisoning over V_2O_5-WO_3-TiO_2 was investigated by Kong et al. [109]. As was introduced onto the catalyst's surface by heating arsenic ore in air for 3000 h. The results of XPS analysis showed that both As^{3+} and As^{5+} were present on the surface and the pentavalent species were dominant. These outcomes suggested that the catalyst can be poisoned by arsenic by two mechanisms that involve the formation of As_2O_3 deposits and their further oxidation to As_2O_5 or isolated cations of As^{5+} [110]. Additionally, the poisoning effect was confirmed by the consumption of surface chemisorbed oxygen that plays an important role in the NH_3-SCR mechanism. The results of catalytic tests showed that the introduction of As severely decreased the activity towards NO reduction, since the conversion of only 22% was reached at 400 °C. Lower catalytic activity was explained by the disappearance of the FT-IR peak from V=O bonding, highly significant for the effective reduction of NO. The phenomenon of the diminished amount of V=O was explained by their interaction and further deactivation by As_2O_3. Textural analysis showed that under the influence of arsenic, the total pore volume of the poisoned material decreased in comparison to the fresh catalyst and additionally, the average pore size showed an increase. It was probably the result of the deposition of bulk particles of arsenic oxide on the internal surface of the catalyst. Based on the physicochemical properties of the contaminated material, the authors attempted to explain two pathways of the poisoning with arsenic. They proposed that (1) As_2O_3 is oxidized to As_2O_5 by the oxygen present on the catalyst's surface or (2) oxidation of As_2O_3 to As_2O_5 is promoted by V_2O_5 and as a result the pentavalent vanadium species are reduced to V^{3+}, the latter being inactive in NO conversion. It can be noticed that in both pathways As_2O_5 deactivates the catalyst due to the consumption of active oxygen, which severely interrupts the catalytic cycle of NH_3-SCR. Additionally, in the case of the mechanism (2), the deposition of arsenic pentoxide limits the access of the gas-phase oxygen to the reduced vanadium centers in their trivalent form and hinders the re-oxidation to V^{5+}.

Another deactivation mechanism was proposed by Peng et al. [32]. The authors suggested that the layer of arsenic oxides is transformed to As-OH groups of low activity that contain high amount of active oxygen and act as the weak Brönsted acid centers. Subsequently, the NH_4^+ cation generated upon Eley-Rideal mechanism forms NH_2^- that are oxidized to N_2O during the catalytic reaction, especially above 300 °C. Similarly, the surface-active oxygen of As_2O_5 can react with ammonia and cause its unselective oxidation. Additionally, when the fresh monolithic SCR catalyst was doped with 1.4% of As, the NO conversion at 450 °C was reduced from 85% obtained for the fresh material to 60% for the poisoned one. When the catalytic tests were carried out in the presence of water stream, the deactivation effect was even more severe. The results of H_2-TPR studies showed that As^{5+} cations present on the surface of the poisoned material increased the reducibility of the active sites. Thus, arsenic cations promote the formation of N_2O during the catalytic reaction. The elevated ability to NH_3 oxidation during the process was observed to vary for the catalysts contaminated with As [110]. In case of the samples that contain less than 1 wt.% of arsenic, As^{3+} species are the predominant and appear mainly in the catalyst's channels in bulk form. On the other hand, high concentration of arsenic results in the formation of surface covering pentavalent As^{5+} moieties and only for these materials the contaminated catalysts exhibit the tendency to the formation of N_2O from ammonia oxidation. The effect can be explained by the fact that As^{5+} species formed at high concentration of arsenic generate the monolayer on the catalyst's surface and are ready to adsorb NH_3, acting as weak Brönsted species. In summary, the content and the type of arsenic species does not influence the level of decrease in NO conversion but significantly influences the ability of the catalyst to oxidize ammonia and produce N_2O.All of the proposed pathways of deactivation by arsenic are presented in Figure 4.

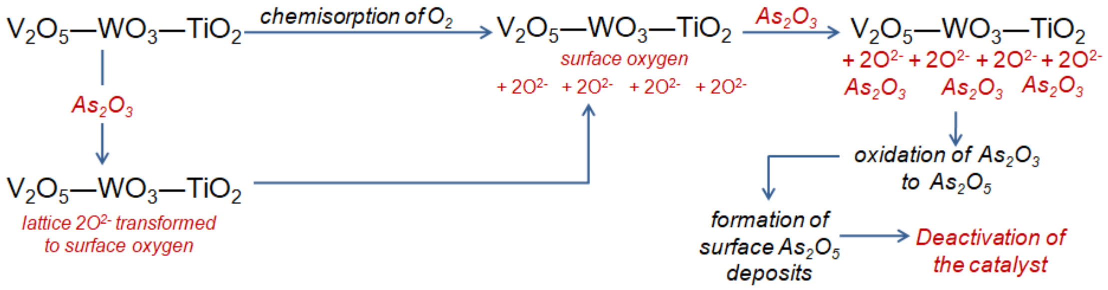

Figure 4. Deactivation of V_2O_5-TiO_2 by arsenic species (scheme based on Reference [32]).

According to the newest studies, As species can deactivate the catalyst in both physical and chemical understanding. Moreover, analyzing the amount of research carried out in that field it can be concluded that the problem of poisoning with As compounds is rather serious and the development of the effective method of the removal of arsenic from the exhaust gas or its removal is needed. The major changes in the catalytic activity of V_2O_5-TiO_2 in NO reduction via NH_3-SCR are presented in Table 6.

Table 6. The most important findings on the interaction of arsenic with V_2O_5-TiO_2.

No.	Important Assumption	Reference
1	As_2O_5 and As^{5+} species cause the deactivation of V_2O_5-TiO_2	[107]
2	Oxidation of As_2O_3 to As_2O_5 on the surface of V_2O_5-TiO_2 leads to the consumption of surface active oxygen and disruption of the catalytic cycle of NH_3-SCR	[108]
3	The presence of As-OH species accelerates the formation of N_2O, decreasing the selectivity of V_2O_5-TiO_2 to N_2	[30,108]

7. The Effect of Halogens

The content of halogens in the flue gas is considered to be an important issue regarding the catalytic activity of V_2O_5-WO_3-TiO_2. Hydrochloric acid can appear in the flue gas due to the combustion of halogenated organics in industrial and municipal wastes. Nevertheless, their effect on the catalytic performance was not widely investigated. It is mainly due to the fact that the operating window of vanadium-based SCR catalyst is 280–400 °C and the remarkable interaction of halogens with the catalyst surface was observed below 300 °C [111]. Despite the acidic character of halogens (HCl or HBr) and generation of the new acid sites on the surface of the catalyst, their presence in the outgases can cause a partial loss of vanadium oxide [112]. Cl^- and Br^- can also interact with the active centers of the catalyst and change their nature and distribution.

In 1990 Chen et al. [83] performed one of the first studies on the influence of chlorides on the catalytic activity of V_2O_5-WO_3-TiO_2 in NH_3-SCR. The authors introduced 12 vol.% of HCl into the stream of the flue gas and observed that the conversion of NO decreased from 98% to 22% after 30 min of the process carried out at 350°C and the increasing temperature accelerated the poisoning impact of HCl. According to the authors, the main reason of the decreased catalytic activity was the formation of NH_4Cl. The effect was especially severe in the temperature range of 300–350 °C due to the fact that 340 °C is the sublimation temperature of ammonium chloride. The negative influence of NH_4Cl was caused by its accumulation on the active surface of the catalyst and blocking of the active sites. Moreover, the interaction of Cl^- with NH_3 resulted in the consumption of the reducing agent and suppressed reduction of NO. Another reason of the decreased catalytic activity was the interaction of chloride anions with vanadium species and formation of volatile vanadium chlorides—VCl_4 and VCl_2 and thus, removal of the active phase from the catalyst's surface.

The formation of vanadium chlorides as the major reason for deactivation of V_2O_5-WO_3-TiO_2 was studied in more detail a few years later by Lisi et al. [113]. The catalyst was poisoned by HCl in a fixed bed reactor by the treatment with 10 vol.% of HCl in He at 300 °C for 12 h. Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) analysis confirmed that the treatment of the material with hydrochloric acid resulted in the decrease of vanadium content from 1.88 wt.% for the fresh sample to 1.07 wt.% for the poisoned one. Therefore, it was assumed that vanadium and chlorine formed VCl_4 and VCl_2 which decreased the number of active sites. Additionally, the tendency to form volatile organic species by the polyvanadate species of the catalyst was higher in comparison to the monovanadate moieties. NH_3-TPD experiments confirmed that chlorine changed the nature of the acid sites of the catalyst, reducing the number of Brönsted centers and leaving Lewis sites unchanged. The summary of the influence of halogens on V_2O_5-TiO_2 is presented in Table 7.

The interaction of halogens with the vanadium-based catalyst of NH_3-SCR was not extensively studied over the recent years which can find its reason in the earlier mentioned difference in the operating temperature window of the catalyst and the remarkable influence on the catalyst below that range. However, due to the poisoning and harmful influence of halogens on the wide range of surfaces, there is a probability that even before the catalytic reaction the active phase of the catalyst is reconstructed which can result in lower activity in NO conversion. Nevertheless, there is still a high demand for new and updated research in that field to confirm that speculations.

Table 7. The most important findings on the interaction of halogens with V_2O_5-TiO_2.

No.	Important Assumption	Reference
1	HCl and HBr tend to cause partial loss of vanadium species from the surface of V_2O_5-TiO_2	[110]
2	HCl reacts with gas-phase NH_3 which leads to the consumption of the reducing agent and the formation of NH_4Cl on the catalyst surface below 340 °C and blocking of the active sites	[81]
3	Consumption of vanadium active species by their interaction with Cl and formation of VCl_2 and VCl_4 that block the active sites of the catalyst	[111]

8. Critical Findings

Concerning the most recent findings of the studies published in the scientific literature in the last 10 years, it can be concluded that the presence of different chemical compounds in the exhaust gas can significantly influence the efficiency of NH_3-SCR installation. In order to present transparently the impact of each discussed contamination on the commercial vanadium-based catalyst, the critical findings were summarized in Table 8.

Table 8. Summary of the contaminations of V_2O_5-TiO_2 NH_3-SCR catalyst and their influence on the catalyst.

No.	Name of the Poison (Chemical Formula)	General Influence on the Catalyst	References
1	Water vapor (H_2O)	Reconstruction of the vanadium sites, competitive adsorption on the acid sites with NH_3 and changing of Brönsted to Lewis sites ratio	[46,47,54]
2	Sulphur dioxide (SO_2)	Oxidation to SO_3 by vanadium species, its interaction with NH_3 and deposition of $(NH_4)_2SO_4$ and NH_4HSO_4 on the catalyst surface	[58,59,62]
3	Alkali metals (K, Na, Ca)	Adsorption on the active sites of the catalyst, formation of metal oxides, blocking of the catalyst pores	[34,44,76]
4	Heavy metal oxides (PbO, As_2O_5)	Accumulation on the active sites and inside the pores of the catalyst, occupation of the active centers and inhibition of the adsorption of NH_3 and NO	[37–39]
5	Halogen compounds (HCl, HBr)	Removal or changing the distribution of the vanadium oxide, reconstruction of monovanadate into polyvanadate species	[111–113]

9. Summary and Conclusions

In summary, the efficiency of the commercial V_2O_5-WO_3-TiO_2 catalyst of NH_3-SCR, can be gradually decreased with time of its utilization. Apart from the physical deactivation, such as high temperature sintering, attrition and loss of the active elements by volatilization, the system can suffer from chemical poisoning. The compounds that most severely affect the catalytic activity are H_2O, SO_2, alkali metals, heavy metals and halogens. Water that is present in exhausts in the form of vapor tends to adsorb on the acid sites and creates a competition for NH_3 to interact with the active centers. The problem of SO_2 is even more complex, due to the ability of V_2O_5-WO_3-TiO_2 to oxidize it to SO_3 that interacts with ammonia and metal cations forming ammonium sulphates/sulphites and metal sulphates/sulphites, respectively. Therefore, pores of the catalyst can be irreversibly plugged and the access of gas molecules to the active sites can be severely limited. The alkali metal compounds, as the common components of the fly ash, the catalytic performance of vanadium-based catalyst as the result of their interaction with V–OH and V=O sites and their poisoning. Among sodium, calcium and potassium, the latter is confirmed to be the most severe in terms of the deactivation effect on the NH_3-SCR catalyst. Also heavy metals, such as lead or arsenic, accumulate on the surface of the catalyst and decrease NH_3 adsorption capacity. Pb can form deposits with the components of the exhausts, such as $PbCl_2$ and block the catalyst's channels, inhibiting the flow of reactants to the active surface, whereas As_2O_3 promotes oxidation of ammonia, simultaneously diminishing selectivity to N_2 and consuming the reducing agent for NO elimination. The combustion products can also contain considerable amounts of halogens. However, the impact of these compounds on V_2O_5-WO_3-TiO_2 remains unclear, due to the insufficient information about their interaction with the catalyst's surface. On one hand, Cl^- and Br^- should enhance the acidic properties due to their chemical character. On the other hand, it was confirmed that chloride anions tend to remove the particles of V_2O_5 from TiO_2, causing a significant loss of the active phase and catalytic activity. In conclusion, there is a number of elements and compounds that can have highly negative impact on the efficient work of vanadium-based SCR catalyst and not only regeneration methods but also the advanced techniques of the abatement of those gases in exhausts are needed.

10. Future Perspective of the Studies over Deactivation of V_2O_5-TiO_2

To date, all of the presented deactivating agents pass for the most severe poisons of V_2O_5-WO_3-$TiO_{2.}$ Thus, in order to minimize the harmful influence of these compounds, a number of methods has been developed. Some of them improve the resistance to poisons and some are focused on recovery of the catalytic system. Nevertheless, since the amount of highly contaminated fuels combusted in power plants and industry gradually increases, more effective poisoning-preventing measures are still in high demand. In fact, some findings published in the scientific literature proposed a couple of methods of the catalyst regeneration or inhibition of the deactivation. However, the most important problem with the utilization of V_2O_5-TiO_2 is related to its placement in the gas purification installation. Therefore, the future perspective of studies should be directed into cost-effective modification of the catalyst composition, in order to extend its temperature window. The research should be focused on the introduction of additional components that will not significantly increase the price of the catalyst and, at the same time, will improve its catalytic performance. Additionally, the components should not catalyze side reactions of NH_3-SCR. If the operating temperature of the FFcatalyst was dilated, the problem of SO_2 oxidation or contamination by alkali-metal containing compounds would be resolved, due to placement of the catalyst after ESP and FGD units. The solution would considerably lower the costs spent on regeneration of the catalytic system and enable to avoid off-times. Additionally, this wide operating temperature window allows to avert additional demand for energy for the re-heating of the flue gas passing through SCR unit placed in "tail end" position. Hence, the future studies should be definitely focused on the activation of V_2O_5-TiO_2 in both low- and high-temperature range of NH_3-SCR with preservation of high selectivity to N_2.

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