Editorial

Selective Catalytic Reduction of NO$_x$

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The recent diesel scandal made the public aware of the fact that NO$_x$ emissions from combustion processes are a major threat to human health and by no means easy to avoid. The most efficient process to reduce NO$_x$ emissions from lean exhaust gases is selective catalytic reduction (SCR) with ammonia, which has undergone tremendous development over the past few decades. Originally only applied in stationary power plants and industrial installations, SCR systems are now installed also in millions of mobile diesel engines, ranging from off-road machineries, heavy-duty and light-duty trucks, and passenger cars, to locomotives and ships. All these applications involve specific challenges due to tighter emission limits, new internal combustion engine technologies, or alternative fuels. The review articles and original research papers in this edited book contribute to the solution of these challenges with a broad range of innovative ideas, covering many aspects of SCR technology.

One of the bottlenecks of the application of SCR technology in vehicles, and particularly passenger cars, is the threshold temperature of about 200 °C for injection of the urea solution in hot exhaust gas, which is above the exhaust gas temperature for some modes of engine operation. Sala, Bielaczyc, and Brzezanski have addressed this problem by preheating and evaporation of the urea solution before injection into the engine's exhaust gas [1]. The concept was checked at a diesel test rig and significantly improved NO$_x$ reduction efficiencies were observed. A critical factor for the efficiency of SCR systems is the uniformity of the reducing agent distribution across the frontal area of the catalytic converter. To this end, Sala et al. have developed an automated sampling and analysis system to probe the NO$_x$ and NH$_3$ concentration profiles of a passenger car SCR catalytic converter indirectly from the downstream side of the converter [2].

Regarding stationary SCR applications, firing of biomass is a special challenge due to the high concentration of impurities and particularly potassium contained in this type of fuel, deactivating the used vanadia–titania-based catalysts. Schill and Fehrmann reviewed different strategies for SCR systems to cope with the high potassium loading from biomass with a focus on intrinsically potassium-resistant SCR catalysts [3]. Such catalysts can be prepared by coating vanadia–titania systems with thin protective layers of, for example, magnesia or sepiolite, using zeolites as support, replacing tungsta with heteropoly acids, and preparation methods to achieve unusual high surface areas.

Zhao, Mao, and Dong have worked on ways to improve vanadia–titania systems and achieved good low-temperature activity combined with water and sulfur tolerance, when adding manganesia and ceria [4]. The low-temperature SCR activity of this catalyst type can also be enhanced by promotion with heteropolyacids of the Keggin structure, as shown by Wu et al. in their study [5]. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) revealed that addition of the heteropolyacids increased the number of Brønsted and Lewis acid sites, in addition to other beneficial effects. Selectivity to nitrogen is another important property of SCR catalysts. Kim and Young added iron oxide to a vanadia–titania system and observed suppression of N$_2$O formation at high temperatures, which was assigned to the formation of strong V–O–Fe interactions and tetrahedrally coordinated polymeric vanadates [6].

When deactivation cannot be prevented, the regeneration of SCR catalysts is an interesting option. Ye et al. successfully demonstrated that treatment of a deactivated vanadia–titania catalyst in a stationary SCR application with solutions containing a vanadia precursor and oxalic acid as well as a tungsta or molybdena precursor completely reactivated the used catalyst [7].

The combination of NO_x reduction and soot oxidation activity in a single device is particularly attractive for mobile applications, where weight and construction space is limited. Casanova, Colussi, and Trovarelli addressed this topic in their study and showed that when iron vanadates were combined with $CeZrO_2$ as active components on titania support, good SCR activity and soot oxidation activity could be reached with one single material [8].

In the last few years, rare-earth metal oxides have started to emerge as SCR catalysts. Mosrati et al. found remarkable low-temperature activity at excellent nitrogen selectivity over a niobium-modified ceria–titania system [9]. On one side, the introduction of niobium decreased the surface area, but on the other side the surface acidity was strengthened, which was explained by strong ceria–titania interactions and high concentration of highly dispersed niobia.

Manganese-based oxides are in the focus of interest since a few years due to their excellent low-temperature SCR activity at moderate costs. However, this type of catalysts suffers from insufficient nitrogen selectivities and moderate water and sulfur resistance. Gao et al. provided a comprehensive review of the state of knowledge about water and sulfur resistance of manganese-based SCR catalysts and potential solutions to overcome, or at least mitigate this problem [10]. They concluded that, at the current state of development, much research is still required to reach a level where commercial application of manganese-based SCR catalysts comes into sight. The research article of Zhang et al. deals with an economically interesting manganese-based catalyst system, combining manganesia and iron oxide as active components with natural vermiculite ore as support. Despite the low costs of the components, the catalyst material excels by considerable low-temperature activity and sulfur resistance [11].

When the costs for the raw materials are the main development target, even waste materials such as Bayer red mud from the aluminum industry can be used for the manufacture of SCR catalysts, as demonstrated by Wu et al. in their research paper [12]. Iron oxide is the main component in this type of catalyst, whose activity can be enhanced by cerium addition.

At the other end of the scale, Cu–SSZ-13 catalysts are used in automotive SCR applications, where the highest volumetric activity and high hydrothermal stability are required, but costs are less of an issue compared to stationary applications. Gao and Peden reviewed the recent progress in the understanding of the mechanistic functionality of Cu–SSZ-13 in the SCR reaction with a focus on the work of their own group [13]. In addition to the coherent explanation of NO–SCR, the review also addresses catalyst deactivation and the description of possible fast-SCR reaction mechanisms over Cu–SSZ-13. Rizzotto, Chen, and Simon add an interesting facet to the understanding of the unique activity of Cu–SSZ-13 for the SCR reaction by applying in situ impedance spectroscopy to explore the mobility of NH_3-solvated Cu^{II} ions [14]. The found out that the unique cage structure of Cu–SSZ-13 favors the local motion of $Cu^{II}(NH_3)_n$ species, which has been described before as an important factor for the SCR activity of this type of material.

In the years to come, an increasing fraction of biofuels is expected in the market. Since biofuels are produced from biomass containing significant amounts of inorganic impurities, such as alkaline metals, there is a higher risk of poisoning the SCR catalysts. This motivated Tarot et al. to investigate the influence of sodium poisoning on the activity of copper-exchanged zeolites at the example of Cu–FER [15]. They found a decrease in NO_x reduction efficiency, which is governed by a loss of ammonia adsorption capacity at low temperatures and a change of the ratio of exchanged copper due to copper oxide formation at high temperatures, respectively.

Despite the success of the established SCR process with ammonia or urea as reducing agents for NO_x, research is ongoing to develop alternatives for future applications. Ström et al. have studied alumina-supported silver and indium catalysts, which are interesting catalysts for SCR with

hydrocarbons as a reducing agent [16]. The activity of these catalysts can be promoted by hydrogen addition. Since ammonia has been identified as intermediate in hydrocarbon–SCR, the researchers have used ammonia as a reducing agent in this study and added hydrogen to the model exhaust gas. Their fundamental study comprising detailed characterization of the catalysts revealed interesting structure–function relationships which may help to improve SCR activity and the development of systems which work without hydrogen addition. The activity of alumina-supported silver catalysts in hydrocarbon–SCR can be improved not only by hydrogen addition, but also by application of cold plasma. The study of Lee, Kang, Jo, and Mok traced back the effect of the plasma on the decomposition of the long-chain hydrocarbon fuel and formation of partially oxidized hydrocarbons, particularly aldehydes [17].

The diversity of contributions in this book reflects the plethora of research questions in the SCR process, whose development potential is still not exploited. Considering all the important work on SCR done in the world, which is partly reported in this book, it is probably not too daring to predict that SCR will also, in the future, remain the most important process to clean lean exhaust gases from NO_x emission.

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