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Is advanced SCR technology at a standstill? A provocation for the academic community and catalyst manufacturers

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Abstract

Despite extensive contributions to the literature since 1975 regarding selective catalytic reduction (SCR) catalysis with ammonia for NO_x removal from combustion gases, there is still on-going, controversial discussion in academia concerning both catalytically active sites in the SCR mechanism and deactivation phenomena with regard to practical SCR applications. New developments such as SCR of NO_x by hydrocarbons are still thwarted by problems relating to the development of suitable materials. Efforts to replace SCR technology by selective catalytic decomposition (SCD) for NO remain confused in both theory and experiment. © 1998 Elsevier Science B.V. All rights reserved.

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1. SCR of NO_x by NH_3 is practiced worldwide

A vast amount of research findings on NO_x removal has been published since 1975. However, none of these findings offer a completely satisfactory commercial solution. Currently, the best approach to NO_x abatement is selective catalytic reduction (SCR) with ammonia. This is a widely practiced technology.

More than 130 SCR plants with over 30 000 m^3 of catalyst were retrofitted in power plants in Europe and the US between 1987 and 1996 by Siemens alone. To provide an optimum solution for catalytic performance, Siemens decided to manufacture two types of catalysts, plate-type and honeycomb-type catalysts (Fig. 1). The fact that there were only few operational problems despite the short introductory phase is surprising considering the specific characteristics of German power plants in terms of operating mode, type of furnace and fuel, since the Japanese experience known at that time had to be expanded upon. Some of the exemplary highlights of the developments made with Siemens catalysts up to the beginning of the 1990s include an increase in the SCR efficiency to 94%, tolerable ash contents up to a maximum of 50 g/m^3 and arsenic contents up to a maximum of 1 mg/m^3. Additional requirements were also verified on an industrial scale to account for new configurations and areas of application. These include in-duct SCR, air heater SCR, compact SCR and flue gas cleaning in waste incineration plants, which currently allow such operating parameters as incident velocities of up to 10 m/s for gases containing ash.

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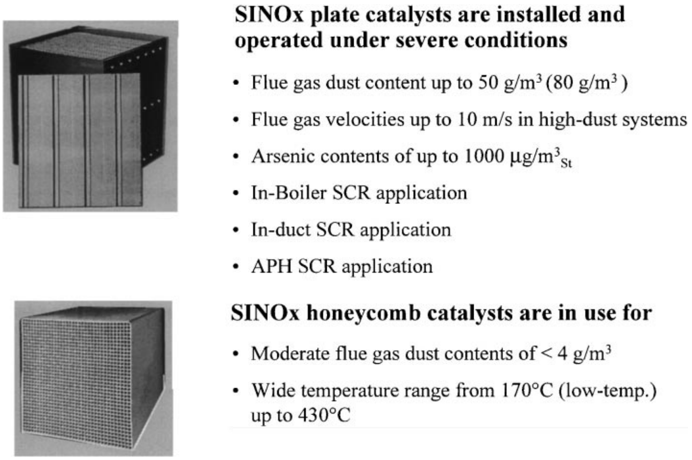

SINOx plate catalysts are installed and operated under severe conditions

- Flue gas dust content up to 50 g/m^3 (80 g/m^3)
- Flue gas velocities up to 10 m/s in high-dust systems
- Arsenic contents of up to 1000 $\mu g/m^3_{St}$
- In-Boiler SCR application
- In-duct SCR application
- APH SCR application

SINOx honeycomb catalysts are in use for

- Moderate flue gas dust contents of < 4 g/m^3
- Wide temperature range from 170°C (low-temp.) up to 430°C

Fig. 1. Key requirements imposed on SINOX catalysts for plate-type and honeycomb-type catalysts.

However, there are still open questions on advanced SCR technology, which suffers from some serious faults. These concern not only the catalysis mechanism and its practical use in SCR for the most varied applications, but also the understanding of the phenomena of catalyst deactivation caused by flue gas constituents.

2. Explanations of deactivation phenomena on a molecular level remain unsatisfactory

Attempts to explain deactivation by loss of surface area, originating from pore clogging or condensation in pores, turned out to be unsatisfactory, because decreasing activity could not be correlated with surface area in a simple manner [1]. Laboratory tests had indicated that there should be an exponential correlation between the relative activity constant k/k_0 and arsenic oxide absorption for TiO_2–MoO_3–V_2O_5 catalysts, obtained by the formation of a monomolecular dispersion (monolayer) of V_2O_5 and MoO_3 on TiO_2 (anatase), when exposed to As_2O_3. A corresponding correlation is expected when the catalysts are exposed to the flue gas of a coal-fired power plant with a slag tap furnace [2].

When using a furnace with ash recirculation, the concentration of trace elements in the gas phase is higher by an order of magnitude than with conventional firing. This offers the possibility of studying contamination effects over short power plant operating times. In this case, it is inevitable that at least some of those elements suspected to be involved in catalyst deactivation are adsorbed on the catalyst surface. With this purpose in mind, the catalyst specimens were positioned in the catalytic reactor such that they came into contact with ammonia-free flue gas. After certain exposure times they were removed from the flue gas for the analysis of the contaminated surface of the catalyst. Because of its detection depth of only a few atomic layers, X-ray photoelectron spectroscopy (XPS) was used to investigate the trace elements adsorbed by the catalysts. The presence of detectable amounts of Cr, Mn, Fe, Co, Ni, Cd, Sn, Sb, Ba, W, Tl and Pb in the surface layer was ruled out. Fig. 2 shows how the atomic fractions of S, As, Mo, V and Ca change with time. It is evident that X_S and X_{As} exhibit very similar dependence on exposure time [3]. Contrary to the other elements, they steadily accumulate in the surface layer, which might be an indication of strong attractive interactions. Arsenic apparently originates predominantly in the gas phase, since As entrained by fine dust would also be expected to contribute to an increase in X_{Si}. But it is significant to note that the atomic fraction of silicon remains relatively constant over the entire exposure time. This is an indication of surface deposition, although it is also a part of the catalyst material, and suggests that equilibrium was reached between erosion and redeposition.

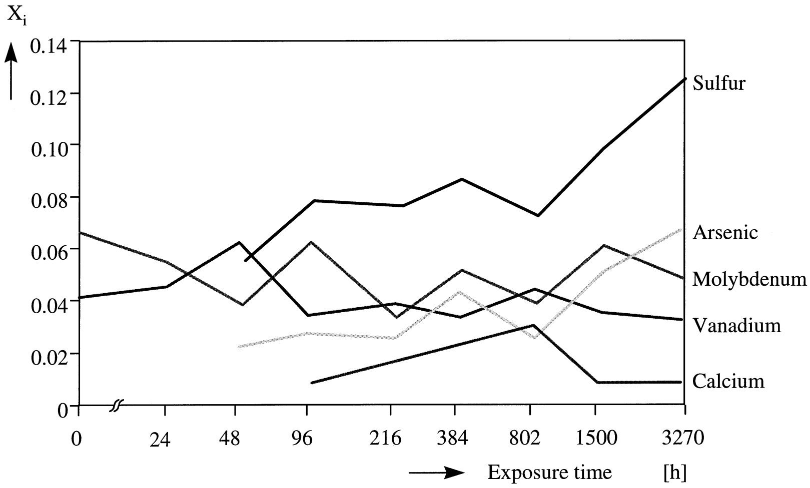

Fig. 2. Atomic fractions X_i of selected elements as a function of the exposure time to flue gas of a slag tap furnace. The specimens were measured by XPS with Al K_α irradiation. Specimen preparation and XPS technique is described elsewhere [3,43].

3. Active sites for SCR of NO_x by NH_3 are still under discussion

Most questions concerning the nature of the catalytically active site are addressed to the fresh catalyst. However, these questions should focus on the entire operating time. On the other hand, academic research has focused primarily on binary systems such as vanadium oxides on titania (anatase), tungsten oxide on titania (anatase) or MoO_3 on titania (anatase), characterizing surface properties by X-ray diffraction, IR and UV/visible diffuse reflection, Raman spectroscopy, X-ray absorption spectroscopy, temperature-programmed oxidation/reduction concerning trace reactions and photoelectron spectroscopy [4–11]. These systems do not necessarily permit comparison with industrial SCR catalysts. Working conditions were also not reflected.

In the case of supported vanadia, Raman spectroscopy was stressed by Went et al. [12] who concluded that both monomeric vanadyl and polymeric vanadate surface species present on the titania (anatase) are involved in the SCR process. In particular, they proposed that the polymeric species is about 10 times more active than the monomeric species and that the polymeric species is less selective towards N_2 formation [13]. This focused attention on the surface vanadia coverage on titania (anatase) as an important factor in increasing SCR activity. A maximum in SCR activity was assumed to be reached when a molecular dispersion (monolayer) covers the oxidic support, a hint first stressed by Russel and Stockes [14] for dehydrocyclization reactions catalyzed by molybdenum alumina.

The strength of the terminal V=O bond has been proposed as one of the factors controlling the reactivity of vanadium oxide catalysts. Miyamoto et al. [15] stated that NH_3 is strongly adsorbed onto V=O sites as NH_4^+ and the reaction rate is directly controlled by the number of surface V=O bonds. Partial oxidation of methanol was used as a trace reaction by Wachs et al. [16] to estimate the redox behavior of vanadium oxide supported on titania. Attention was focused on the position of the Raman band of the terminal V=O bond and its V=O bond strength, which indicate a stronger V=O bond for a transition to a higher Raman band position. Wachs et al. [16,17] deny that the V=O bond is responsible for SCR catalysis. They stated that the vanadium–oxygen-support bridging bond appears to strongly influence reactivity, and that the reducibility of supported vanadium oxide catalysts should be responsible. Lietti et al. [18] proposed that the redox properties of the catalysts are the major factor governing activity and that the reaction primarily involve a coordinated ammonia species on Lewis acid sites. However, participation of a protonated ammonium species on a Brönsted acid site was also proposed. Ramis et al. [19] stated that promoters affect the Lewis acidity of V=O sites, which in turn affects the adsorption of ammonia as the initial step in the SCR reaction. In contrast, others have favored unsupported V_2O_5 with respect to crystallographic planes possessing V–O–V or V–OH bonds rather than V=O bonds as being responsible for the SCR reaction [6,20].

For the discussion about a dual mechanism, Chen and Yang [21] stated that V=O sites are not adjoined to V–OH sites under SCR reaction conditions. They obtained experimental evidence that there is no correlation between SCR activity and the density of V=O sites. Instead of V=O sites, V–OH sites by themselves were brought into discussion. Chen and Yang [21] concluded with the help of poisoning experiments by alkali metals that the Brönsted acid sites of the V–OH groups are the active sites for the SCR reaction. They denied that alkali metal poisoning can be interpreted on the basis of V=O being the active site as discussed above. Martin et al. [22] showed by XPS analysis that the addition of alkali metals to V_2O_5 stabilizes the 5+ valence. Chen and Yang [21] interpreted the basicity of dopants as the important factor which decreases the Brönsted acidity and, logically, the catalytic activity.

A large number of publications are cited by Kim et al. [4] concerning the investigation of the surface structures of the supported molybdenum oxide species on various supports by Raman spectroscopy. It is generally accepted that the symmetric stretching mode of the terminal M=O bond at 940–960 cm^{-1} under hydrated conditions shifts to the higher wave number region of 980–1000 cm^{-1} upon dehydration at elevated temperatures. Independent of supports such as TiO_2 (rutile), TiO_2 (anatase) or Al_2O_3, polymolybdate clusters decompose under dehydrated conditions to form species with terminal Mo=O bonds and bridging Mo–O-support bonds. When K_2O was added to a V_2O_5/TiO_2 system, Deo and Wachs [5] observed a decrease in the Raman band of the V=O bond to lower wave numbers due to the direct interaction of potassium to the terminal V=O bond. The shift of the Raman bands to lower wave numbers by basic additives simultaneously was caused by strong bonding and a decrease in Brönsted acidity. For the MoO_3/TiO_2 system, Kim et al. [4] pointed out that in a similar aspect the stretching mode of the terminal Mo=O bond increased by direct coordination with sodium. Vuurman et al. [23] characterized the V_2O_5–WO_3–TiO_2 system by Raman spectroscopy for dehydrated systems. They pointed out that the surface vanadium oxide and tungsten oxides on TiO_2 were present as separate phases independent of all WO_3 loadings. Similarly, sequences of impregnation of vanadium oxide and tungsten oxide did not influence the nature of either site. Ramis et al. [24] confirmed this with the presence of V=O and W=O vibration in exactly the same position as the individual supported metals. Deo and Wachs [7] drew attention to impurities such as sodium and potassium oxide and pointed out that impurities like these favor the formation of surface orthovanadate species. Upon adding acidic WO_3 or MoO_3 to V_2O_5/TiO_2, preferentially octahedral surface vanadium oxide species should be formed wherever there is vanadium oxide coverage. On the other hand, Deo and Wachs [7] stated that acidic additives such as WO_3 do not significantly influence the structure of the surface vanadium oxide species on oxidic supports under dehydrated conditions. With respect to structural analysis, the polemic of Wachs [25] and Ramis et al. [26] seems to support the discussion in greater detail.

But under SCR conditions the catalyst is not available for a dehydrated species. Dependency on the variation of the water content was investigated in a wide range up to more than 20 wt% H_2O. In this context, the terminal V=O bond is perturbed by reduction as well as by adsorption of NH_3 and H_2O. Deo and Wachs [27] pointed out that these observations do not prove that the terminal V=O bond is directly involved in the rate determining step of the SCR catalysis. Addition of water to the reacting gas mixture results in a decrease in the SCR turnover frequency of approximately 40–50%, which is independent of the vanadia surface coverage. In situ Raman results suggest that such a decrease can be attributed to the competitive adsorption of water on the active vanadia sites. The presence of large amounts of water in the reacting gas mixture may also lower the rate of SCR reaction by slowing the reoxidation of vanadia [28]. Analogous questions should definitely be addressed concerning the dependence of NO conversion on WO_x/TiO_2 with WO_x loading.

Hilbrig et al. [29] studied the acidity of the WO_x/TiO_2 (anatase) systems in the absence of water vapor by adsorption of CO at a very low temperature of 83 K and adsorption of ammonia at temperatures up to

673 K. They concluded that the acid properties of such supported oxide materials are strongly modified as compared to those of pure metal oxide, in the sense that not only new strong Lewis acid sites are created but also Brönsted acidity is induced. They brought the lack of Lewis acid sites, on which the adsorption of ammonia takes place, in the context with the loss of activity of the SCR reaction for simple systems such as tungsten oxide or molybdenum oxide supported on titania (anatase). Nor do the results for the poisoned catalyst yield any answers for industrial catalysts, which differ substantially from those studied in academia. Along with slight quantities of vanadium, industrial catalysts contain at least tungsten or molybdenum oxide as additional catalyst components. The addition of a slight amounts of vanadium exhibits clear synergy effects on the catalytic behavior. Also, the interaction between vapor containing flue gas and active sites during catalysis under operating conditions was mostly neglected with respect to industrial catalysts [30,31]. Therefore the W=O rule must be considered controversial with regard to W–O–TiO_2. Some evidence for the formation of W–O–Ti bonds was obtained by EXAFS as Knözinger agreed in the discussion [29]. But these bonds are unknown in the creation of acidity, although they might by hydrolyzed in the presence of water vapor at elevated temperatures. This process may lead to the formation of acidic OH-groups.

A considerable lack of knowledge of industrial catalyst systems continues to be felt in the apparently highly fabricated understanding of the deactivation processes of tungsten and molybdenum-containing titania catalysts in flue gases containing arsenic. Although the use of molybdenum-containing catalysts in arsenic-laden flue gas has found an industrial application, there is still apparent discontent, as the material developers are unable to sufficiently explain the deactivation phenomena on a molecular level and hence to provide an impetus for further innovative development beyond the current state of the art.

4. Deactivated sites are detectable in altered reaction kinetics

Along with mass transport, deactivation behavior also has a significant influencing factor for catalytic behavior, where a distinction can be made between selective and non-selective poisoning. A significant prerequisite for non-selective poisoning is that the catalyst has an energetically homogeneous surface. If the activation energy is taken as a measure of the energetic condition of the surface, this parameter does not change in non-selective poisoning. Poison uptake is therefore not directly proportional to the number of active sites under the condition that the same number of active sites is always deactivated by a specific quantity of poison. In this case poisoning generally changes the mass transport characteristics. Poisoning decreases the BET surface area, and also results in a detectable shift in pore size distribution to narrower radii. Pores are thus narrowed to the point that specific catalyst areas become partially or completely inaccessible for the reactants. The regression lines in an Arrhenius plot are thus parallel for varying degrees of poison uptake. This parallel orientation of the individual lines in an Arrhenius plot does not hold for an energetically uneven surface. In the case of selective poisoning, an Arrhenius plot would yield plots of differing slopes before and after poisoning (Fig. 3).

It is obvious that in many catalytic processes a minority of the population participates in the catalytic process. No references at all are known from the literature, indicating that this must be viewed differently in the case of SCR catalysis. Investigations must therefore be targeted to determine which functions the population of the metal species can take on under differing reaction conditions. Such functions may be restricted exclusively to providing adsorption sites for NH_3, which the analyses used should then be able to

$$k = k_0\, e^{-E/RT}$$

$$\ln k = \ln k_0 - E/RT$$

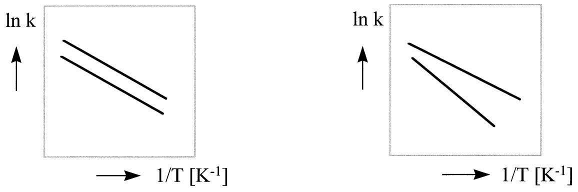

Fig. 3. Arrhenius plots for non-selective and selective poisoning effects.

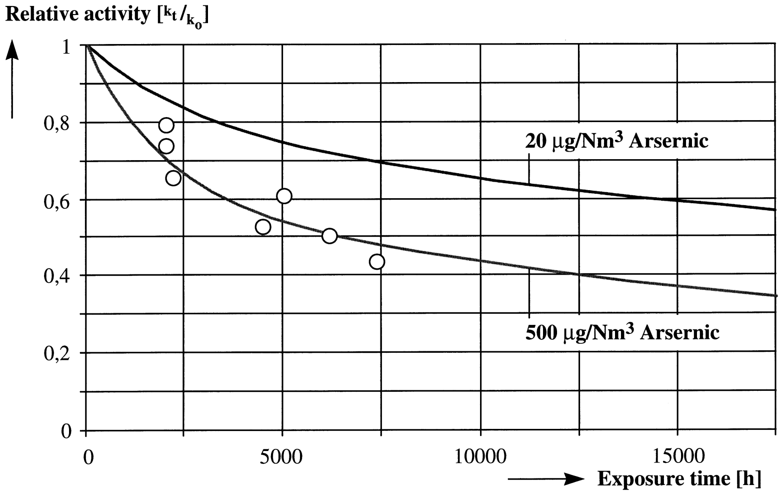

Fig. 4. Relative activity [k_t/k_0] as a function of the exposure time of a V_2O_5–MoO_3–TiO_2 (anatase) catalyst to a slag tap furnace with various arsenic content in the flue gas. Catalytic activity of the catalysts before and after power plant exposure was measured in a test system (gas composition 400 vpm NO, 400 vpm NH_3, 500 vpm SO_2, 5.4 vol% O_2, 10 vol% H_2O, balance N_2, linear velocity (LV) 4 m/s, SV value 4.355 Nm^3/h).

distinguish. The occupation of adsorption sites on the catalyst by components in the flue gas thus need not necessarily affect the catalytically active species. Therefore only specific substances in the flue gas will degrade the SCR reaction. This is shown for the example of non-Siemens V_2O_5/MoO_3-supported TiO_2 (anatase) catalysts as a function of arsenic content in the flue gas (Fig. 4). In any case, the deposited arsenic does not demonstrate stoichiometric poisoning of active sites (Fig. 5). All of the remaining materials in the flue gas hence only occupy adsorption sites which do not participate in the SCR reaction. As the analysis methods usually used do not necessarily enable a distinction to be drawn, kinetic investigation of the deactiviation phenomenon is the method of choice.

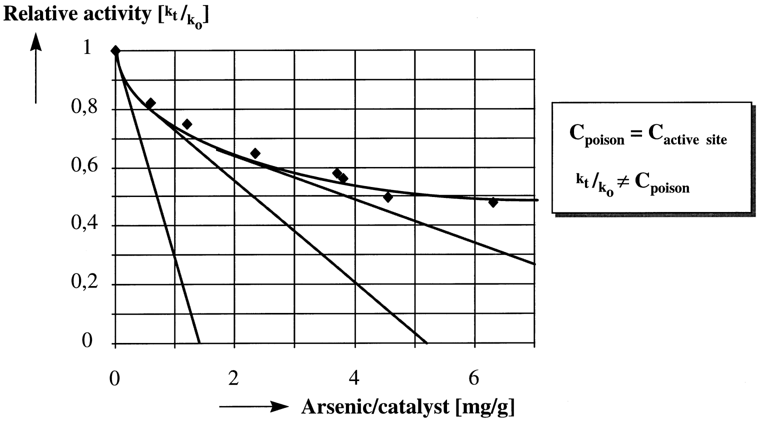

Fig. 5. Relative activity [k_t/k_0] as function of the deposited arsenic on a V_2O_5–MoO_3–TiO_2 (anatase) catalyst in a slag tap furnace. To determine the arsenic content in the catalysts, the specimens were ground in a ball mill, dissolved by HNO_3 and analyzed using AAS hybrid technique.

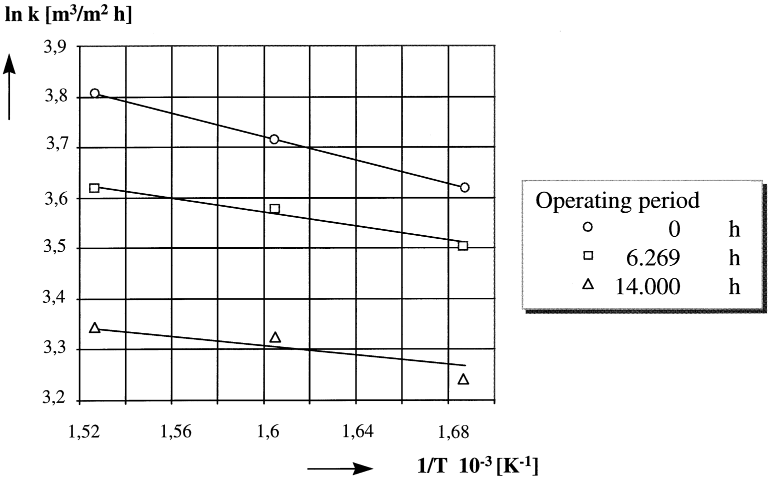

Fig. 6. Arrhenius plot as a function of the exposure time of a V_2O_5–MoO_3–TiO_2 (anatase) catalyst in a slag tap furnace. Catalytic activity of the catalysts before and after power plant exposure was measured in a test system (gas composition 400 vpm NO, 400 vpm NH_3, 500 vpm SO_2, 5.4 vol% O_2, 10 vol% H_2O, balance N_2, linear velocity (LV) 4 m/s, SV value 4.355 N m^3/h).

5. Discussion of arsenic-poisoned sites

As has been shown for the present case, poisoning must have resulted in a modification of the active sites, which are still functional (Fig. 6). This also indicates that there is also no uniformly poisoned species on a molecular level. Such a variety of modified species has been observed before. However, it was not possible to detect various arsenic structures by X-ray absorption spectroscopy (XAS) after poisoning as performed by Hilbrig et al. [32]. After poisoning, arsenic was assigned a valence of +5 based on reference compounds. It was postulated that As^{5+} is bonded to the titania surfaces as an isolated arsenate structure by hydroxyl groups. Results recently published by the above authors pointed out the formation of a new type of As–OH stretching mode for molybdenum oxide supported on titania (anatase). It was concluded that the arsenate species should interact with terminal metal oxide units. However the formation of bonds between arsenic and the active components of the catalysts has not yet been demonstrated. The discovery of a molybdenum arsenate phase which underwent phase transformation is published elsewhere [33]. Up to now it is unclear if this is the result of a segregation process. Obviously, this phase does not exist in the presence of vanadia.

Given this background, it does not appear very helpful to correlate surface sites which can be characterized by Lewis and Brönsted properties with the deactivation phenomena induced by arsenic oxide without being able at the same time to discuss the influence of the active vanadium species on the structural characteristics. Instead of this, the investigations have concentrated primarily on pure molybdenum oxide- or tungsten oxide–TiO_2 (anatase) systems, mostly with regard to the formation of monomolecular coverage on the titanium oxide surface. Both systems seem to be relatively well understood. They exhibit oxo group vibrations in the Raman and DRIFT spectra which can be assigned to polytungstates or polymolybdates. While the harmonic vibrations yield very uniform values for tungsten (2005 cm^{-1}) and for molybdenum (1965 cm^{-1}) independent of the degree of coverage, the fundamental frequencies react extremely sensitive to the degree of polymerization of the supported species [8]. This has given rise to the theory that the tungsten species aligns itself in a tetragonal pyramidal system with an oxo group on the TiO_2 (anatase) surface in monomolecular coverage. The W=O(-O) groups are bridged by oxygen atoms [9,10]. With reference to the overtone bonds cited above, these are not due to polytungstate or polymolybdates, but to monomeric mono-oxo species [34–

37]. In fact, polymeric species invariably give rise to several coupled M–O stretching modes which result in multiple fundamentals and even more (and rather weak) harmonic bandwidth. If monomolecular coverage is not achieved, additional OH vibrations can be detected which can be assigned to a TiOH species. In cases such as this, if the surface of the catalyst is covered with arsenic oxide, the OH groups associated with the TiO_2 disappear. As–OH vibrations are detected instead, the vibration frequency of which should depend on the substrate. Ammonium ions can subsequently be detected following the adsorption of NH_3. The As_2O_3 coverage is therefore spoken of as enabling the creation of an additional type of Brönsted site on the catalyst surface. The NH_3 is protonated by the acidic As–OH groups [38,39]. It has not been demonstrated whether or not these species contribute to the degradation of the SCR reaction.

It is known from other experiments by IR that the Lewis acid sites of MoO_3 on TiO_2 (anatase) are far less acidic than WO_3 on TiO_2 (anatase) [29]. On the other hand, the Brönsted acidity of MoO_3 on TiO_2 (anatase) is significantly less than WO_3 on TiO_2 (anatase). These properties can only apparently be influenced by the addition of V_2O_5. No results on this have yet been discussed in the literature to date. Only a few projects deal with catalyst systems consisting of vanadium/tungsten oxides or vanadium/molybdenum oxides on titania. Unfortunately the mixing ratios in these projects were selected so unfavorably that vanadium constitutes more than 80% of the supported species and therefore does not bear any significant resemblance to the industrial catalysts. Here in particular, the impression is far more that the detection limits of the analytical methods used in each case was the determining factor for the vanadium contents set. The high dispersion of the supported oxides considerably restricts an exact determination of the surface species by conventional methods. It has not yet been possible to demonstrate a direct interaction between species such as vanadate and molybdate on oxidic supports, which is possible as a general rule for unsupported systems. A series of interesting experimental results is known for systems which very nearly match the composition of industrial catalysts, even though these results could be criticized for the excessive attention to bulk characteristics. In the case of arsenic oxide resistant DeNO$_x$ catalysts, these investigations are particularly pertinent to the molybdenum oxide/vanadium oxide systems [33,40–43].

6. SCR of NO$_x$ by hydrocarbons is still restricted by obstacles in material development

Ammonia or its analogs were reported to be the only reducing agent for SCR of NO$_x$ in an oxidizing atmosphere before the discovery of SCR by hydrocarbons [44]. A variety of ion-exchanged zeolites such as Cu, Fe, Pt, Co, Ga, Ge and H exchanged zeolites are summarized in a review article of Amiridis et al. [45] as being active for SCR catalysis by hydrocarbons. Non-zeolitic systems were also reported elsewhere. But at least currently most of these catalytic systems do not posses sufficient activity for commercial application. Although Cu–ZSM-5 is an active catalyst for the selective reduction of NO by hydrocarbons in the presence of oxygen, there are significant limitations to its use in commercial applications, primarily due to the inhibiting effect of water, its low hydrothermal stability and the vulnerability to poisoning by SO_2. It should also be considered that selectivity is obtained only with selective hydrocarbons. Noble metal based catalysts appear to overcome most of these problems, but still face additional ones due to their narrow window of operability and high selectivity for N_2O formation and oxidation of SO_2 to SO_3.

7. Experimental and theoretical efforts to improve selective catalytic decomposition (SCD) of NO

Efforts to improve on SCR technology are receiving worldwide attention. The principle of SCD is superior to the other nitrogen oxide conversion methods. Recently, the catalytic activity of metal-exchanged zeolites was discovered [46–48]. The initial impetus came from the discovery by Iwamoto and Yahiro [49] that Cu–ZSM-5 catalyzes the decomposition of NO into N_2 and O_2. Cu(II)-exchanged ZSM-5 in particular exhibited remarkable stability and high decomposition rates [50–53]. Iwamoto found Cu(I) to be the active site of the catalyst. This scheme does not explain the process of NO decomposition. Although many experimental attempts have been made to explain the decomposition, the data did not lead to an exact mechanism explaining charge transfer and decomposition in detail. Copper dinitrosyls and nitrosyl–nitric complexes have been detected as adsorption complexes under an NO atmosphere at low and high temperatures, but no evidence has been presented indicating that they are real reaction intermediates [54,55]. Regarding NO decomposition, there is currently no discussion as to whether all reaction steps are catalyzed or if some of them take place in the homogeneous gas phase.

Yokomichi et al. [56] recently performed theoretical studies. Using ab initio quantum chemical methods, they proved that Cu is activated by the zeolite skeleton and reproduced the poisoning of the catalyst by oxygen. A simple model was used for these calculations; zeolite was modeled by $Al(OH)_4^-$ binding Cu(I) as an active site. A cluster of Cu^+–OH–Cu^+ was also tested as an active site model. The group stated that the limitations of these models prevented them from explaining the decomposition route of NO.

The homogeneous gas reaction of $NO \rightarrow N_2+O_2$, which is thermodynamically preferred, is nearly completely inhibited by its high activation energy. The modest yield can be increased if it is possible to lower the activation energy with the use of catalysts. Unfortunately, current yields from Cu–ZSM-5 are still too

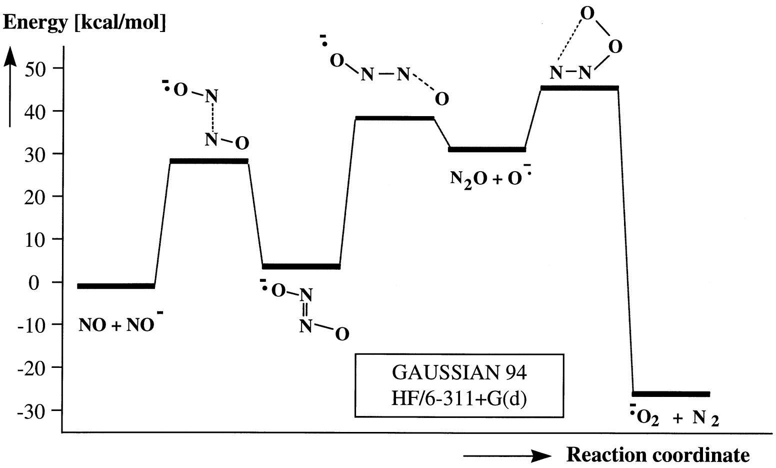

Fig. 7. Mechanism of NO decomposition via $N_2O_2^-$.

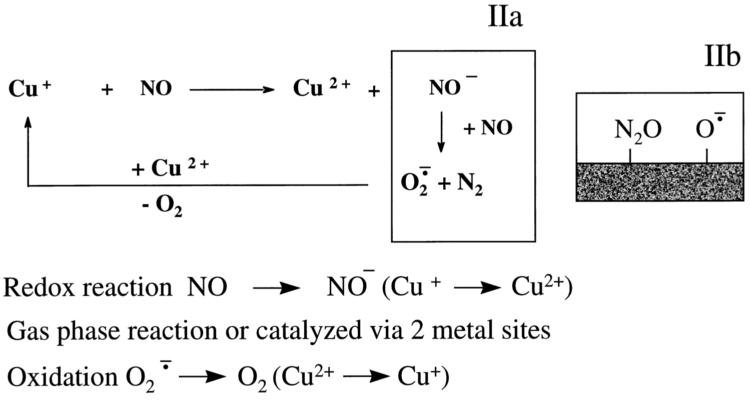

Fig. 8. Proposed reaction scheme for NO decomposition via homogeneous gas reaction step (IIa) and catalytic reaction step (IIb).

low for practical applications. Although much work has been done on kinetic studies, little is known about the molecular properties of the catalytic process. A semi-empirical calculation was therefore performed to obtain an overview of the reaction path with respect to intermediates and activation energies [57]. *Trans* and *cis* complexes are discussed on the basis of this calculation. But the homogeneous gas phase reaction favors *trans* complexes along the reaction path $NO^- + NO \rightarrow O_2^- + N_2$ (Fig. 7). Only the subsequent reaction step $N_2O + O^- \rightarrow N_2 + O_2$ requires metal sites if supported catalytically (Fig. 8). However, there is considerable room for improvement, especially when one considers that there is basically no scientific understanding of this technology and that there is a need for theoretical efforts to support further materials development [58–61].

8. Conclusions

Extensive efforts continue to be made in exploring the improvement of both transition and noble metal catalysts for selective catalytic reduction (SCR) of NO_x by hydrocarbons, including durability under such realistic operating conditions as the presence of 10–15% H_2O and 25–50 ppm SO_2. Significant efforts have been also directed towards understanding the associated reaction mechanisms. Material development is needed before a breakthrough for applications such as catalytic converters for diesel trucks and passenger cars can become a reality. Efforts to replace SCR technology with NH_3 and its homologs are receiving worldwide attention. Although the reaction scheme proposed by Iwamoto looks very simple at the first glance, it gives rise to speculations regarding adsorption and desorption at the catalytic sites. But details of the charge transfer effects are also still unknown. Concerning NO decomposition, there is currently no discussion of whether all reaction steps are catalyzed or if some are performed in a homogeneous gas reaction. The mechanism of NO decomposition is still under discussion. The results have been obtained at far from realistic conditions such as the presence of O_2, H_2O and SO_2. The first choice for NO_x abatement is therefore SCR catalysis with ammonia and its homologs. Critical examination is needed for further promotion of advanced SCR technology.

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