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Deactivation of V_2O_5–WO_3/TiO_2 DeNOx Catalyst under Commercial Conditions in Power Production Plant

Maciej Zyrkowski [1,2,*], Monika Motak [1], Bogdan Samojeden [1,*] and Krzysztof Szczepanek [2]

[1] Faculty of Energy and Fuels, AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Kraków, Poland; motakm@agh.edu.pl

[2] PGE Energia Ciepla S.A., ul. Ciepłownicza 1, 31-587 Kraków, Poland; krzysztof.szczepanek@gkpge.pl

* Correspondence: maciej.zyrkowski@agh.edu.pl (M.Z.); bogdan.samojeden@agh.edu.pl (B.S.)

Received: 2 November 2020; Accepted: 23 November 2020; Published: 25 November 2020

Abstract: Nitrogen dioxide is one of the most dangerous air pollutants, because its high concentration in air can be directly harmful to human health. It is also responsible for photochemical smog and acid rains. One of the most commonly used techniques to tackle this problem in large combustion plants is selective catalytic reduction (SCR). Commercial SCR installations are often equipped with a V_2O_5–WO_3/TiO_2 catalyst. In power plants which utilize a solid fuel boiler, catalysts are exposed to unfavorable conditions. In the paper, factors responsible for deactivation of such a catalyst are comprehensively reviewed where different types of deactivation mechanism, like mechanical, chemical or thermal mechanisms, are separately described. The paper presents the impact of sulfur trioxide and ammonia slip on the catalyst deactivation as well as the problem of ammonium bisulfate formation. The latter is one of the crucial factors influencing the loss of catalytic activity. The majority of issues with fast catalyst deactivation occur when the catalyst work in off-design conditions, in particular in too high or too low temperatures.

Keywords: SCR-NH_3; DeNOx; deactivation; power plants; vanadium-based catalyst; ammonium bisulfates; commercial catalyst

1. Introduction

Fossil fuel power plants are subjected to increasingly rigorous NOx emission limits. In Europe there are still plenty of coal-fired power generation units that produce significant amounts of nitrogen oxides. Two major types of NOx removal technology are used in such plants: selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR). As the name suggests, the latter takes advantage of a catalyst. The decision of choosing one over the other comes down to economic and technical aspects. While SNCR technology is much more affordable for power plant operators, it may struggle to deliver the required NOx emission reduction nowadays. The emission limits in current European Union (EU) regulations are 150 mg/Nm^3 for an existing large coal-fired boiler, 180 mg/Nm^3 for a medium-sized boiler and 270 mg/Nm^3 for small ones. For newly built units, limits are respectively 85, 100 and 150 mg/Nm^3 [1]. These limits favor utilization of SCR technology for medium and large existing units, as well as for all newly built ones.

Catalysts are a well-known technology in a variety of industries, and there is still a lot of ongoing research regarding the development of new catalysts and improvement of existing ones. Despite many advantages, catalysts tend to lose their activity over time. Kiełtyka et al. [2] indicated, that in a typical coal-fired power plant with biomass co-firing, V_2O_5–WO_3/TiO_2 commercial catalyst can lose 10% of its

activity already after 2000 h of operation, and 20% after nearly 5000 h. According to Zheng et al. [3], the rate of deactivation of V_2O_5−WO_3/TiO_2 catalyst installed on a straw-fired boiler can be as high as 1% per day of operation. Eventually catalytic layers need to be replaced every 2–3 years (in commercial installations), and new ones are relatively expensive [4,5].

Commercial catalysts installed on coal-fired boilers are subjected to rapidly changing and rather unfavorable conditions. The reactor is usually placed at the end of the boiler second pass (high-dust configuration). There are two main factors that are responsible for SCR catalyst deactivation—flue gas physical parameters and flue gas composition. The former is derived from various process parameters, boiler construction, as well as boiler load. The latter is derived mainly from fuel composition and the combustion process itself. The composition of flue gas is responsible for chemical deactivation of the catalyst (poisoning, plugging) as well as mechanical deactivation (erosion caused by coarse particles). Flue gas physical parameters are responsible for thermal deactivation (sintering due to the high temperature) and mechanical deactivation (uneven flue gases distribution) [5,6]. During the boiler operation, it is feasible to control both factors to a certain extent, depending on the boiler. One of the most commonly used catalysts in the power industry are vanadium-based catalysts, with 1 ÷ 2.5 wt.% of V_2O_5 as an active material, 8 wt.% of WO_3 as a promoter and anatase TiO_2 as a supporter. They can be a plate-type or have the shape of a honeycomb [7]. Vanadium concentration is crucial for the NOx reduction [8], however its high content may cause loss of the selectivity and thermal stability of the catalyst, as well as increased conversion of SO_2 to SO_3 [9–12]. The major drawback of V_2O_5-WO_3/TiO_2 catalyst is its toxicity and the poor stability of vanadium, reduced activity at low temperature (below 250 °C) as well as a relatively narrow temperature window [10,13,14]. However, the catalyst is known for its high activity and resistance to SO_2 [5,15–18]. According to literature, V_2O_5−WO_3/TiO_2 catalysts work best in temperatures 300 ÷ 400 °C [19,20]. Operation at higher temperatures can cause sintering, while operation at lower temperatures may result in catalyst plugging due to ammonium bisulfate formation [21,22].

This paper gives detailed overview of the commercial V_2O_5−WO_3/TiO_2 catalysts used in DeNOx process in industrial boilers, with focus on the mechanisms of its deactivation. The mechanisms of SO_2 oxidation, as well as ammonia slip from SCR reactors, are also described, as they are vital to understand the catalyst deactivation process. Furthermore, the authors describe the effect of boiler operation conditions on the overall catalyst performance.

2. Catalyst Performance

Overall, an SCR catalyst's performance can be simply described by its ability to reduce concentration of NOx from flue gas stream. This is a derivative of the catalyst's activity, which for heterogeneous catalysts can be approximated as the amount of active centers that the catalyst has. Active sites are regions of the solid catalyst, where free (unbalanced) chemical bonds exist allowing the adsorption process. In practice, active centers can be found in all distorted spots of the catalyst's surface, such as cracks, peaks and corners. The higher the surface area of the catalyst the more active centers it may comprise. Active centers can be also easily damaged by a variety of factors [23].

According to Odenbrand et al. and Li et al. catalyst deactivation is a mainly chemical phenomenon [24,25]. The role of active component in the catalyst is to provide sufficient amount of active sites. For the V_2O_5−WO_3/TiO_2 catalyst, most important are V-OH acid sites and V^{5+} = O sites [15,26]. Vanadium oxide content is, therefore, responsible for catalyst activity, and its reduction during the SCR reactor's operation results in activity loss. For the V_2O_5−WO_3/TiO_2 catalyst, the role of WO_3 supporter is also considerable, as it interacts with TiO_2 to enhance electron transfer as well as it helps with NO oxidation to NO_3− and further decomposition of NO_3− to NO_2. This is beneficial for catalyst activity and to widen the temperature window for the reaction [27,28].

The main reactions occurring in SCR installation in the presence of a catalyst, are:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \quad (2)$$

Ammonia reduction over the $V_2O_5{-}WO_3/TiO_2$ catalyst is highly selective, which means the NO is reduced before the O_2. Therefore reactions (1) and (2) proceed at the highest rate. Side reactions occurring in the SCR reactors are the following [29]:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad (3)$$

$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O \quad (4)$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad (5)$$

$$4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O \quad (6)$$

$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \quad (7)$$

Side reactions (4)–(7) are undesired, as they lead to formation of nitrogen oxides (N_2O, NO, NO_2) instead of elementary nitrogen. Most often it is possible to detect some N_2O downstream the SCR reactor, and it is a strong greenhouse gas but it is hard to detect NO or NO_2 in flue gas. However, increased consumption of reagent (particularly when SCR operating temperature exceeds 380 °C) can be an indication of their formation, according to Media et al. [29]. All the above equations indicate the key role of ammonia in the process [30]. To ensure the best performance of the SCR reactor, the proper NH_3/NOx molar ratio is required. The highest NOx reduction efficiency can be achieved for NH_3/NOx molar ratio between 1.0 and 1.1. For a value of NH_3/NOx higher than this, reduction efficiency remains constant but the ammonia slip strongly increases [31]. To start SCR reactions, ammonia must first be activated, which can occur either through Lewis-type interaction or over a Brønsted acidic site, of which the second mechanism is more favorable [32]. According to adsorption theory, a desired reaction is boosted by a catalyst wherever ammonia molecules (in Lewis-type interactions) or ammonia ions (in Brønsted acidic site) can adsorb on the surface [33,34]. Also the presence of sulfates increase Lewis and Brønsted acidity, which is beneficial for NOx reduction capabilities as well as the catalyst lifetime [35,36]. Some authors refer to the catalyst storage capacity as the total amount of NH_3 that can be adsorbed on the catalyst surface [37,38]. Another factor, important from the DeNOx reaction point of view, is a proper contact time between flue gas and the catalyst surface, therefore, too high a flue gas velocity can result in decreased NOx removal efficiency [31].

Referring to the basics of the catalysis process, some more interesting facts can be derived. According to literature, the idea of the catalytic process is to reduce energy of activation required for a given reaction. Without the catalyst (i.e., in the SNCR method), the temperature in DeNOx reactions is equal to about 950 °C [39,40]. For vanadium-based catalysts, maximum efficiency can be achieved in about 350 °C [41]. However, NO conversion decreases from 100% at about 270 ÷ 300 °C to only 20% at about 120 °C [27]. According to Song et al. [42], who tested a $V_2O_5{-}MoO_3/TiO_2$ catalyst, NO conversion can drop significantly also when temperature higher than 350 °C is reached.

In pulverized coal boilers, it is difficult to maintain constant flue gas temperature and distribution. The temperature at which flue gas enters the reactor depends on multiple boiler parameters, such as for instance a coal mills configuration, the amount of air supplied to combustion and to over-fire nozzles, the cleanliness level of heating surfaces, the load of the boiler or feed water inlet temperature. Volatile matter content in coal can also influence flue gas temperature. If there are some regions of the SCR reactor that are exposed to lower flue gas flow, it may lead to faster deactivation of those regions due too. On the other hand, many of the above parameters can be controlled during the boiler operation, which gives room for optimization of SCR working conditions.

Because the catalyst's performance declines over time, it is important to measure its ability to reduce NOx from flue gas by means of an absolute factor. The performance of SCR catalysts, can be expressed as follows [23]:

$$X = 1 - \frac{C_{NO}^{out} + C_{NO2}^{out}}{C_{NO}^{in} + C_{NO2}^{in}} \quad (8)$$

$$\text{Varea} = \frac{V}{A} \quad (9)$$

$$K = -\text{Varea} \ln(1 - X) \quad (10)$$

where:
Varea—area velocity [m^3/m^2h]
A—total surface area of the catalyst [m^2]
V—flue gas volumetric flow through the catalyst [m^3/h]
X, X0—efficiency of the catalyst (used, fresh)
C—concentration of inlet and outlet NO/NO_2
K, K0—catalyst activity coefficient (used, fresh)

By dividing the activity coefficient K of an used catalyst by K0 of a fresh catalyst, overall loss of activity can be calculated for the catalyst. As long as both the fresh and used catalysts are exposed to exactly the same volumetric flue gas flow and have exactly the same total surface area A (not the surface area measured by BET isotherm method), area velocity Varea (Equations (9) and (10)) can be neglected. When a set of catalyst layers is under consideration, K values for each layer should be added to obtain the activity coefficient for a whole installation. Equation (10) can only be applied when NH_3/NOx ratio is between 1.00 and 1.02, while Equation (8) can be used for a general assessment of the catalyst's performance [23].

Most desired improvements that are under research for vanadium-based catalyst are aimed to ensure its appropriate operation in the temperature range 200–250 °C [43]. According to Koebel et al. [44], rate of reaction at temperatures below 300 °C is limited by reoxidation of vanadium sites, which can be partially compensated by introducing NO_2. However, almost all of NOx generated in combustion chamber is in the form of NO [45]. The way to improve a vanadium-based catalyst's performance at lower temperatures is to take advantage of the so-called "fast SCR" reaction. By increasing the fraction of NO_2 before the SCR reactor, which can be done by placing additional oxidation catalyst, the "fast SCR" reaction will occur [44,46]:

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \quad (11)$$

The activity of a vanadium-based catalyst at low temperature can be also improved by doping with elements, such as Co, Ce, Cr, Mo or Ni [47]. According to Li et al. [48], a small addition of silica to the TiO_2 supporter can improve catalyst selectivity towards N_2. Activity of the vanadium-based catalyst can be increased by the addition of CeO_2, done by the impregnation or co-precipitation methods. This allows us to increase activity of the catalyst, widen the temperature window of the reaction, as well as improve resistance to sulfur [49,50].

3. Problem of Ammonia Bisulfate Formation

3.1. Ammonia Slip

In order to abate NO_x emission by employing selective-catalytic reduction methods, the flue gas from a power plant is mixed with liquid ammonia (NH_3) in the presence of catalyst. Ammonia is injected to the flue gas stream at the inlet of the SCR reactor by means of spray nozzles. Typically, not all of the injected ammonia reacts and a part of it is carried over by the flue gas stream and escapes

the SCR reactor. This amount of NH_3 is usually called the ammonia slip [51,52]. As already mentioned, ammonia slip appears when NH_3/NO_x ratio is higher than 1 [31]. There are several reasons why this phenomenon is highly undesired from the power plant operation point of view. Escaped ammonia would react with SO_3 in flue gas, creating sticky ammonium bisulfates that can easily collect dust and plug not only SCR catalysts, but also devices such as rotating air preheaters. Besides the formation of sulfates, ammonia can also adsorb on the fly ash. In particular, adsorption occurs when there is amorphous structure in fly ash particles. Therefore, it is also linked with the combustion process and boiler load, as faster flue gas cooling leads to the presence of amorphous phase in the particles [53–58]. Escaped ammonia may thus affect the quality of fly ash from the power plant—the material that is typically sold on the market. A strong smell of ammonia may hinder fly ash from being utilized, which would generate additional costs for the power plant. It is worth mentioning that total ammonia adsorbed by fly ash depends not only on the level of ammonia slip from SCR reactors, but also on the fly ash structure and composition. An acceptable value of ammonia slip from SCR reactor is in the range of 1–2 ppmv while slip higher than 5 ppmv should be avoided [59]. A typical reason for ammonia slip that is too large are poor ammonia distribution in flue gas, catalyst age and contamination, low flue gas temperature, inlet NO_x level higher than SCR reactor design point as well high flue gas flow.

3.2. Sulfur Trioxide

One of the crucial factors for both boiler and SCR catalysts' operation is the concentration of sulfur trioxide (SO_3). Its presence in the flue gas stream is derived from the SO_2 to SO_3 conversion. There are several factors determining this phenomenon. The most important is sulfur content in coal which is mostly converted to SO_2 in the combustion chamber. Another is oxygen concentration—the more oxygen present in the combustion process, the higher the SO_3 concentrations will be [60]. Most of the SO_3 formation in the combustion chamber takes place at temperatures above 530 °C. A high content of alkaline/earth-alkaline compounds (CaO in particular) would result in lower SO_3 concentration, due to formation of sulfates. These reactions are most likely to happen in the temperature range 300–800 °C. The SO_2/SO_3 conversion is, on the other hand, catalyzed by the presence of iron oxide (Fe_2O_3) in flue gas. This catalytic conversion is most intense at about 600–700 °C (it does vary depending on the Fe_2O_3 particle size) and it has the most significant effect on the final SO_3 concentration in flue gas [60]. Also the presence of alumina, CuO and V_2O_5 results in a higher SO_2/SO_3 conversion rate. Typical conversion upstream of the SCR reactor in a pulverized coal boiler is within the range of 1–2% [55,61–64]. In a coal-fired boiler, all the aforementioned parameters are subjected to dynamic changes. Therefore, SO_3 concentration at the outlet of the combustion chamber may vary significantly and cannot be robustly predicted without a dedicated measurement system [65].

Downstream of the combustion chamber, the concentration of SO_3 in a flue gas further increases when passing the SCR reactor. Next to the ammonia slip, high SO_2/SO_3 conversion is another undesired parameter of the SCR installations. Depending on the catalyst wear and operating conditions, SO_2/SO_3 conversion rate can reach up to 2% for the V_2O_5-WO_3/TiO_2 catalyst. The conversion rate increases with temperature—at the temperature of 400 °C it can be more than twice the value obtained at 300 °C. Also, the SO_2/SO_3 conversion increases proportionally to NH_3 concentration. According to Lu et al. [66], conversion can increase from 1.1% to 2.1% when NH_3 concentration increases from 40 ppm to 140 ppm. Furthermore, the content of TiO_2 and V_2O_5 can significantly affect the conversion. On the other hand, the SO_2/SO_3 conversion in a SCR reactor increases by roughly 30% in the absence of ammonia injection. This occurs because the lack of NH_3 makes the catalyst pores more accessible for SO_2 adsorption and, therefore, contact with TiO_2 and V_2O_5 is increased [55,63,66–68]. According to the results published by Electric Power Research Institute [69], SO_2/SO_3 conversion rate increases also with catalyst age as well as for the regenerated catalysts. The effect of H_2O on the SO_2/SO_3 conversion is not consistent. According to Qing et al. [70], a rise in conversion can be visible for H_2O concentration in a flue gas between 7.5% and 15%, while for higher concentrations a visible drop can be noticed.

Sulfur trioxide is responsible for the formation of sulfuric acid in a flue gas from coal-fired power plants and it participates in ammonium bisulfate formation. The pure form of SO_3 gas exists at the temperature higher than 427 °C. As the temperature drops along the boiler path, SO_3 combines with water vapor forming H_2SO_4. This process ends when temperature reaches about 200 °C, when almost all SO_3—that has not reacted with ammonia in the meantime—is converted to sulfuric acid [67,71]. The latter may condense at temperature below ca. 200 °C [72], which can lead to serious corrosion issues [71].

3.3. Ammonia Bisulfate Formation

Both ammonia slip and sulfur trioxide influence the formation of ammonium bisulfates (ABS), sticky and corrosive substances that block active sites on the catalyst [17,42,73,74]. According to Wang et al. [75], the deposition of 30% wt. NH_4HSO_4 on the catalyst results in a pore volume drop of more than 50% and a significant reduction in BET surface area. When ABS starts depositing, firstly the larger pores are affected and smaller pores remain untouched. If the temperature of flue gas is above the ABS dew point, condensation can still occur inside the catalyst pores. Crucial chemical reactions that describe ABS formation in a coal-fired boiler are [76]:

$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4 \quad (12)$$

$$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4 \quad (13)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad (14)$$

The obvious way to abate issues with ABS is to avoid or decrease its formation. The latter is proportional to the concentration of SO_3, moisture and H_2SO_4 in the flue gas, as well as ammonia slip from SCR reactors. The latter increases when the catalyst activity drops, which indicates the relation between ammonia slip and other mechanisms of deactivation, such as a decrease in Brønsted acid sites for instance. The higher the concentration of NH_3, SO_3 and moisture in flue gas, the higher the temperature of ABS condensation [76,77]. It is important to determine the accurate temperature of ABS condensation, because the temperature of flue gas varies significantly with the boiler load [61]. Knowing the edge temperature allows to operate the boiler in a manner that could prevent ABS condensation. However, there is no consistency in the literature about the temperature of ABS condensation. Furthermore, the temperature of NH_4HSO_4 decomposition on the catalyst surface can be higher due to the specific pore structure. If catalyst pore size decreases below 10 nm, the decomposition temperature increases due to the capillary forces [55,65]. According to Menasha et. al. [77], ABS can precipitate in the temperature range of 262–327 °C, with peak intensity in the range of 284–300 °C. Shi et al. [78] pointed out that the temperature of ABS condensation is in the range of 190–240 °C. It can be concluded that at the temperature below ca. 330 °C, there is a risk of ammonia bisulfate precipitation. Producers, knowing the actual pore structure, can define the minimum safe operating temperature for a catalyst, such as presented in Figure 1 [65]. Power plant operators may consider closing NH_3 injection if the actual temperature of the flue gas is lower than the minimum safe temperature, as operating the SCR reactor below the ABS dew point can be seriously damaging for catalyst activity. Results of laboratory tests show that after 20 h of operation in such conditions, coefficient K/K0 is equal to ca. 0.6 for the first layer and 0.8 for the second layer of the SCR reactor [76,77]. Ammonium bisulfates is also dangerous for devices placed downstream the SCR reactor. In a coal-fired power plant, the rotating air preheater is typically affected due to increased fouling, which is a highly undesirable phenomenon [79].

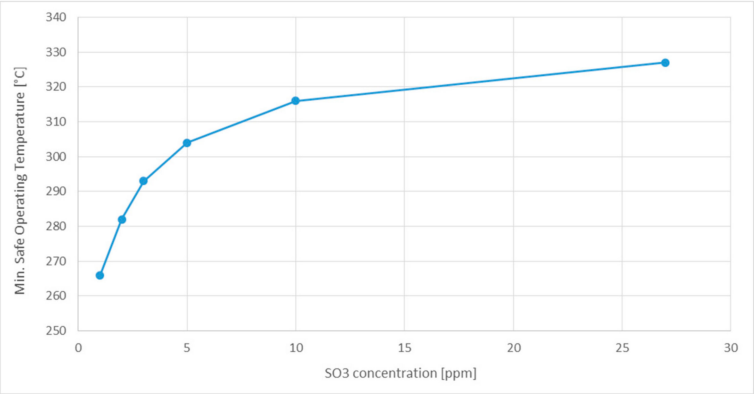

Figure 1. Minimum safe operating temperature for selective catalytic reduction (SCR) reactors as the function of SO_3 concentration, according to Charles [65].

4. Deactivation Mechanisms

Catalyst deactivation phenomena can be divided into three major types—mechanical, chemical and thermal deactivation [6]. As far as chemical deactivation is concerned, it is vital to discuss issues related with catalyst poisoning which, besides already discussed ammonium bisulfates formation, are crucial for the $V_2O_5–WO_3/TiO_2$ catalyst operation.

4.1. Poisoning

Poisoning of the SCR catalyst is mainly associated with alkali metals and sulfur. Also, water present in the flue gas can affect activity of the vanadium-based catalyst as it occupies acidic sites [80]. The concentration of water vapor equal to 8% in a flue gas can decrease activity by roughly 15% after 3 h of operation. If water is removed from the flue gas, however, activity is restored to the initial level [41]. At temperature above 450 °C, however, moisture can enhance NO_x conversion [81]. The V_2O_5-WO_3/TiO_2 catalyst is well known for its resistance to SO_2 poisoning. Despite that, such catalysts are still affected by sulfur dioxide content in the flue gas, particularly when the flue gas temperature drops below 300 °C [82]. Its presence allows compounds to form that are directly responsible for catalyst deactivation or plugging. The role of pure SO_2 is also significant. According to Zang et al. [83], SO_2 adsorption on the catalyst occurs and SO_4^{2-} ions are formed as the result, particularly in the presence of oxygen, and they can occupy active sites of the catalyst. Xiao et al. [84] indicated, that when adding roughly 1000 ppm of pure SO_2 to the flue gas stream, the activity of the catalyst can drop by ca. 20%. The major reason for $V_2O_5–WO_3/TiO_2$ catalyst deactivation is, however, related to interactions with alkali metals present in flue gas. As the temperature required by the $V_2O_5–WO_3/TiO_2$ catalyst is relatively high, the most common position of the SCR installation is upstream of the dust collector (called a high-dust SCR) [2,6,85]. Because of that, the catalyst surface interacts with alkali and earth alkali metals carried out by the flue gas stream. Along with the SO_2, alkali metals can poison the catalyst and, in consequence, reduce its activity. One of the major reasons for that is the neutralization of acid sites. Sodium, calcium and potassium are known to have the most damaging effect on the vanadium-based catalysts [86–91]. Tang et al. [92] confirmed that cations Na^+ and Ca^{2+} can affect the activity of the catalyst, due to neutralization of Brønsted acid sites as well as a decrease of vanadium reducibility. The $CaSO_4$, responsible for plugging the catalyst as well as increased emission of N_2O, is formed when Ca combines with SO_2 and O_2 [89,93–95]. Also the CaO and $CaCO_3$ reduce catalyst activity [95]. Deng et al. studied the effect of NaCl, KCl, Na_2CO_3, K_2CO_3, Na_2SO_4 and K_2SO_4 on the catalyst's performance. In the worst case scenario, the V_2O_5-WO_3/TiO_2 catalyst exposed to the stream of pure KCl and NaCl aerosol for 5 h lost, respectively, about 26% and 16% of its initial efficiency. At low K/V molar ratios (range 0.02–0.1), $K_2S_2O_7$ is formed and it interacts with V_2O_5. The product of this interaction—eutectic V_2O_5-$K_2S_2O_7$—decreases NH_3 adsorption on Brønsted acid

sites [25]. Zheng et al. [95] tested deactivation of a catalyst exposed to a pure KCl and K_2SO_4 stream and concluded that the main reason for deactivation was reaction between poison and Brønsted acid sites. The compounds, such as Na_2CO_3, K_2CO_3, Na_2SO_4 or K_2SO_4, as well as the presence of KCl and NaCl in coal, results in lower, but still clearly noticeable deactivation [6,87]. According to Xiao et al. [84], Na_2O can decrease the number of V^{5+} = 0 bonds as well as the surface oxygen, which affect NO_x conversion. Li et al. [41] compared the loss of V_2O_5–WO_3/TiO_2 catalyst activity due to poisoning by different alkali metals. Tests revealed that the most damaging effect on the catalyst was from NaOH, followed by Na_2O, $Al(OH)_3$ and Al_2O_3. Already 0.5% concentration of NaOH in flue gas is sufficient to decrease catalyst activity by 20% at 400 °C temperature and almost 40% at 350 °C. The presence of SO_2, despite its negative effect in other situations, can abate deactivation caused by K, Na and Ca [2,96]. On top of that, Guo et al. [32] suggested, despite the negative effect of $CaSO_4$, that sulfation can be actually beneficial for the catalyst activity as it increases the number of active Brønsted acid sites. According to Liu et al., the presence of Cl in flue gas can inhibit adsorption of NH_3 and NO_x on the catalyst, which would affect its activity as well [90,97]. Another element that is capable of decreasing catalyst activity is phosphorus [30,98]. Also, arsenic has been reported as a poisonous element for vanadium-based catalyst which, along with the toxicity of vanadium, is the reason why spent catalysts are treated as a hazardous waste [5,99,100].

4.2. Mechanical Deactivation

In coal-fired boilers, flue gas entering the SCR reactors contains a significant amount of particulate matter, such as fly ash particles, cenospheres or unburnt coal particles [57]. They hit the surface of catalysts at some point with a given momentum and can damage the surface, cause surface attrition or result in dust build-up in some areas of the SCR reactors [101]. Mechanical damage of the catalyst's surface, dust accumulation as well as attrition will result in the decrease of activity, affecting the number of available active sites. In an ideal situation, flow through the catalyst's plates should be optimized in such a way that the interaction between flue gas and SCR reactor surface has minimal impact on the catalyst's performance. Besides that, the amount of ammonia injected per unit of flue gas volume should be uniform. In industrial reality, flue gas distribution and velocity are usually uneven, which can affect a catalyst's performance [101–103]. In order to ensure a uniform distribution of flue gas entering the SCR reactor, installations are typically equipped with guide vanes directing the flow [104]. This solution might not be sufficient, however, as the flue gas distribution can pivot between left and right side of the boiler during its operation, so theoretically vanes should be able to dynamically adjust to the inlet flue gas distribution.

4.3. Thermal Deactivation

Thermal deactivation of the catalyst is related to TiO_2 phase transition (or sintering). The TiO_2 most commonly occurs as one of two polymorphs—rutile or anatase. The rutile form is stable, while the anatase is stable only below certain temperature and can undergo irreversible phase transition to rutile. This process is influenced by the temperature at first place, but also particle size and shape, surface area, excess of oxygen or presence of promoters and inhibitors. Temperature of the transition can vary from 400 °C to 1200 °C, although it is mostly expected at roughly 600–750 °C. Elements, such as K, Na, Ni, Li, Fe, Zn, Cu, Cd, Mn and Cr, may act as promoters while elements, such as Ca, Si, P, S, Zr, Al, Ba, B and Ce may act as inhibitors [105–109]. Du et al. [110] pointed out that if the structure of TiO_2 is hollow, it could be possible to avoid phase transition at temperatures below 800 °C. Also, an amorphous carbon coating can prevent transition, by hindering the access of oxygen. One of the roles of tungsten in the V_2O_5–WO_3/TiO_2 catalyst is to reduce phase transition of TiO_2 at high temperature [111,112]. However, according to Khutan et al. [113], temperature of the transition can be decreased by vanadium doping, which might be unfavorable for SCR catalysts containing both anatase TiO_2 and V_2O_5.

Thermal deactivation can result in overall surface area decrease and changes in surface structure resulting in a larger share of NH_3 adsorbed on Lewis-type sites. High temperature can also provoke

vanadium volatilization [14,114–116]. As a result, the activity of the catalyst is affected as well as the temperature window for DeNOx reaction becoming narrower. Besides that, the SO_2/SO_3 conversion increases, which can make the catalyst eventually unusable [117].

5. Industrial Boilers Characteristics

SCR reactors equipped with a V_2O_5-WO_3/TiO_2 catalyst are widely used in the power production sector. A pulverized coal boiler is a good example of SCR application unit with its rather difficult and rapidly changing operation conditions. According to Ma et al. [118], NO_x specific emission from coal-fired units is lower for high capacity units, as well as for units burning bituminous coal. In typical configuration, the standard SCR reactor is placed at the end of the boiler, upstream of the air preheater. It must be designed specifically for each unit in order to locate reactors in the best temperature conditions. There are plenty of issues related to such configuration.

In the coal-fired power plant, temperature variation is a common problem. In the combustion chamber temperature can be as high as 1700–1900 °C and it decreases along the flue gas path [57]. The SCR reactors are typically installed close to the boiler outlet or the economizer (water heater). The temperature of flue gas entering the reactor depends on a variety of factors. The first is the combustion process itself, where the temperature depends mainly on the amount of air (oxygen) in the process as well as volatile matter content in coal [119]. The temperature of flue gas leaving the combustion chamber will depend on the firing system configuration and whether there is air staging or auxiliary air supply. Afterwards, flue gases are cooled down by means of heat exchangers (superheaters, economizers) along their pathway. If heating surfaces in the boiler are contaminated, temperature of the flue gas downstream of a given heat exchanger will be higher due to reduced heat transfer. Temperature in the combustion chamber may also fluctuate rapidly due to the difference in fuel properties, as coal fed to the boiler does not have a consistent composition most of the time. Any temperature fluctuation in the combustion chamber is going to propagate and probably affect the temperature of flue gas before the SCR reactors. Another factor that may influence this parameter is steam—its flow and temperature in the boiler, as well as cooling water injection level. Finally, the load changes. Depending on the boiler construction, the load level can decrease to about 40%. In older constructions equipped with a drum, this is usually 60%. The decreased load also results in lower flue gas temperature entering the SCR reactor [61]. Figure 2 presents a correlation between flue gas temperature, measured in the second pass of the boiler, and the load level for a medium-size, 120 kg/s nominal steam capacity, pulverized coal-fired boiler (hard coal). As can be seen, maximum flue gas temperature variation is equal to about 41 °C. Taking this into account, it can be concluded that the operation of the SCR reactor within optimal temperature range in coal-fired boilers can be difficult to achieve.

Moreover, in coal-fired boilers it is not easy to maintain an even flue gas distribution in the cross-section of the duct. It is a common knowledge that most of the time, the parameters of the flue gas in the boiler are offset to the right or left side, and hardly ever are they distributed evenly. This depends on the burners' configuration (tangential or front wall), as well as appropriate pulverized coal and air distribution in each of the burner and auxiliary air nozzles. The flue gas distribution can also depend on the cleanliness of the boiler heating surfaces. For instance, an intense dust built up on the one side of superheater causes additional pressure drop and thus disturbs the flue gas distribution downstream of this superheater [120]. It is also difficult to control the flue gas distribution during boiler operation and it is often impossible to obtain real-time information about this distribution. Some estimations can be made, however, by taking into account the temperature measurement along the boiler or ID fans' power consumption. CFD (Computational Fluid Dynamics) modelling is often employed to get knowledge about the real flue gas distribution, but it would be rather difficult to have such model working on-line in the power plant (although technically possible).

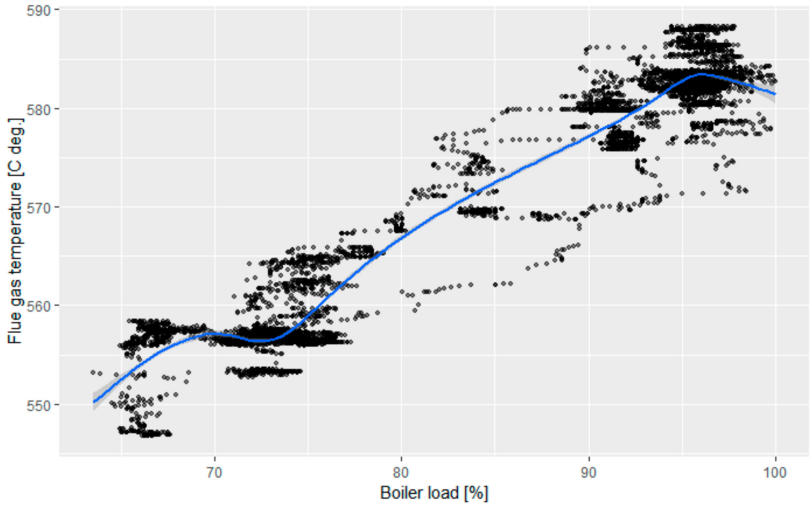

Figure 2. Correlation between flue gas temperature and the load level of pulverized-coal boiler with 120 kg/s nominal steam capacity (own source).

6. Conclusions

In the article, deactivation factors of vanadium-based catalyst for the DeNOx process have been comprehensively reviewed. They can be divided into three major categories: chemical, mechanical and thermal deactivation. As suggested by literature, the main problems influencing the operation of SCR reactors are the formation of SO_3 and ammonia slip. Both have a crucial effect on the formation of ammonium bisulfates, which is one of the most undesired side-products of DeNOx processes in coal-fired power plants. Ammonia bisulfate is a sticky substance, capable of clogging the surface of the catalyst as well as other equipment downstream of the SCR reactor. It is also responsible for a vast share of chemical deactivation of the catalyst, next to the poisoning arising from the presence of alkali and earth alkali metals in flue gas. The role of sulfur is ambiguous. On the one hand, it contributes to the ammonia bisulfate formation, but on the other hand, sulfation can increase the number of active Brønsted acid sites which is beneficial for catalyst activity. The latter can be also decreased by operating the SCR reactor at too high or low temperatures. Above 400 °C there is a risk of TiO_2 phase transition, while below 300 °C activity drops due to reaction kinetics as well as the effect of sulfur, alkali metals and ammonium bisulfates. A commercial SCR reactor installed on a pulverized coal boiler, is subjected to rapid and vast flue gas temperature fluctuations. Also, uneven flue gas distribution can result in a significant temperature difference along the reactor cross-section. Besides that, uneven flue gas distribution is responsible for faster deactivation of some parts of the catalysts due to attrition or dust build-up.

Author Contributions: Conceptualization, M.M. and B.S.; methodology, M.Z.; formal analysis, M.Z.; investigation, M.Z.; resources, M.Z.; data curation, M.Z.; writing—original draft preparation, M.Z. and B.S.; writing—review and editing, B.S and K.S.; visualization, M.Z.; supervision, M.M. and K.S.; project administration, M.M.; funding acquisition, M.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was founded by the grant of the Ministry of Science and Higher Education no. 0039/DW/2018/02.

Conflicts of Interest: The authors declare no conflict of interest.

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