

Secondary Ways of Nitrogen Oxides Reduction

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Abstract : Nitrogen oxides are combustion pollutants that play an important role in many atmospheric processes that affect climate change, ecosystem stability and population health. Their occurrence is highest in industrial and densely populated areas. Nitrogen oxides undergo chemical reactions in the atmosphere, leading to a greenhouse effect and global warming. The paper contains an overview of reactions in which nitrogen oxides are involved in atmosphere, as well as an overview of methods for nitrogen oxides emissions reducing into the environment.

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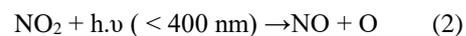
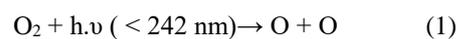
1 Introduction

Nitrogen oxides play an important role in many atmospheric processes with strong implications for ecosystem stability, climate change and public health. Nitrogen oxides are produced in large quantities by combustion, primarily in the form of NO, which is oxidized to NO₂. In a lower atmosphere, nitrogen oxides contribute to the formation of acid rain, as well as to the formation of ozone and aerosol. In addition, nitrogen oxides are toxic at high concentrations. In higher atmospheric layers, nitrogen oxides contribute to the decomposition of the ozone layer [1]. The most important nitrogen oxides are N₂O, NO, NO₂.

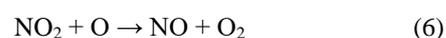
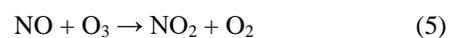
2 Reactions of the Nitrogen Oxides at Atmosphere

Small particles and gases are emitted daily into the atmosphere by industrial activity, internal combustion engines, energy production, building heating, agricultural activity. The monitored gases also include nitrogen oxides. More than 90% of the nitrogen oxides are from internal combustion engines emitted in the form of nitric oxide (NO), which in the stratosphere is oxidized to nitrogen dioxide (NO₂). It has a negative effect on the respiratory tract of living organisms. NO₂

emissions destroy the ozone layer and also represent greenhouse gas causing climate change. Excessive occurrence of NO₂ in the troposphere leads to an undesirable increase in the concentration of tropospheric ozone. The following reactions occurring in the troposphere are sources of ozone [2,3]:



The neutral collision particle (M) balances the energy ratios of the reaction. Increased ozone concentration in the troposphere, causes diseases of the respiratory tract and nervous system. Nitrogen oxides from the flue gases of the supersonic aircraft reach the stratosphere, where N₂O reacts with atomic oxygen to form nitric oxide, which reacts with ozone, thereby contributing to the depletion of the ozone layer in the atmosphere [3].



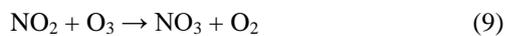
The following equation expresses the resulting reaction.



Nitrogen oxides and volatile organic compounds react in the presence of sunlight to produce photochemical smog, a significant form of air pollution. The presence of photochemical smog increases in summer when the incident solar radiation is higher. Hydrocarbons emitted from industrial activities and transport react with NO_x rapidly and increase the concentration of ozone and peroxide compounds, in particular peroxyacetyl nitrate [4]. Children and people with lung diseases such as asthma, are particularly sensitive to the adverse effects of smog, which causes damage to lung tissue and decreased lung function. Nitrogen dioxide is also involved in the formation of nitric acid and acid rain. NO_2 is oxidized in the gas phase during the day by reaction with a hydroxyl radical.



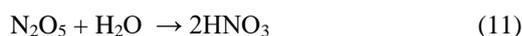
M is the molecule required to stabilize the addition product. Nitric acid (HNO_3) is highly soluble in liquid water in aerosol particles or in clouds [5]. NO_2 also reacts with ozone to form a nitrate radical [5].



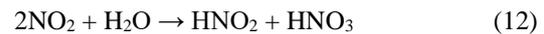
During the day, the NO_3 radical rapidly undergoes photolysis, but at night it can react with the NO_2 molecule to form nitric oxide.



N_2O_5 reacts rapidly with liquid water (in aerosol particles or in cloud drops, but not in the gas phase) to form nitric acid.

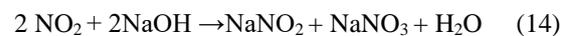
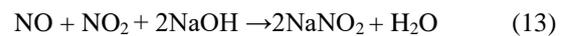


The reaction is considered to be the major route of nitric acid formation in the atmosphere [5]. Nitric acid contributes to acid rain or can be deposited in soil where it generates nitrates which are taken up by plants. The reaction in the aqueous phase is too slow to have any significance in the atmosphere [5].



3 Methods for Reducing Nitrogen Oxides

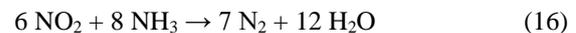
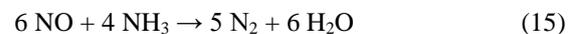
Emission regulations for unburned hydrocarbons, nitrogen oxides and particulate matter are increasingly stricter worldwide. Transport (mobile source) and fuel combustion (stationary source) are the main sources of nitrogen oxide emissions [6]. Power generation, stationary engines, industrial boilers, process heaters and gas turbines are the main stationary sources of NO_x [2]. Several technologies have been applied to reduce nitrogen oxide emissions from both stationary and mobile sources. Methods of reducing nitrogen oxides in flue gases are divided into primary and secondary. The primary measures adjust the combustion process to produce the lowest NO_x content. Secondary measures reduce the already formed NO_x from flue gas. These are divided into wet and dry. Wet methods utilize absorption into solutions. Sodium hydroxide is most commonly used as an absorbent. This process proceeds according to the following reactions:



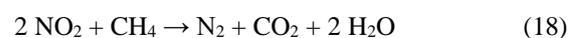
The dry processes include adsorption and reduction methods. The most commonly used techniques for reducing nitrogen oxides are:

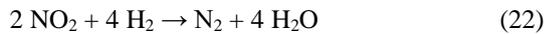
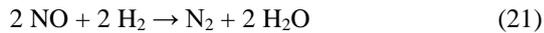
- a) non-catalytic reduction
- b) catalytic reduction
- c) wet cleaning

In the non-catalytic reduction of a mixture of nitrogen oxides and ammonia, nitrous oxide is converted to elemental nitrogen and water vapor at temperature interval $800^\circ\text{C} - 1000^\circ\text{C}$ according to the equations [7]:

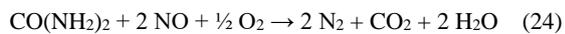
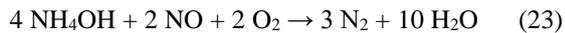


In the catalytic reduction of the mixture of nitrogen oxides with methane, carbon monoxide and hydrogen, the oxides of nitrogen are converted to nitrogen, carbon dioxide and water according to the equations: [7]:

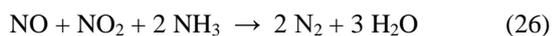




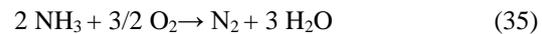
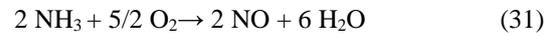
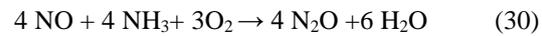
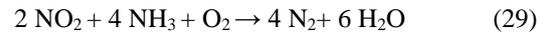
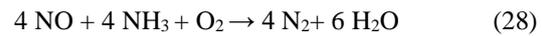
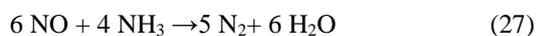
According to literature, SNCR technology is currently the best available technology that meets the required level of environmental protection [2]. Selective reduction is achieved by reaction with aqueous ammonia or urea solution according to the reactions:



he reaction proceeds either at temperatures of about 850°C in the combustion chamber of the boiler without catalyst, but with lower efficiency, or at about 350°C on the surface of the catalyst with high efficiency. Thus, from a chemical point of view, denitrification can be catalytic or non-catalytic. Particular attention is paid to selective catalytic reduction with an emphasis on catalysts for the reduction of NO from stationary sources. The catalyst is needed due to the high activation energy of the direct decomposition reaction. The reducing agent is injected in front of the catalyst, which then gives rise to events which can be described by reactions [2]:



The most commercial devices use a $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst, although there are many devices that use zeolite technology [6]. V_2O_5 levels also play a role in minimizing SO_3 formation [4]. In addition, modifiers such as Mo and W are added to improve the long-term performance of the device [4]. Introducing an additional reductant in the exhaust of combustion process can circumvent the thermodynamic and kinetic difficulties in reducing NO_x . By selectively promoting the reaction of NO_x with a reductant over the reaction of NO_x with O_2 , SCR catalysts can achieve NO_x concentrations that are below the thermodynamic equilibrium concentration [9]. However, the reaction mechanism of selectively reducing NO is complicated and still not well understood because of the many side reactions occurring between different proportions of NO, NH_3 , and O_2 across different temperatures. Set of reactions was observed by Wang et. al. over a Cu-V/ γ - Al_2O_3 catalysts[10].



SCR systems need to be constantly improved in the light of the gradual tightening of emissions regulations. Their performance can be improved by adjusting the various processes that occur in these complex systems. Computational Fluid Dynamics (CFD) provides a cost-effective means to achieve more efficient NO_x conversion by the SCR system. SCR systems usually consist of multiple catalyst layers. The results of the study show a significant effect of the second catalyst layer on the overall performance of the SCR system. The second catalyst layer plays an important role in the reduction of NO_x as well as ammonia [8].

4 Catalyst Processes Utilizing Zeolites

Dry catalyst processes include processes utilizing surface-treated sorbents, for example zeolites after incorporation of metal elements such as Co, Pt, Cu. Various catalytic materials have been investigated, and both the carrier and the catalyst component have been shown to be critical for degradation at a lower operating temperature. These catalysts, such as Co / Beta zeolite, are deposited on a ceramic support and accelerate the reduction of nitrogen oxides to nitrogen. The use of zeolite materials finds application especially in mobile sources. According to recent research, the most effective method appears to be SCR catalyzed by a zeolite catalyst. Superior activity and selectivity of a Cu ion-exchanged SSZ-13 zeolite in the selective catalytic reduction (SCR) of NO_x with NH_3 were observed, in comparison with Cu-beta and Cu-ZSM-5 zeolites. Cu-SSZ-13 was not only more active in the NO_x SCR reaction over the entire temperature range studied (up to 550°C), but also more selective toward nitrogen formation, resulting in significantly lower amounts of NO_x by-products (i.e., NO_2 and N_2O) than the other two zeolites. In addition, Cu-SSZ-13 demonstrated the highest activity and N_2 formation selectivity in the oxidation of NH_3 . The results of this study strongly suggest that Cu-SSZ-13 is a promising candidate as a catalyst for NO_x SCR with great potential in after-treatment systems for either mobile or

stationary sources [11]. More recently, Cu²⁺-exchanged beta zeolite (Cu-beta) has been shown to have excellent activity in the SCR of NO_x with NH₃, and metal-exchanged beta zeolites are generally found to have greater hydrothermal stability than similar ZSM-5 catalysts. In the very recent patent literature, Cu²⁺ ion-exchanged SSZ-13 (Cu-SSZ-13) has been reported to exhibit NO_x conversions of 90–100% over a wide temperature range in the NH₃-SCR process, and its activity exceeded 80% even after extensive high-temperature hydrothermal aging [12]. The SSZ-13 zeolite has chabazite (CHA) structure with a relatively small pore radius (~3.8 Å) in an eight-membered ring [13]. Copper ions were exchanged into the zeolite in an aqueous ion-exchange process [11]. The activity and selectivity of the Cu-SSZ-13 catalyst for both NO_x SCR with NH₃ and NH₃ oxidation are superior to those of both Cu-beta and Cu-ZSM-5. The Cu-SSZ-13 catalyst maintains its high conversion (>90%) up to 500 °C, while the NO_x conversion of Cu-ZSM-5 begins to decline above 300 °C [11]. The order of high-temperature NH₃ SCR reactivity is the inverse of the order in pore size, i.e., SSZ-13 having the smallest pores (~4 Å, 8-membered ring) being the most active, ZSM-5 with medium size pore opening (~5.5 Å, 10-membered ring) having medium activity, and beta with the largest pores (~7 Å and ~5.5 Å, 12-membered ring) having the lowest activity [11]. Under the same reaction conditions for NO_x SCR with NH₃, Cu-SSZ-13 demonstrates superior activity and N₂ formation selectivity in comparison with Cu-beta and Cu-ZSM-5 zeolites [11].

5 Conclusion

Nowadays, as environmental problems are increasingly important, it is particularly important to reduce emissions of gaseous substances that not only harm health but also contribute to the greenhouse effect and global warming. Such gaseous substances also include nitrogen oxides. Therefore, the efforts of scientific teams are constantly improving the equipment for reducing nitrogen oxides. Currently, the best available technology is SNCR technology. The efforts of scientific teams are to improve this technology, but also to introduce new technologies. In particular, the combination of catalytic conversion with sorption is promising. Suitable sorbents are zeolites with incorporated metal cations which influence the reaction of the conversion of nitrogen oxides to nitrogen catalytically. Currently, the combination of SCR technology with zeolites is mainly used in mobile sources.

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