

Selective catalytic reduction for NO_x abatement: a review of the technology and modeling approaches

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Abstract: To address the problems of NO_x emission from stationary sources and comply with ever stringent emission limits, operating and new boilers are being retrofitted with selective non-catalytic and/or catalytic reduction (SNCR and SCR) methods, often in addition to primary measures. Common, well-optimized SCR reactor designs usually yield much higher NO_x reduction rates compared to other technologies, but at the cost of additional power consumption for unit operation. In addition to the SCR configurations, the catalysts used in power plant SCR reactors are discussed in the paper, together with the chemistry behind the SCR process. The selection of catalyst and the design of honeycomb structure highly depends on the local conditions, mainly the operating temperature, particulate matter, and the concentration of the other chemical compounds found in flue gas, such as the SO₂ which may cause problems with catalyst poisoning. The chemistry within the SCR systems consists of selective catalytic reduction reactions, which should be optimized to have high reaction rates. These reactions occur at the catalyst wall surfaces. However, undesirable reactions, such as conversion of ammonia and NO to N₂O can be also expected. Reactions of non-selective ammonia oxidation into the N₂, NO, and N₂O in the presence of O₂ at high temperatures occur, as well. The modeling approaches such as porous medium model, source-in-cell model, and density functional theory are also reviewed and explained regarding their application to problems in SCR reactor.

Key words: selective catalytic reduction, SCR reactor design, catalyst, reactions, modeling, review

1. INTRODUCTION

The emission of gasses from stationary sources, among which are NO_x (nitrogen oxides), is identified as the one of major sources contributing to environmental pollution, and as such is identified and regulated globally through strict national and international legislatives mandating allowed emission levels from individual sources, all in effort to alleviate some of the environmental concerns and reduce

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the impact. In Europe this is done through the Directive 2010/75/EU, which gives referent emission levels which must be met, depending on the age of individual large combustion plant. BAT [1] document is the report on best available technologies, and it is updated regularly with newest information when necessary. From the current revision of this document, it can be found that lignite combustion should be conducted at sufficiently low temperatures with primary measures applied to achieve 200 mg/Nm^3 , should this not be possible, the plant must be further retrofitted with SNCR and/or SCR to fully comply with the emission limits from the Directive 2010/75/EU. With this in mind, continuous efforts are made to provide better technologies for pollutant gasses reduction, especially NO_x , through the application of different primary and secondary measures.

While the some of the NO_x technologies are based on fuel treatment prior to the combustion process, they are not commonly found on the full-scale utility boilers. Majority of technologies in use focus on treatment of flue gas during and/or after various stages of the combustion process. They can be classified as the primary measures [2], influencing and modifying the combustion process, and the secondary measures, focusing at the flue gas treatment during various post-combustion stages. Gholami et al. [3] refer to the latter as the post-combustion NO_x removal technologies, and classify them according to the applied NO_x control method. From their classification, the selective catalytic reduction, selective non-catalytic reduction, and wet scrubbing are the technologies most commonly found on large scale utility boilers, as they are robust and reliable over longer periods of time, while the technologies such as electron beam, adsorption, electrochemical method and non-thermal plasma are not commonly found on full-scale utility boilers, and are more likely to be found on smaller scale research and experimental plants, as they are promising evolving technologies, but still in early development stages.

Different emission control options for NO_x were considered by Srivastava et al. [2] over the range of coal-fired utility boilers located in the US, reporting the efficiency for primary measures below the 65% at the time of research, of which most commonly used low NO_x burners and air staging/overfire air, with their improved variations aimed towards higher process efficiency. The secondary measures they considered include reburning, SNCR, and SCR. Depending on the applied technology, or their combination, the reported NO_x reduction efficiency varied significantly, with highest achieved being around 92% with SCR. Further considerations in their paper cover emerging NO_x technologies, such as layered NO_x control for cyclone boilers, applicable to a relatively small group of boilers with specific combustion organization, oxygen enhanced combustion intended to provide some cost savings compared to the SCR, refinements intended for Low- NO_x tangentially fired systems in general, and the preheat combustion systems, targeting precursors of NO_x before it can be formed, as well as the newly built or proof of concept modern multipollutant control technologies at different stages of market readiness.

Considering the SCR technologies Gholami et al. [3] separate them into the groups based on the reactant used, as NH_3 -, H_2 -, HC -, and CO -selective catalytic reduction. They identify major advantages of SCR as the highly efficient systems with low operating cost and relatively simple installation, with disadvantages being high catalyst cost and its limited lifespan, ammonia slip, large amount of generated waste, and high equipment costs.

From the catalyst side catalysts with different active component and carrier can be found in use, depending on their properties and behavior under different conditions that may occur. Thus, the catalysts used on power plants may or may not perform well if applied to automotive industry and vice versa, due to different gas temperature ranges, and other problems that may appear. Most commonly the V_2O_5 - TiO_2 catalyst or some modified form of it is used on the power plants, due to its reactivity at temperatures often found in boiler before the air preheater. However, due to high wear of honeycomb, and problems caused by the ash, there is an idea to place the SCR system after the air preheater and probably the filters, in order to prolong the lifespan of catalyst. This leads to a use of different catalyst, more suitable to new temperatures range and local conditions. The Mn-based catalysts for this application are reviewed by the Lee and Bai [4], providing the detailed insight into their applicability with analysis of different supports and doping metals effects. Mohan et al. [5] review the behavior of copper zeolite catalyst in NH_3 -SCR system as a low temperature catalyst.

Considering the performance of SCR catalyst, especially under the conditions that are likely to occur on a full scale plant, Benson et al. [6] analyzed the pressure drop over time for several catalyst honeycomb configurations, as well as the deposit characteristics.

To better understand the SCR, in a form of hybrid SNCR-SCR system, Nguyen et al. [7] use CFD simulations of entire process, with SCR part based on a V_2O_5 - WO_3 / TiO_2 catalyst in form of the honeycomb monolith combined. Their numerical research is based on an experimental pilot scale reactor.

The efficiency of the catalyst utilization highly depends on the flue gas and ammonia distribution. With this in mind Liu et al. [8] conducted a numerical case study of several SCR gas distribution strategies, in order to provide as uniform as possible flow through the honeycomb.

Effectiveness of selective catalytic reduction is highly influenced by the catalyst preparation and synthesis procedures. Thus, He et al. [9] conducted an experiment focusing on investigation of several synthesis procedures for preparation of supported WO_3 / TiO_2 catalyst. Their work shown the influence of catalyst synthesis method on the SCR process.

2. SCR DESIGNS AND CONFIGURATIONS

Schreifels et al. group SCR reactors in the three typical, distinctive configurations [10], based on their position within the boiler system as the whole are commonly used on newer power plants. The

difference between them, considering the SCR reactor, is in the inlet gas temperature, flue gas composition, and the amount of particulate matter. In this respect we distinguish **the high dust configuration**, where the SCR system is placed before the air preheater (Figure 1). This configuration has highest particulate matter concentration as the ESP in such configuration is installed after the air preheater. Such positioning of SCR leads to intensive abrasion of materials and special care must be taken into account at design and materials selection stage.

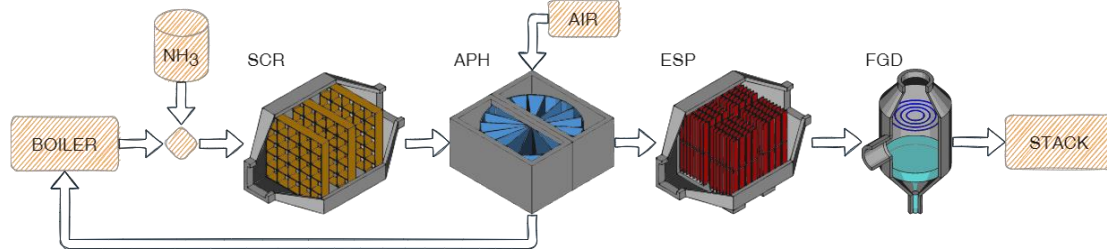


Figure 1. The high dust configuration (the SCR reactor is positioned before the ESP filter)

More beneficial configuration, considering the particles presence, is **the low dust configuration**, since the hot-side ESP is installed before the SCR (Figure 2). In such configuration no significant temperature drops should be expected, thus no gas reheating should be necessary. In both of these cases sulfur oxides are not treated prior to entering the SCR reactor and may lead to catalyst poisoning in certain catalysts, depending on their resistance [4, 11], unless the FSI is used to control SO_2 content in the furnace during the combustion [12]. Other components, such as alkali and heavy metals in the flue gas may also react chemically with catalyst [13], but their presence in the flue gas is significantly lower, if present at all.

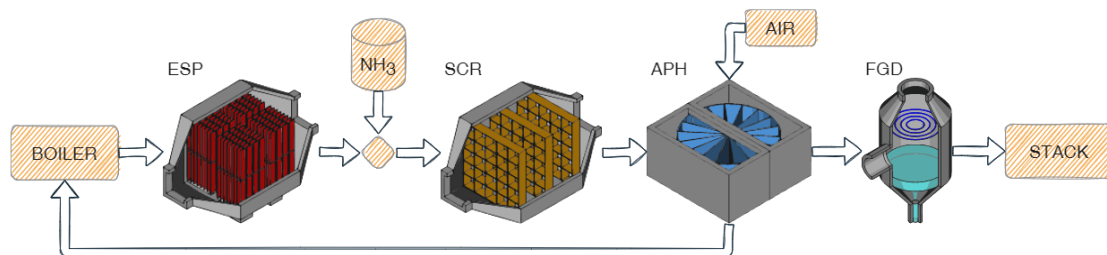


Figure 2. The low dust configuration (the ESP filter is positioned before the SCR reactor)

Tail end configuration is the name commonly used for SCR reactors positioned further down the gas stream, behind the air preheater and FGD system (Figure 3). Benefit of such organization is that most of the sulfur from the flue gas is removed in the FGD, and the problems with sulfur poisoning that may occur in some catalysts, are virtually removed. This configuration, in wet bottomed boilers is used to prevent arsenic poisoning of the catalyst. However, the problems arising from this placement of the reactor may be the low flue gas temperatures, leading to a necessity to

reheat the flue gas, in order to provide stable and efficient operation, and/or consider the use of different catalysts that may provide more efficient process reactions at given temperatures.

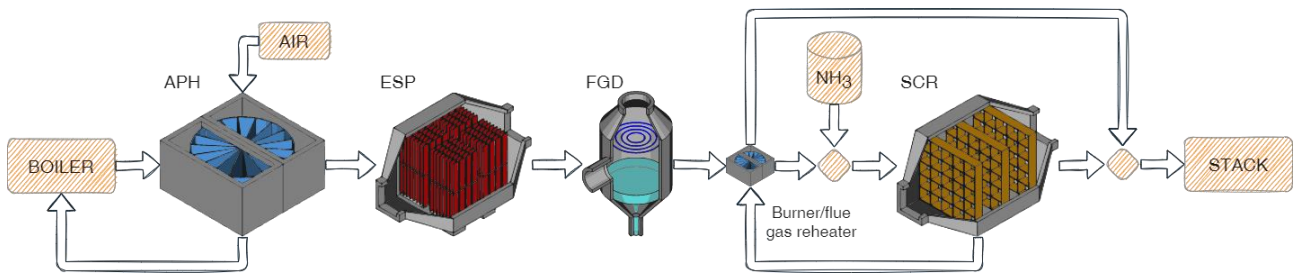


Figure 3. The tail end configuration (The SCR reactor is positioned after the FGD reactor)

2. CATALYSTS COMMONLY USED ON POWER PLANTS

Depending on the catalyst working conditions – the local temperatures and flue gas composition, different catalysts and supports are used, to provide best NO_x reduction, maintain high reaction rates for long periods, and resist local wear caused by the particles.

Based on these differences we can noticeably distinguish catalysts used for power plant boilers and those better suited for internal combustion engines. The $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ is most commonly used to treat flue gas from large scale boilers [14, 15]. Temperatures range, depending on the boiler design, in this section is around 300°C , and this catalyst is well suited for the application in high dust and low dust configurations. The honeycomb support [16] or parallel plates [6] are used for structure to provide good mechanical properties, low pressure drops and avoid problems with particles deposition and plugging. Considering the tail end configurations, the different catalyst should be used, as the gas temperatures are significantly lower. Another problem is the catalyst poisoning, i.e., and it should be addressed by appropriate catalyst selection. In order to partially alleviate the problems commonly found in high and low dust configurations, some authors opt for Mn-based catalysts, most commonly used in tail end SCR configurations [4, 17, 18]. Depending on the catalyst and the preparation method the performance and the range of temperatures can vary greatly. Gao et al. [18] gave comparative review of Mn-based catalysts, from which it can be seen that MnO_x as catalyst can operate in temperatures range $75 - 175^\circ\text{C}$, while the Mn-Ce-O_x is more suitable in the range $100\text{-}150^\circ\text{C}$. In this list is also the Mn/ZSM-5 which can withstand temperatures up to the 390°C . All of these catalysts have near 100% NO_x conversion rate.

The treatment of internal combustion engine flue gas introduces new and somewhat different challenges that can differ significantly from those on power plants, as these engines can sometimes produce hot gasses exceeding 500°C , and because of that, and different fuels used introduce new problems to tackle. Thus, catalyst that are stable at those temperatures, and not prone to excessive poisoning should be used. Kim et al. [19] propose the use of novel catalysts such as CeVO_4 , ErVO_4 and TbVO_4 , to alleviate the problems of the commercial Vanadium based catalysts. Given the wide

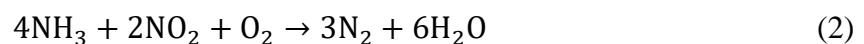
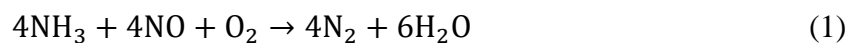
range of temperatures, the selectivity of these catalysts was analyzed in their paper. They also discuss the problems of TiO₂ support at high temperatures. While these catalysts are viable solution for internal combustion engine products, their use in power plants may prove difficult or not possible at all, due to operating conditions and different chemical compounds found in combustion products.

3. CHEMISTRY BEHIND THE NO_x REMOVAL FROM FLUE GAS

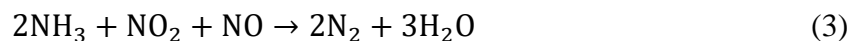
Understanding of underlying chemical reaction is necessary to be able to better understand the SCR process itself. While there are major similarities and agreement among the different authors about the chemical reactions that are used to describe the processes, some differences can be found in models. Here we try to summarize the most common models and approaches to SCR.

3.1. Expected catalytic chemical reactions

Conversion of NO and NO₂ to N₂ is done on the surface of the catalyst. To allow for SCR reactions to occur an NH₃ or another reactant should be added to the flue gas. In the case of NH₃ addition the stoichiometric SCR reactions are [2, 4, 14]:

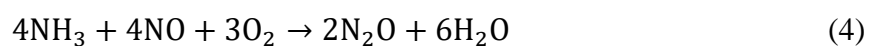


Lee and Bai [4], and Schreifels et al. [10] add the third reaction where NH₃ reacts with NO and NO₂ at the same time to form N₂ and H₂O, without the presence of the O₂:



Chen et al. [11] model the reactions of NO and NO₂ with NH₃ as two separate reactions, each producing N₂ and H₂O without the presence of O₂. To simplify the model, some authors add NO₂ contents to the NO and use only the first equation in their reactions model [14]. This is also the case in work of Koebel and Elsner [20] who also use single reaction for the SCR, mainly due to the fact that flue gas consists mostly of NO. However, they do notice that second reaction for NO₂ should be used if its content becomes significant. This simplification is justified, as the NO is predominant nitrogen oxide in power plant flue gas, contributing over 90% to all nitrogen oxides formed [3, 10].

At lower temperatures the SCR reaction also produces N₂O concurrently on catalyst surfaces [14], and even though its presence is low, recently there is interest to follow and analyze the production, mostly due to its global warming potential [14], as it belongs to a group of GHG (Green House Gasses) [21].

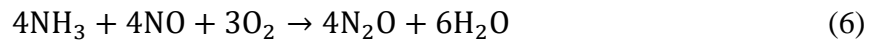
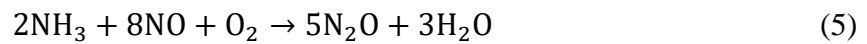


While the N₂O is mostly understood to form in the presence of NH₃, following the above reaction, Yates et al. [22] offer different scheme, under the assumption that N₂O is formed from two NO molecules, without the NH₃ involvement in the process during the reaction with polymeric

vanadyl species. To avoid significant N₂O production the selectiveness of individual catalysts is carefully considered at expected temperature operation ranges.

3.2. Undesirable side reactions that occur during catalytic NO_x reduction

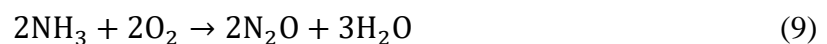
Aside from the reduction of NO_x to N₂ and water, the nitrogen oxides can react with NH₃ to form N₂O instead [4], which is undesirable, as previously mentioned:



This is an unselective behavior, which occurs when the molar ratio of NO and NH₃ is lower than 1.

3.3. Non-selective ammonia oxidation

The non-selective ammonia oxidation appears over non-selective sites with certain catalyst structures, such is the Co₃O₄ in Mn based catalysts [4, 17]:



The intensity of above reactions highly depends on the catalyst used and local temperatures. In the NH₃-SCR it may lead to an imbalance in molar ratio of NO and NH₃, thus decreasing the conversion of NO. It is important to predict the rate of these reactions, in order to provide the needed NH₃.

3.3. Selective non-catalytic reduction

The selective non-catalytic reaction of nitrogen oxides with NH₃ at higher temperatures leads to the formation of N₂ and H₂O steam, following the 4NH₃ + 4NO + O₂ → 4N₂ + 6H₂O mechanism [2], which is similar to the SCR reactions, but occurs at higher temperatures, without need for catalyst. Srivastava et al. also notice that this SNCR reaction can contribute to the overall SCR efficiency when the NH₃ is injected at higher flue gas temperatures. Other authors experiment with hybrid SNCR-SCR systems as well, to achieve optimal emissions [7].

4. MODELLING APPROACHES TO THE SCR REACTIONS

Several different approaches to SCR reactions modelling on the reactive surfaces can be found in the literature. The complexity and the amount of information about the process provided by them varies, depending on the way they treat reacting surfaces. Kim and Choi researched the different amount of Vanadium oxide loading and its effects on catalyst selectivity towards N₂ and N₂O over the range of temperatures [23]. With proper catalyst structure N₂O formation can be significantly suppressed, and this was researched by the Lee et al. [24].

To be able to properly select a good model for simulations it is important to understand both the macroscopic and microscopic structure of the catalyst that will be modeled. The catalyst is usually

formed in honeycomb or plate structures on large power plant boilers, while in some other applications it may be put in packed bed in form of spherical granules, or some other suitable shape. However, the latter is not suitable for use on boilers combusting solid or liquid fuels, as it would prove difficult to operate and maintain. Commonly used models are the porous medium model, source-in-cell model, and density functional theory studies. The choice of the proper model for exact problem is influenced by the needed model accuracy, the data it provides, as well as the catalyst structure, and to a certain point by the available computational resources.

4.1. Porous medium model

Liu et al. [8] use the porous medium model to simulate the flow of gas through the the honeycomb structure of SCR catalyst and rectangular flow rectifiers. In such model all reactions are considered to be volumetric, as the honeycomb and rectifier structures are simulated through the additional pressure drop equation along the SCR reactor. While this model is applicable to all reactor types honeycomb and packed bed alike, it would be expected to give better results for packed bed reactors, as they have less pronounced inlet and outlet velocity profiles.

4.1. Global kinetic model

Roduit et al. [15] investigate the inner structure of the catalyst with corresponding reactions and species concentrations, leading to a very detailed model, that gives significant information both about the NO_x conversion, and the changes in catalyst over the time. Such model is able to simulate catalytic reactions both on surfaces and inside of catalyst structure, depending on local species concentrations. Such complexity of the model, may carry a hefty penalty in computational time if used to simulate full scale reactors.

4.2. Source-in-cell model

The source-in-cell models used in CFD in general provide a good balance between the amount of information they provide, and the computational time. Such models take into account both heterogenous and homogeneous reactions, in order to model reactions both near the wall and further in the fluid volume. Such model can be found in [25] where the authors model heterogenous catalytic reactions as in fluid cells touching the catalyst walls, while the reactions in the rest of fluid volume are homogenous.

4.3. Density functional theory studies

Some authors use the density functional theory to study the reaction mechanism of catalytic denitrification [13, 18]. The studies based on these models focus on geometric optimization, electronic structure, surface characteristics and the related chemical processes. Density functional theory itself is a computational quantum mechanical modelling method commonly used to investigate electronic structure, and is one of more popular approaches in computational chemistry, due to its versatility.

5. CONCLUSION

In this paper we made a short review of technologies and approaches to selective catalytic reduction technologies used for flue gas treatment, with focus on NO_x abatement. Given the flue gas temperatures at the SCR reactor inlet, as well as the presence of particulate matter, an appropriate design of the honeycomb and catalyst must be selected, in order to provide uninterrupted and efficient operation. Good candidates for use on power plant boilers are V and Mn based catalysts, as they provide wide temperature reaction window well matching the local gas temperatures. Another problem to consider is the SO₂ poisoning where newly developed catalysts show great resistance, extending operation times.

Honeycomb support structure is used on power plant boilers, especially if the SCR configuration is such to allow dust passing through the reactor. This prevents physical plugging of the catalyst over longer periods of the time, and provides lower pressure drops.

Considering the overall chemical reactions on catalytic surfaces most authors model NO reactions as it is the predominant nitrogen oxide. Other nitrogen oxides are proportionally added to the NO concentration. The ratio between the NO and NH₃ should be closely monitored, to prevent undesirable reactions that would produce N₂O instead of N₂. Certain catalyst structures also have non-selective behavior.

To model the reactions in a SCR reactor, from the fluid side, probably the more appropriate are the porous medium and source-in-cell models. The latter, is well suited for catalytic surfaces structured as the walls surrounding the fluid containing the reactants. Other models shown, while giving more details about the catalyst itself, have significantly higher computational power demand, especially coupled with CFD.

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