Catalysis for NOx abatement

Selective catalytic reduction of NOx by ammonia: fundamental and industrial aspects

Emission of NOx is a major global pollution problem. The most efficient commercially proven method of removing NOx from flue gases today is still the Selective Catalytic Reduction (SCR) of NOx by ammonia over vanadia/titania catalysts. What are the future challenges of SCR and can we today understand why such catalysts are especially efficient and do we have sufficient fundamental insight into the nature of the active sites and the mechanism such that we can bridge our fundamental knowledge with actual industrial application? These questions will be addressed presently. The substantial progress which has been made in the molecular understanding of SCR will be discussed and it will be shown that the microkinetic approach is a useful framework for incorporating the fundamental insight.

Introduction

Nitrogen oxides (NOx) belong to some of the most troublesome pollutants and their damaging effects on our health and environment are substantial. For example, NOx plays an important role in the Earth’s atmospheric chemistry. A high concentration of NOx increases the tropospheric ozone levels via photochemical oxidation of NOx, while depleting the stratospheric ozone through thermal reaction of nitrous oxide with oxygen atoms in the upper atmosphere. This may have many serious consequences for global warming. NOx also contributes substantially to acid rain (formed via reaction involving HO2 or OH radicals) leading to acid deposits which contribute to forest dying around us, destruction of fresh and coastal water life, deterioration of building materials, and causing the reddish brown smog in urban areas (due to NO, formed by the photochemical oxidation of NO). The direct health hazards relating to NOx range from bronchitis and pneumonia, to effects on the immune system resulting in increased susceptibility to viral infection and hay fever[1]. NOx is produced not only in all combustion processes involving fossil fuels and, burning of biomass (including field burning and forest fires), but also by lightning, microbial decomposition of proteins in the soil, and volcanic activity[2]. However, the first two man-made sources contribute to almost three-quarters of the total amount of NOx emitted into the atmosphere[3]. The total amount of NOx emissions from the European Community, Japan, and the United States is about 35 million metric tons per year (based on NO2). The United States alone emit about 60% of this amount[4]. Guidelines for maximum allowable NOx emissions from both mobile and stationary sources were already introduced in the early 1970’s, and these guidelines have since then been continuously revised and tightened. This situation has provided significant incentive for both research and commercial developments in the area of NOx abatement. However, emission guidelines are not always sufficient driving forces for actual installation of the quite costly NOx control technologies and as a result regulating laws usually have to be passed first. Furthermore, if such laws are not global, the production costs and the competitive situation of the producers will vary from country to country. Thus, solutions to the environmental problems are complicated by local as well as global political issues.

Various technologies have been developed to control the emission of nitrogen oxides; and these may be classified either as primary or secondary measures. The primary technologies (“clean technologies”) are aimed at reducing the initial formation of nitrogen oxides, for example, by modifications of the fuel quality or the combustion processes. The secondary measures are aimed at removing the produced nitrogen oxides from the flue or exhaust gases (“clean-up techniques” or “flue-gas treatments”). Although the primary measures are in principle more attractive than
the NOx removal by secondary measures, the progress in the development of primary measures has not been sufficient to meet the more stringent emission regulations. Thus, NOx reduction has mainly been carried out by use of secondary or clean-up technology.

Secondary control measures include both wet and dry methods. So far the wet methods are limited to small waste stream cleanup and are not suitable for NOx removal from large volumes of flue gases. The dry methods consist of catalytic and non-catalytic types. Details of the various methods have been described in a review by Bosch and Janssen [3]. Among the various secondary processes, the Selective Catalytic Reduction (SCR) of NOx by ammonia over vanadia/titania catalysts is by far the most important commercial process today for removing NOx from flue gas.

The SCR process has been commercially implemented in Japan since 1977 [5] and the first installations of such units in the U.S., West Germany and Austria came about ten years later [6,7]. Nowadays, SCR installations for over hundred thousand MW capacity have been made worldwide. The market for SCR catalysts and systems is expected to increase as stricter regulations are being enforced in an increasing number of countries. The present article focuses on the removal of NOx from flue gas by the SCR process. First, a short description of the industrial aspects of this process and the catalysts will be given, followed by a discussion of some fundamental aspects of the catalyst system, in particular with regard to the nature of the active sites and the SCR reaction mechanism. It will be shown that it is possible to translate this insight to the industrial operation.

The Selective Catalytic Reduction Process

In the SCR process, NOx is reduced by ammonia over a catalyst to form harmless nitrogen and water vapor without creating any secondary pollutants. This process has the following overall stoichiometry [3]:

$$4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$$

Figure 1 shows a schematic diagram of the SCR process. The main components of the SCR process basically consist of a reactor with the catalyst and an ammonia storage and injection system. The reducing agent can be either liquid, water-free ammonia under pressure or it can be a 25% aqueous ammonia solution at atmospheric pressure. A solution of urea can be used as well. The ammonia (e.g. aqueous NH3) is volatilized in an electrically steam or hot water heated evaporator and is subsequently diluted with air before it is injected into the exhaust gas duct. The injection of the mixture normally takes place through a system of nozzles in the NOx Out Signal

**Figure 1**

Schematic process diagram for Selective Catalytic Reduction (SCR) of NOx.

**Figure 2**

Schematic diagram of the deNOx process for high dust and low dust/tail end operations for coal fired boilers.

SCR = reactor for SCR, APH = air preheater, ESP = electrostatic precipitator (dust filter), FGD = flue gas desulfurization, H = heater.

The numbers give the gas temperature in °C.
In order to achieve a uniform mixing of the ammonia with the exhaust gas. A static mixer may be placed in the exhaust gas duct to further improve mixing. In order to ensure efficient NOx removal and minimum NH3 slip ("leakage") from the SCR reactor, it is very important that the flue gas-ammonia mixture has a uniform NH3/NOx ratio.

In practice, the degree of conversion of the nitrogen oxides depends on the amount of ammonia added and it increases with increasing NH3/NOx ratio. One should not, however, add NH3 above the stoichiometrically required amount in order to avoid the slip of unreacted ammonia.

The SCR process arrangement depends on the particular industrial applications\(^{3,8}\). For example, for coal-fired boilers, there are the so-called high dust and low dust/tail end processes (Fig. 2). In the high dust operation, the SCR reactor is placed immediately after the boiler and upstream of the electrostatic precipitator (or the dust filter), whereas in the low dust/tail end operation the SCR reactor is placed downstream of the flue gas desulfurization (FGD). The high dust position is preferred from an economical point of view. However, if flue gases contain a significant amount of catalyst poisons (particularly in molten slag coal fired boilers), or if utility plants offer inadequate space around the boiler, the low dust/tail end process is adopted.

Other important applications of SCR include NOx emission control from gas- and oil-fired boilers, gas turbines, chemical plants (e.g. HNO3 plants), and internal combustion engines. The growing importance of the last application which removes NOx from diesel engines is demonstrated in installations of reciprocating engines on several marine vessels in California and Sweden (an example is illustrated in Fig. 3). Besides the applications mentioned above, SCR is also used in connection with the treatment of emission from industrial plants and waste incinerators. SCR may also be integrated in a process (e.g. SNOX from Haldor Topsøe and DESONOX from Degussa) for the combined removal of nitrogen and sulfur oxides from flue gases with the production of H2SO4. The typical flue gas composition from a coal-fired boiler is as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>400-700 ppm</td>
</tr>
<tr>
<td>NO2</td>
<td>2-5 ppm</td>
</tr>
<tr>
<td>SO2</td>
<td>500-2000 ppm</td>
</tr>
<tr>
<td>SO3</td>
<td>2-20 ppm</td>
</tr>
<tr>
<td>H2O</td>
<td>6-8 %</td>
</tr>
<tr>
<td>O2</td>
<td>4-5 %</td>
</tr>
<tr>
<td>CO2</td>
<td>10-12 %</td>
</tr>
<tr>
<td>Dust (low dust)</td>
<td>5-20 mg/Nm³</td>
</tr>
<tr>
<td>Dust (high dust)</td>
<td>10-20 g/Nm³</td>
</tr>
</tbody>
</table>
In the SNOX process\[9\] (shown in Fig. 4), the flue gas after dust removal enters the SCR reactor where 99% of the NOx is reduced by NH3 in the presence of O2. The sulfur is converted to concentrated commercial grade sulfuric acid. The conversion involves the catalytic oxidation of SO2 into SO3, which is subsequently hydrated to sulfuric acid and condensed as 95% sulfuric acid in the air-cooled multi-tube WSA (Wet Sulfuric Acid) condenser. The SNOX process has the advantage that it can operate at NH3/NOx ratios slightly above 1.0 without ammonia slip, because all of the surplus ammonia will be oxidized to nitrogen and NOx in the downstream SO2 oxidation reactor\[10\]. This combined process gives an overall deNOx degree of about 97%, and the higher NOx removal efficiency achieved by the higher NH3/NOx allows the use of smaller catalyst volume as compared to conventional SCR.

A zeolite based catalyst is used in the DESONOX process\[11\] which produces about 70% H2SO4.

**SCR Catalysts**

The SCR reactor usually consists of one or more layers of catalysts. The catalyst volume, and consequently the size of the reactor, depends among other things on the activity of the catalyst, the desired degree of NOx reduction, the NOx concentration, the flue gas pressure, the acceptable level of NH3 slip and the dust content. Typically, very large volumes of gas have to be treated (e.g. 1,000,000 Nm3/h for a 300 MW, power plant) and reliable operation of the SCR unit is a key issue, in order not to interfere with the operation of the power plant itself. To minimize problems in high dust plants arising from the deposition of dust contained in the exhaust gases, monolithic catalysts are necessary in combination with regular “soot-blowing”.

SCR catalysts may be made in several ways\[8\]. The catalyst material can either be extruded into honeycomb monoliths or be deposited onto perforated metal plates or nets. Another procedure involves wash coating a layer of catalyst onto a monolithic matrix consisting of cordierite or corrugated ceramic paper\[8\].

**Figure 4** Schematic diagram of the SNOX™ process.

**Figure 5** Schematic sketch of an SCR reactor loaded with monolithic catalysts.
lysts of the latter type. The catalyst may be manufactured with different channel diameters since this will influence the volume activity of the catalyst, the pressure drop and the dust deposition (plugging of channels). Thus, the choice of the channel diameter depends on the dust content of the exhaust gas, the characteristics of the dust and the allowable pressure drop across the SCR reactor.

Many different types of catalysts have been investigated for use in the deNOx process. (For a review, see e.g. Bosch and Janssen[3]). The active components may be based on, for example, iron, chromium or vanadium, while support materials tested include TiO$_2$, Al$_2$O$_3$, SiO$_2$, zeolites and various combinations of these oxides[12]. However, the most commonly used catalyst we have today for the reduction of NOx from flue-gas is titania-supported vanadia[3]. This catalyst has high SCR activity and is resistant to poisoning by SO$_3$.[14]. The titania used is predominately in the anatase form, since anatase is easier to produce with high surface areas than rutile.

Figure 6 shows some typical NOx removal behavior[10] for vanadia/titania catalysts at two different space velocities, plotted as the NOx conversion against the NH$_3$/NOx ratio. The curves show that NOx conversions above 95% can be achieved at space velocities (i.e. NHSV, expressed as normal cubic meter of flue gas per hour per cubic meter of catalyst) below 10,000 Nm$^3$/m$^3$h with NH$_3$/NOx ratios ~1. However, high NH$_3$/NOx ratios are not desirable, since as discussed above and shown in the figure, a large increase in the ammonia slip occurs above NH$_3$/NOx ~1. In industry, the maximum allowable ammonia slip is often the decisive factor for determining the required minimum catalyst volume. As mentioned previously, it is also very important to avoid an uneven flow distribution and poor NH$_3$ mixing, since such effects may also lead to large increases in the NH$_3$ slip.

**Process Constraints and Catalyst Deactivation in SCR**

Normally, an ammonia slip above 5-10 ppm cannot be tolerated since it can react with SO$_2$ to give ammonium bisulfate which causes corrosion and fouling problems in downstream equipment. Furthermore, in the high dust application, a too high ammonia slip contaminates the fly ash, making it unsuitable for cement production. In power plants with wet bottom boilers and ash recirculation, diarsenic trioxide is a severe poison[13] for the deNOx catalysts. Other causes of deactivation include poisoning by alkali metals present in the flue gas, thermal sintering, and plugging of catalyst pores and/or channels by dust deposit. The alkali metal problem is especially severe in connection with the utilization of biomass.

**SCR Reaction Kinetics**

The very large volumes of flue gas to be treated require the installation of a huge amount of catalyst (e.g. about 250 m$^3$ of high dust catalyst in a 300 MW$_e$ power plant). Hence, it is important to be able to describe in detail the degree of NOx removal for a given installed catalyst volume. Thus, to design industrial deNOx reactors, it is essential to have detailed kinetic information. For this purpose power law kinetic expressions are often used in industry. However, the simple power rate law has severe inherent limitations and seldomly it describes the reaction kinetics adequately over wide range of reaction conditions[16]. This is especially so in environmental processes (e.g., ultrapurification or zero emission processes) where one or several of the components have to be removed down to the ppm-level[17,18]. The above problems are also important for the SCR reaction and in fact, apparent reaction orders ranging from 0.5 to 1 and -0.15 to 1 have been reported for nitric oxide and ammonia, respectively. Reaction kinetics has thus been one of the controversial issues in SCR. In the subsequent section, we show that the microkinetic approach[19] is a useful framework for introducing fundamental knowledge on the SCR reaction and, consequently, many of the controversies could be resolved.

**Earlier proposals regarding SCR mechanism and active sites:**

Many different types of reaction mechanisms have been proposed in the literature for the SCR reaction over vanadia/titania catalysts and still today no general consensus has been reached. Proposals have ranged from Eley-Rideal type mechanisms involving gas phase NO, surface-mediated mechanisms involving weakly adsorbed NO to Langmuir-Hinshelwood type mechanisms, with different types of adsorbed NH$_3$ and NO species. For example, based on separate results on TiO$_2$ and V$_2$O$_5$ samples, Odriozola et al.[20] considered V$_2$O$_5$/TiO$_2$ as a bifunctional catalyst and suggested a Langmuir-Hinshelwood mechanism involving reaction between adsorbed NO on TiO$_2$ and adsorbed NH$_3$ on V$^5+$. Went et al.[21] proposed a similar mechanism involving a reaction between adsorbed NH$_3$ on Lewis acid sites and adsorbed NO on other, non-specified sites. Such proposals are however not in agreement with the failure to observe significant amounts of adsorbed NO under reaction conditions[19,20]. Recent TPD studies[21] have also shown that the adsorption of NO is weak. Takagi et al.[22,23] proposed a reaction of the Langmuir-Hinshelwood type between adsorbed NO$_2$ and adsorbed NH$_3$. However, Inomata et al.[24,25] did not observe oxidation of NO to NO$_2$ by O$_2$ in a flow of dilute gases with concentrations (1000 ppm NO in 1% O$_2$) resembling those encountered under industrial conditions. Also, in our own work[26] we did not observe NO$_2$ on the vanadia/titania catalyst surface under typical SCR conditions. Eley-Rideal mechanisms between adsorbed NH$_3$ and gas phase NO were proposed by Inomata et al.[24,25] and later by Gasior et
Microkinetic analysis

Our earlier kinetic analysis of the deNOx reaction\cite{33}, made to evaluate the various mechanisms, showed that a simple two-step Eley-Rideal mechanism involving reaction between adsorbed NH₃ and gaseous (or weakly adsorbed) NO is not consistent with the available information. Rather, a three-step mechanism could give an adequate representation of the data\cite{33}. This mechanism consists of an equilibrated ammonia adsorption step, followed by an activation step and a subsequent reaction between the activated ammonia species and NO to form the products. The three-step mechanism was written as below:

$$\text{Step 1: } \text{NH}_3 + M \rightarrow \text{NH}_3-M$$

$$\text{Step 2: } \text{NH}_3-M + S \rightarrow \text{NH}_3-S + M$$

$$\text{Step 3: } \text{NO} + \text{NH}_3-S \rightarrow \text{Products} + S$$

where M represents an ammonia adsorption site, and S represents a reactive site on which ammonia subsequently becomes activated.

It was not possible to distinguish kinetically whether Step 3 was a true Eley-Rideal step, involving reaction with gaseous NO, or a reaction with weakly adsorbed NO. The three-step mechanism was able to quantitatively describe the NO conversion data\cite{33} under industrially relevant conditions for operating the vanadia/titania catalysts. Furthermore, it gave a very good description of the ammonia slip\cite{33} behavior, which previously has been found more difficult to describe than the conversion of NOx. However, despite the good fit of the kinetic data, the mechanism was still semi-empirical in nature, since direct information concerning the nature of the M and S sites not provided.

Lewis acid sites (VO²⁺) were proposed by Ramis et al.\cite{29} as the active sites which coordinate molecular ammonia. Inomata et al.\cite{24,26} proposed that NH₃ adsorption occurs on dual sites involving V=O and an adjacent V=O, which assists in the activation of NH₃. They found that the rate of the NH₃-NO reaction is proportional to the amount of V=O. Other studies\cite{25,30,31}, however, could not find a correlation between V=O and SCR activity. Gasior et al.\cite{20} proposed V=O to be the active site. This suggestion has since been supported by several investigators\cite{25,30,31}. The interaction of ammonia and V=O was confirmed by our IR studies\cite{32} which revealed a direct correlation between the concentration of V=O groups and the Brønsted acidity.

Not surprisingly, it has been difficult to use any of the proposals on the SCR reaction mechanism and the nature of the active sites to explain the industrial SCR operation. It is likely that the disagreement in the literature relates to the fact that many of these studies were done under conditions which are not representative for the industrial application.

![Figure 7a](image1.png)

On-line mass spectrometry results on the 6% V₂O₅/TiO₂ during TPSR in (a) O₂/Ar, (b) NO + O₂/Ar, and (c) NO/Ar, shown as concentrations vs. temperatures. (Reprinted with permission from ref.\cite{32}).

![Figure 7b](image2.png)

![Figure 8a](image3.png)
In view of these ambiguities, we decided to perform in situ infra-red spectroscopic studies [25,32] to elucidate the nature of the surface interactions of the various reactant molecules such as ammonia, nitric oxide, and oxygen. Information about the reaction intermediates and the reactivity of the surface sites was also obtained by combining the infrared studies with simultaneous analysis of reactants and products. Adsorption of ammonia has shown that both Brønsted and Lewis acid sites are present on the surface of vanadia/titania catalysts as reflected by the infrared absorption bands of ammonium species and coordinatively bonded ammonia species, respectively [25,32-37]. The relative concentrations of these sites depend on the concentration of vanadia and the state of oxidation. Specifically, more Brønsted acid sites are found on oxidized vanadia catalysts with a high loading [25]. Only Lewis acid sites are observed on the titania support itself [25,38]. The question that has been frequently raised in the literature is: which of these sites is responsible for the SCR activity?

This issue was addressed by the use of in situ Fourier transform infrared spectroscopy [32,39,40] and by monitoring simultaneously the changes in catalytic activity and the changes in the concentration of surface sites and adsorbed species. The results show no simple correlation for the Lewis acid sites, but they do reveal a direct correlation between the concentration of Brønsted acid sites (as indicated by the intensity of a band at 1430 cm⁻¹) and NOx conversion [39]. Clearly, the Brønsted acid sites appear to be the catalytically important sites for NH₃ adsorption. Separate experiments have shown that the V-OH groups on the vanadia surface are the Brønsted acid sites [32]. Thus, the M sites in the above semi-empirical mechanism are V-OH groups.

Further information on the surface sites and their catalytic significance was obtained by looking at the changes in the nature of adsorbed species and the changes in gas composition over the catalyst during temperature-programmed surface reaction (TPSR). For example, Figure 7 compares the in situ infrared results obtained during the course of such TPSR studies over a preoxidized 6% vanadia/titania catalyst pre-saturated with ammonia, in O₂, N₂, and a mixture of NO+O₂. The initial spectra of the catalyst saturated with ammonia show absorption bands due to NH₄⁺ species (bands at 3020, 2810, 1670, and 1430 cm⁻¹) and coordinated NH₃ (bands at 3364, 3334, 3256, 3170, and 1602 cm⁻¹). Clear differences are seen in the manner that these spectra change when the temperature is raised in the different gases. In general, the ammonia absorption bands disappear gradually with increasing temperature, but at different rates. The results show that the preadsorbed ammonia species are removed fast in the mixture NO and O₂ (Fig. 7b), and slowly in O₂ alone (Fig. 7a). The corresponding gas compositions during TPSR are shown in Figure 8. The production of N₂ parallels that of water during the initial exposure of the ammonia-saturated catalyst surface to the mixture of NO and O₂ (Fig. 7b), and slowly in O₂ alone (Fig. 7a). The corresponding gas compositions during TPSR are shown in Figure 8. The production of N₂ parallels that of water during the initial exposure of the ammonia-saturated catalyst surface to the mixture of NO and O₂ (Fig. 8a). Thus, the disappearance of ammonia absorption bands in mixture of NO and O₂ in the infrared spectra (Fig. 7) is attributed to the SCR reaction, while...
their disappearance in O2 is mainly due to desorption of ammonia. Figure 8c shows that some SCR reaction also occurs when the ammonia pre-saturated catalyst surface is exposed to NO alone, but to a lower extent than in the NO - O2 mixture.

A closer examination of the infrared spectra reveals important changes in both the V-OH and the V=O groups during the reaction cycle\[32,39\]. It is seen that after the initial intensity decrease of the V-OH band (at 3640 cm\(^{-1}\)) due to interaction with ammonia, a new, more reduced V-OH is formed (at 3660 cm\(^{-1}\)). At the same time, a downward shift is seen in the V=O band reflecting a weakening of the V=O bond. This observation indicates that the V cations have undergone reduction, most probably by the transfer (perhaps partial) of H from the adsorbed NH\(_3\) to the surface vanadyl groups to form an activated ammonia species. The formation of new reduced V-OH is consistent with this. Thus, the S sites in the mechanism appear to be V=O groups. Upon further increase in temperature during the TPSR, V=O groups reappear with the simultaneous appearance of the original V-OH.

These experimental observations have been summarized in a catalytic cycle for the SCR reaction over vanadia/titania catalysts (Scheme 1)\[32,39\]. Basically, the reaction involves both acid-base and redox catalytic functions. The reaction is initiated by the adsorption of ammonia on Brønsted acid sites (V\(^{5+}\)-OH), followed by “activation” of ammonia via reaction with redox sites (V=O). This “activated” form of ammonia then reacts with gaseous or weakly adsorbed NO, producing N\(_2\) and H\(_2\)O while releasing V\(^{4+}\)-OH. To complete the catalytic cycle, the V\(^{4+}\)-OH species is oxidized by either NO or O\(_2\) to regenerate the original V=O species. Our studies\[40\] also show that the type of activity correlation changes at high and low O\(_2\) pressures. At high oxygen pressure (8%), a rather good correlation is seen between the NOx conversion and the product of the concentration of the Brønsted acid sites and the partial pressure of NO at the reactor outlet, whereas at low O\(_2\) pressure, the activity appears to correlate better with the product of the concentrations of the Brønsted acid sites and vanadyl groups. These results suggest that the relative importance of the different steps in the catalytic cycle changes depending on the pressure conditions.

**Scheme 1** Catalytic cycle for the SCR reaction over vanadia/titania. (Adapted from ref. [40]).

![Scheme 1](image-url)
oxygen concentration. Changes in the significance of the reaction steps may also be expected upon other variations in reaction and catalyst parameters. Such effects have been recently observed by Amiridis and Solar[41] for V₂O₅/TiO₂, V₂O₅/TiO₂/SiO₂ and V₂O₅-WO₃/TiO₂ catalysts with varying vanadia loadings. The two examples above illustrate why simple power law kinetic expressions will not always apply over a wide range of reaction conditions. However, a recent microkinetic analysis[42] using the catalytic cycle proposed in Scheme 1 showed that one can quantitatively describe both the laboratory (Fig. 9) and industrial kinetic data for the SCR reaction over a wide range of conditions.

### Questions and answers

**What are the major future challenges for the Selective Catalytic Reduction process?**
The main challenges will continue to depend on politics and on environmental legislation. We still need to find satisfactory solutions to NOx removal from mobile diesel engines. This will no doubt require an integration and coupling of the operation of the engine and the SCR process. Also, in response to the environmental debate over CO₂ emissions, burning of biomass has in some countries been considered as an alternative to the combustion of fossil fuel. This poses new challenges for SCR since, for example, alkali metals, which are serious catalyst poisons, are present in fairly large quantities in bio-fuels. Separate alkali metals removal procedures may thus have to be introduced. The use of V-containing fuels like heavy oil or Orimulsion also presents a challenge, as accumulation of V₂O₅ is a problem with these fuels.

**Why is the vanadia/titania system the most widely used catalyst for SCR?**
Today vanadia/titania is still the most active and economical SCR catalyst and it exhibits the best resistance to water vapor and to poisoning by sulfur. Other catalysts based on noble metals, metal oxides and zeolites have been widely investigated. However, none of these systems can meet the performance of vanadia/titania yet.

**How do we reduce the “ammonia slip” from SCR processes?**
The “ammonia slip” or the unreacted ammonia from the SCR process can be reduced by installing either more or improved catalysts. Furthermore, it is very important to optimize the design of the ammonia injection system to ensure good mixing of the ammonia with the exhaust gas such that a uniform distribution of NH₃/NOx is achieved throughout the catalyst bed. Ammonia slip is eliminated in the SNOX process[49] which combines SCR with SO₂ oxidation to produce sulfuric acid. In this process, surplus ammonia is oxidized to nitrogen and NOx in the downstream SO₂ oxidation reactor.

### Summary

Some industrial aspects of selective catalytic reduction of NOx have been addressed with respect to process layout, catalyst configuration and problems encountered in industrial operation. Furthermore, we discussed the difficulties one often encounters when traditional kinetics is used to describe environmental processes. One source of complication is the necessity to cover large concentration changes, since it is desirable to remove the pollutants to the ppm-range. The widely used power rate laws are often inadequate in these “ppm” processes and the use of such expressions may lead to large errors in the recommended catalyst volume[43]. The problem can be avoided by using the so-called microkinetic analysis, which is based on a good fundamental understanding of the nature of the reaction and the active sites. We also discussed how the use of combined in situ on-line spectroscopic and catalytic activity studies establish the catalytic cycle, which forms the basis for a microkinetic analysis, which is able to provide an adequate description of the kinetic data from both laboratory and industry over a wide range of conditions. Such detailed understanding of the fundamental aspects of the catalyst system and the reaction mechanism under realistic industrial conditions will aid in guiding future reactor design and in developing improved catalysts for the removal of NOx.

**Can one use other reducing agents than ammonia?**
Yes, there has been an interest to replace ammonia with other reducing agents in order to avoid possible hazards associated with the storage and transportation of liquid ammonia. Other nitrogen containing compounds such as urea, melamine and cyanuric acid have been found to give almost similar catalytic performance as ammonia[12]. They can be considered as convenient ammonia storage media and are decomposed to ammonia prior to the SCR reaction. Hydrocarbons have also been tried as reductants for NOx[25], but the performance is still insufficient for commercialization. Although direct catalytic decomposition of NOx seems to be an attractive alternative, and extensive research has been done in this area, it has not yet moved beyond the laboratory phase.

**How relevant is microkinetic analysis for process design?**
Since microkinetic models are based on actual molecular insight, they have the potential of guiding both catalyst and process research and developments. One could add that in catalysis, empirical kinetic models are often sufficient if the goal is mainly to provide the basis for design. However, such empirical models often break down when one has to describe environmental processes like the SCR[15,16], where large concentration changes are encountered. This is in fact seen to be the situation in SCR and it was one of the reasons for obtaining the molecular basis for a microkinetic analysis.
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References