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Inhibiting and deactivating effects of water on the selective catalytic reduction of nitric oxide with ammonia over $\text{MnO}_x/\text{Al}_2\text{O}_3$

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Abstract

The effect of water on the selective catalytic reduction (SCR) of nitric oxide with ammonia over alumina supported with 2–15 wt.-% manganese oxide was investigated in the temperature range 385–600 K, with the emphasis on the low side of this temperature window. Studies on the effect of 1–5 vol.-% water vapour on the SCR reaction rate and selectivity were combined with TPD experiments to reveal the influence of water on the adsorption of the single SCR reactants. It turned out that the activity decrease due to water addition can be divided into a reversible inhibition and an irreversible deactivation. Inhibition is caused by molecular adsorption of water. TPD studies showed that water can adsorb competitively with both ammonia and nitric oxide. Additional kinetic experiments revealed that adsorbed ammonia is present in excess on the catalyst surface, even in the presence of water. Reduced nitric oxide adsorption is responsible for the observed reversible decrease in the reaction rate; the fractional reaction order changes from 0.79 in the absence of water to 1.07 in its presence. Deactivation is probably due to the dissociative adsorption of water, resulting in the formation of additional surface hydroxyls. As the amount of surface hydroxyls formed is limited to a saturation level, the deactivating effect on the catalyst is limited too. The additional hydroxyls condense and desorb in the temperature range 525–775 K, resulting in a lower degree of deactivation at higher temperature. A high temperature treatment at 775 K results in a complete regeneration. The amount of surface hydroxyls formed per unit surface area decreases at increasing MnO_x -loading. The selectivity to the production of nitrogen is enhanced significantly by the presence of gas phase water.

Keywords: Ammonia; Water; Deactivation; Inhibition; Manganese oxide; Nitric oxide reduction

1. Introduction

Today, selective catalytic reduction (SCR) of nitric oxide with ammonia is one of the most effective ways to remove NO_x from flue gases produced by stationary

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sources. As a result of intensive research, catalysts based on V_2O_5/TiO_2 have been successfully commercialised [1]. A disadvantage of most catalyst systems studied is the high operating temperature (> 575 K). As a consequence, reheating of the stack gases is unavoidable if application of SCR catalysts in add-on units is desired. Hence, the search for catalysts active at low temperatures (< 473 K) continues. A recent study, performed at our laboratory [2], revealed that alumina supported manganese oxides are very active in the temperature range 383–575 K. Besides, nitrous oxide formation is almost absent up to 575 K at low manganese loadings [3]. Because of these interesting properties we analysed these catalysts in more detail.

Stack gases always contain a considerable amount of water (5–25 vol.-%). Despite the considerable amount of research in the area of SCR catalysts little attention has been paid to the impact of water on the catalyst performance. Most of the SCR studies on the effect of water were performed at temperatures above 473 K [4–8]. Often, a limited decrease in catalyst activity was observed, the effect being more pronounced at the low temperature side of the experimental window.

Some authors found, on various catalyst systems, that water decreased the SCR reaction rate reversibly [6,7,9] due to competitive adsorption on active sites, mostly on ammonia adsorption sites. However Li et al. [8], studying the effect of water on the reduction of nitric oxide with methane, demonstrated that water could adsorb competitively with nitric oxide too, which was confirmed by adsorption experiments followed by TPD.

Turco et al. [5] argued, on the basis of kinetic studies, the effect of water to be irreversible. However, they did not investigate the long-term consequences of this irreversible adsorption on the reaction rate.

A few studies have dealt with the effect of water on SCR catalysts operating at temperatures below 473 K. For Cu-exchanged Y-zeolite [10], $NiSO_4/Al_2O_3$ [11], unsupported CrO_x [12] and V_2O_5/TiO_2 [13] the reaction rate decreases considerably during addition of water. In all cases the activity is restored after removal of water from the gas stream, suggesting reversible water adsorption, in competition with at least one of the SCR reactants.

A positive effect of the presence of water is the enhanced selectivity towards nitrogen production. Topsøe et al. [4] argued that on V_2O_5/TiO_2 the intermediate NH_xNO complex dehydrates under wet conditions, while it dehydrogenates under dry conditions. Odenbrand et al. [7] attributed the enhanced selectivity to a lower number of oxygen vacancies in the presence of water, which leads to less dissociative adsorption of ammonia and hence to less nitrous oxide formation. On unsupported CrO_x gas phase water is supposed to inhibit undesired reactions, like non-selective reduction to nitrous oxide and ammonia oxidation, more strongly than the SCR reaction [12].

On the surface of $\gamma-Al_2O_3$ distinct types of surface hydroxyls can be present [14,15]. Besides, at low temperatures physically adsorbed water is present, as well as some water chemisorbed on O^{2-} -sites on the $\gamma-Al_2O_3$ lattice. Rossi et al. [16]

observed that on a dry surface of α - Al_2O_3 water initially adsorbs irreversibly on the strongest Lewis acid sites. The total amount of irreversibly bound water decreased with increasing adsorption temperature. Continued addition of water resulted in reversible adsorption. Egashira et al. [17,18] examined the adsorption of water on other oxidic surfaces like TiO_2 and SnO_2 . On TiO_2 the features are comparable to γ - Al_2O_3 . In their TPD experiments [17] these authors observed the presence of physically adsorbed H_2O , chemisorbed H_2O on surface oxygen by H-bonding, and surface hydroxyls formed by dissociative adsorption of water.

Very little was reported on the adsorption of water on supported manganese oxides. Baltanas et al. [19] suggested that water might affect the total amount of coordinatively unsaturated sites. Furthermore, water can hydrolyse the Al–O–Mn bonds at 573 K; the hydrolysis of the metal oxide-support bond was also observed on $\text{CrO}_x/\text{SiO}_2$ systems [20], resulting in clustering of the metal oxide phase. According to Kanungo [21] unsupported MnO_2 loses all physically adsorbed water below 473 K and all chemically adsorbed water and surface hydroxyls at 673 K.

In this paper the effect of water on the activity of and the selectivity for the SCR reaction of γ - Al_2O_3 -supported manganese oxides will be reported in the temperature range 383–698 K, with emphasis on the low temperatures (383–473 K). Moreover, adsorption studies of water and of single SCR reactants in the absence and presence of water, followed by TPD, are carried out to describe the nature of the observed phenomena.

2. Experimental

2.1. Catalysts

The catalysts were prepared by incipient wetness impregnation of dried γ - Al_2O_3 (Ketjen CK300, $S_{\text{BET}} = 194 \text{ m}^2 \text{ g}^{-1}$, pore volume $0.5 \text{ cm}^3 \text{ g}^{-1}$, particle size 177–250 nm) of an aqueous solution of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Aldrich). The catalysts were subsequently dried in air at 400 K and calcined in pure O_2 for 1 h at 573 K and for 3 h at 773 K. Due to the limited solubility of the acetate precursor the impregnation procedure was carried out in several steps with drying in-between. Samples of 1, 2, 6 and 15 wt.-% Mn-loading were prepared by this method.

MnO_2 and Mn_2O_3 , prepared by decomposition of MnCO_3 (Aldrich) according to [22], were used as reference materials.

2.2. Gases

0.40 vol.-% NO/He , 0.40 vol.-% NH_3/He , O_2 (2.6) and He (4.6) were used during the study (UCAR). The O_2 was dried before use by molecular sieves (5A, Janssen Chimica).

2.3. Activity tests

The effect of water on the SCR reaction rate was measured in a set-up described elsewhere [23] containing a flow reactor connected on-line with a mass spectrometer (UTI 100C). The connecting tubing was heated at 385 K to avoid adsorption on the walls.

Before the catalytic tests the samples, containing equal amounts of Mn (1.2 mg), were pre-treated in-situ in 2 vol.-% O₂/He at 673 K during 1 h. Subsequently, the samples were cooled down to reaction temperature at which the standard reaction mixture was added, containing 500 ppm NO, 550 ppm NH₃, 2% O₂ with He being the balance gas; VHSV = 25 000 h⁻¹. Previous measurements and calculations [24,25] indicated that under these conditions internal and external mass transfer limitations can be excluded.

As soon as steady state conditions at a specified temperature were reached (10–15 h) water was added to this mixture by means of a diffusion cell, according to Fortuin [26]. 1–5 vol.-% of H₂O could be added in this way. After stabilisation of the nitric oxide conversion water was removed from the gas stream to find out whether the potential effects of water addition were reversible. The temperature was varied from 383 to 698 K. Moreover, reaction kinetics were established at 423 K in mixtures containing 75–1500 ppm NO, 75–1500 ppm NH₃, 0.25%–5% O₂, 1%–4% H₂O.

2.4. Temperature-programmed desorption

For TPD experiments the same apparatus was used as for activity experiments. Each experiment started with a pre-treatment in 2 vol.-% O₂/He up to 773 K. Subsequently, the sample, containing 100 mg of catalyst, was cooled down to 323 K in the same atmosphere. At this temperature a gas mixture containing 1000 ppm NO + 2% O₂ in He or 1000 ppm NH₃ in He was passed over the catalysts until saturation of the catalyst surface was reached, as apparent from the MS data. This adsorption step was carried out both in the absence and presence of 1 vol.-% H₂O in the gas stream. Subsequently, the sample was purged in He for about 60 min to remove all physisorbed species. Finally, TPD was carried out in pure He at a heating rate of 5 K min⁻¹ up to 773 K, followed by a 1 h isothermal period. All flow rates were 50 cm³ min⁻¹.

TPD experiments were also performed after suddenly stopping the SCR reaction at 423 K. Samples were compared after (see also Fig. 1):

Stage (I) reaction during 15 h in a standard reaction mixture.

Stage (II) Stage (I); followed by 3 h standard conditions in the presence of 2 vol.-% H₂O, followed by 3 h standard conditions.

Stage (III) Stage (I); followed by 3 h standard conditions in the presence of 2 vol.-% H₂O.

Some TPD experiments were performed in a thermobalance, Setaram TG 85. In this case only the adsorption of 0.5–2.0 vol.-% H₂O in Ar was measured at low temperature (323–473 K), followed by TPD in Ar. The samples contained 60 mg of catalyst. The flow rate was 150 cm³ min^{−1}.

2.5. X-ray diffraction (XRD)

XRD spectra were recorded after exposure to 2.5 vol.-% H₂O in air during 170 h. A Philips diffractometer 1710 with Cu K α radiation was used, equipped with a Ni filter to remove the Cu K β radiation.

2.6. BET/N₂ adsorption

BET surface area measurements were performed with a Carlo Erba Sorptometric 1800 after outgassing the samples in vacuum at 473 K. The specific surface area was calculated from the extent of N₂ sorption at 77 K at relative pressures from 0.03 to 0.35.

2.7. Mercury porosimetry

Mercury porosimetry measurements were performed with a Carlo Erba 4000 porosimeter. A wetting angle of 141.3° and a surface tension of 480 mN m^{−1} for mercury was used.

3. Results and discussion

3.1. Expressions of activity

The effect of water on the reaction rate is expressed by a normalized rate constant. In a separate study [24] the kinetics of the SCR reaction were estimated under dry conditions. In its most simple form the reaction rate can be expressed as the following power rate law:

$$r_{\text{NO}} = k p_{\text{NO}}^{\alpha} p_{\text{NH}_3}^{\beta} p_{\text{O}_2}^{\gamma} \quad (1)$$

where k is the reaction rate constant and p_{NO} , p_{NH_3} and p_{O_2} are the partial pressures of nitric oxide, ammonia and oxygen, respectively. At 423 K, the values of the apparent reaction orders α , β and γ are as follows: $\alpha = 0.79$, $\beta = -0.04$, $\gamma = 0.51$. As a result of the approximately zero order in ammonia the ammonia dependency can be neglected. Because of the excess O₂ in all the experiments the O₂ partial pressure term can be replaced by a constant. Hence, Eq. (1) can be reduced to:

$$r_{\text{NO}} = k' p_{\text{NO}}^{\alpha} \quad (2)$$

in which $k' = k p_{\text{O}_2}^\gamma$.

According to Eq. (3):

$$\frac{W}{F_{\text{NO}}} = \int_0^X \frac{dX}{k' \alpha_{\text{NO}}} \quad (3)$$

where W is the amount of Mn (kg), F_{NO} is the molar flow rate of nitric oxide at the entrance of the reactor (mol s^{-1}) and X is the nitric oxide conversion, k' can be determined in the absence and presence of water. The effect of water is then expressed using a normalized reaction rate constant: k'/k'_{ref} ; k'_{ref} represents the rate constant of a reference sample to which no water was added.

In the absence of water, alumina supported manganese oxides show a slowly progressing deactivation during the first 600 h on stream [2]. By use of the factor k'/k'_{ref} this decline is subtracted from the decline due to water addition.

3.2. Two effects of water

The impact of water addition on the SCR reaction rate of a 2 wt.-% Mn/Al₂O₃ sample is demonstrated in Fig. 1. Upon addition of water the SCR rate constant decreases instantaneously to about 30% of its original level, at which it stabilises

Fig. 1. Normalized SCR rate constant as a function of time; $T = 423 \text{ K}$; 2 wt.-% Mn/Al₂O₃; 3 times addition of 2 vol.-% H₂O.

Fig. 2. Normalized SCR rate constant before (filled), during (hatched) and after (crosshatched) supply as a function of H₂O content; $T = 423$ K; 2 wt.-% Mn/Al₂O₃.

quickly (Stage III in the plot). Upon removal of the water supply the activity is rapidly restored to about 80–85% of its original level (Stage II). After repeated cycles the same stable activity levels are reached. The effect of water can clearly be divided in a reversible ‘inhibition’ and an irreversible ‘deactivation’. The original rate constant is not reached again, even after 140 h. The deactivated state of the catalyst is attained after one cycle of water addition. Hereafter, water only exhibits an inhibitive effect on the SCR activity.

Inhibition by water becomes stronger at increasing water content in the gas stream, as shown in Fig. 2. In contrast, the degree of deactivation is independent on the water content supplied before. After all treatments the catalyst can be completely regenerated by heating in He up to 773 K.

To investigate the way in which water adsorbs on the surface of a 2 wt.-% Mn/Al₂O₃ and the γ -Al₂O₃ support, TPD profiles were recorded after saturation of the surface with water vapour at 323 K. The profiles are shown in Fig. 3. Two bands can be distinguished: a sharp peak with a maximum at 404 K and a less pronounced band at 550–750 K. The profiles are quite similar, except for a slightly more intense desorption in the 425–650 K range from the γ -Al₂O₃ support. According to previous studies on the adsorption of water on Al₂O₃ and TiO₂ surfaces [14,16,17] the peak at 404 K can be assigned to the desorption of molecularly adsorbed water. Egashira et al. [17] observed separate peaks of physically adsorbed and chemisorbed water after adsorption at 273 K on TiO₂. According to Peri [14] water can be physically adsorbed at temperatures below 373 K. The adsorption enthalpy of the water species desorbing at 404 K in our experiments was determined by the method of Kovalinka

Fig. 3. TPD after adsorption 1 vol.-% H_2O at 323 K; 2 wt.-% $\text{Mn}/\text{Al}_2\text{O}_3$ (—) and $\gamma\text{-Al}_2\text{O}_3$ (---).

et al. [27] and turned out to be 53 kJ mol^{-1} . Compared to the heat of vaporisation of water at 373 K, 43.8 kJ mol^{-1} , one may conclude that the peak at 404 K represents at least partly the desorption of (molecularly) chemisorbed water. The band at 550–750 K in Fig. 3 can be assigned to the condensation and subsequent desorption of surface hydroxyls [14,16,17]. It should be noted that at 775 K the surface of $\gamma\text{-Al}_2\text{O}_3$ is still covered by 25–35% of a monolayer of (mainly isolated) hydroxyls [15]; as these hydroxyls are already present on the surface after calcination at 775 K and remain after regenerations at this temperature they are not involved in the discussion about the adsorption of gas phase water on the surface.

Taking into account the reaction temperature used in our studies up to here (423 K), the inhibiting effect of water may be ascribed to the molecular adsorption of water. The stronger inhibition observed at increasing water concentrations can also be explained by reversible molecular adsorption.

The deactivating effect of gas phase water could in principle be attributed to:

1. molecular adsorption in micropores, which are emptied very slowly after removal of gas phase water.
2. hydrolysis of the Al–O–Mn bonds leading to sintering of the MnO_x -phase.
3. the formation of surface hydroxyls which are stable up to 525–775 K.

As determined by BET/ N_2 adsorption, the $\gamma\text{-Al}_2\text{O}_3$ support does not contain pores with radii smaller than 2 nm. Analysis of the supported manganese oxide catalysts by mercury porosimetry showed that these catalysts contain few pores with radii in the 2–4 nm range. By consequence, molecular adsorption in micropores, which are very slowly emptied after removal of gas phase water (option 1) can be rejected as possible cause of the deactivation by H_2O .

Two kinds of experiments were performed to discriminate between options 2 and 3. To determine whether sintering occurs, XRD patterns were recorded. However, the XRD pattern of a fresh 2 wt.-% Mn/Al₂O₃ catalyst hardly shows any crystallinity. Sintering due to the presence of water in the gas phase can occur without passing the detection limit of XRD. For that reason, a 6 wt.-% sample was investigated, which shows already some MnO_x lines before water addition; if sintering occurs sharpened diffraction lines are expected. Samples of Al₂O₃, 2 and 6 wt.-% Mn/Al₂O₃ were treated by a 2.5 vol.-% H₂O/air mixture at 423 K during 170 h. After this period XRD spectra were recorded. The spectra do not show any increased crystallinity with respect to the fresh, calcined samples (even for the 6 wt.-% Mn-sample), so sintering seems unlikely.

Repeating the experiment of Fig. 1 at different temperatures is thought to be more decisive on the question whether deactivation is caused by sintering or by the formation of surface hydroxyls. Sintering is expected to increase at elevated temperatures, whereas surface hydroxyls will desorb better at higher temperatures resulting in a lower degree of deactivation.

In Fig. 4 the normalised reaction rate constant of a 2 wt.-% Mn/Al₂O₃ sample during and after the supply of 2 vol.-% H₂O at different temperatures is shown. Inhibition decreases already between 383 and 550 K as a result of reduced molecular adsorption of water. The degree of deactivation is constant up to 550 K, but decreases above this temperature; by consequence, sintering is very unlikely as a cause for deactivation. At 698 K inhibition and deactivation are negligible. Hence, both the reduced degree of deactivation and the desorption of the additionally

Fig. 4. Normalized SCR rate constant before (filled) during (hatched) and after (crosshatched) supply 2 vol.-% H₂O as a function of temperature; 2 wt.-% Mn/Al₂O₃.

formed surface hydroxyls occur in the same temperature range. At 698 K the normalized rate constant even exceeds unity during water addition; due to the stronger suppression of the ammonia oxidation to nitric oxide by water (see also Section 3.5) the observed nitric oxide conversion becomes higher in the presence of water. Rossi et al. [16] studied the adsorption of water on α - Al_2O_3 at 473–773 K by microcalorimetry. They observed an irreversible adsorption at very low water pressures, followed by a pressure dependent reversible adsorption. Furthermore, in the temperature range 473–673 K, the amount of irreversibly adsorbed water tends to decrease with increasing temperature. These findings correspond rather well with the assumption that the deactivation shown in Fig. 1 is caused by the formation of the surface hydroxyls that do not leave the surface at temperatures below 550 K. Moreover, the fact that after all treatments regeneration can be achieved by heating the sample up to 775 K provides additional support for this hypothesis. Rossi et al. [16] noticed that part of the irreversibly bound water at 473 K becomes reversibly bound at higher temperatures. This behaviour may be responsible for the fact that inhibition is still observable at temperatures above 550 K in our experiments. In the past, Haldeman and Hemett [28] reported that the amount of irreversibly adsorbed water at 423 K is independent on the water concentration above 0.5 vol.-%. Following the assumption that the deactivation is caused by irreversible (dissociative) adsorption of water, this result is in agreement with the fact that the degree of deactivation is independent on the water content in the gas stream, as shown in Fig. 2.

3.3. Inhibition by water

Inhibition of the adsorption of the single SCR reactants

The inhibition of the SCR reaction by molecularly adsorbed water was examined in more detail. Attention was focused on the question whether the reversible decrease in reaction rate is attributable to reduced adsorption of ammonia or nitric oxide or of both by the presence of water vapour. In Fig. 5 and Fig. 6 TPD profiles are shown after adsorption of the single SCR reactants at 323 K in the absence and presence of 1 vol.-% H_2O . Desorbed quantities of the different components are reported in Table 1. As shown before at higher Mn-loadings [29], ammonia desorbs in a broad temperature range (Fig. 5), characteristic for the presence of several (up to five) adsorbed ammonia species differing in thermal stability on (low loaded) γ - Al_2O_3 surfaces [30]. In the presence of water the ammonia adsorption decreases considerably, in agreement with the competition between ammonia and water reported on other oxidic surfaces [5,9,31,32]. This competition mainly concerns the adsorption of the weakly bound ammonia species. Nitric oxide does not adsorb on $\text{MnO}_x/\text{Al}_2\text{O}_3$ in any significant amounts in the absence of oxygen [29]. Hence, the influence of water on the nitric oxide adsorption was studied in the presence of O_2 . As observed before [33] nitric oxide can adsorb in two modes in the presence of oxygen. The TPD profile of Fig. 6 shows two peaks, situated at

Fig. 5. TPD after adsorption 1000 ppm NH_3 without (—) and with (---) 1 vol.-% H_2O at 323 K; 2 wt.-% $\text{Mn}/\text{Al}_2\text{O}_3$.

Fig. 6. TPD after adsorption 1000 ppm NO + 2 vol.-% O_2 without (—) and with (---) 1 vol.-% H_2O at 323 K; 2 wt.-% $\text{Mn}/\text{Al}_2\text{O}_3$.

400 K and 615 K respectively, representing two adsorption modes of different thermal stability. In the presence of water, the adsorption of both modes is ham-

Table 1

Amounts desorbed ammonia and nitric oxide during TPD after adsorption at 323 K in the absence/presence of 1 vol.-% H₂O; 2 wt.-% Mn/Al₂O₃

TPD	Adsorption in the absence of H ₂ O ($\times 10^{-6}$ mol m ⁻²)	Adsorption in the presence of H ₂ O ($\times 10^{-6}$ mol m ⁻²)
NH ₃	2.16	1.13
NO 400 K	0.87	0.63
NO 615 K	1.55	0.28
NO total	2.42	0.91

pered, especially the thermodynamically more stable mode. This competition is in agreement with the nitric oxide adsorption phenomena on Co-ZSM-5 observed by Li et al. [8]. In summary, it appears that at low temperatures water can inhibit the adsorption of both nitric oxide and ammonia on MnO_x/Al₂O₃ catalysts.

Inhibition of the adsorption of the SCR reactants under reaction conditions

It is not clear whether the inhibition of both nitric oxide- and ammonia adsorption takes place under SCR standard conditions at 423 K. To investigate the role of water during the SCR reaction TPD was performed after abruptly stopping the SCR reaction. Three samples are compared:

1. one that was never exposed to gas phase water ('dry' sample: stage I in Fig. 1)
2. one that was exposed to gas phase water during 3 h after which dry standard conditions were supplied before stopping the reaction (deactivated sample: stage II in Fig. 1)
3. one that was exposed to gas phase water during 3 h after which the SCR reactants and water were removed simultaneously from the gas stream (inhibited sample: stage III in Fig. 1).

The results for a 2 wt.-% Mn/Al₂O₃ are presented in Fig. 7, Fig. 8 and Fig. 9. The amounts of the desorbed components are given in Table 2. In Fig. 7 the TPD profiles of water are shown. The amount of surface hydroxyls desorbing from the samples that were exposed to water is significantly higher compared to the desorption from the sample only exposed to SCR reaction water. This observation confirms the presence of additional surface hydroxyls in the deactivated state of the catalyst. The difference in the water desorption profiles between the inhibited and deactivated sample is demonstrated in the temperature region 430–530 K. A large amount of molecularly bound water is desorbing from the inhibited sample. In contrast, hardly any molecularly adsorbed water desorbs from the deactivated sample, due to its ability to desorb until a new equilibrium between the partial pressures of the SCR reactants and their partial coverages on the surface is established. These features form additional proof for the assumption that molecularly bound water is responsible for the (reversible) inhibition of the SCR reaction.

In Fig. 8 the TPD profiles of ammonia are shown. The amount of ammonia desorbing from the surface of a deactivated sample is slightly less than from the

Fig. 7. TPD after abruptly stopping the SCR reaction at 423 K; water concentration as a function of the temperature; 2 wt.-% Mn/Al₂O₃. A 'dry' (—), deactivated (---) and inhibited (.....) sample.

Fig. 8. TPD after abruptly stopping the SCR reaction at 423 K; ammonia concentration as a function of temperature; 2 wt.-% Mn/Al₂O₃. A 'dry' (—), deactivated (---) and inhibited (.....) sample.

fresh sample. Probably, the additional surface hydroxyls block some ammonia adsorption sites. Significantly less ammonia desorbs from the surface of the inhibited sample. Especially the adsorption of weakly bound ammonia, desorbing in the

Fig. 9. TPD after abruptly stopping the SCR reaction at 423 K; nitrogen concentration as a function of temperature; 2 wt.-% Mn/Al₂O₃. A 'dry' (—), deactivated (---) and inhibited (.....) sample.

temperature range 425–525 K, is strongly inhibited by the presence of water vapour. The competition for adsorption sites between ammonia and water is clearly shown by comparing the Fig. 7 and Fig. 8. On the surface of the inhibited sample molecular water is abundant while it contains hardly any weakly adsorbed ammonia. On the surface of the deactivated sample the ammonia adsorption is largely restored while molecularly adsorbed water is removed.

As observed before [29,33] nitric oxide reacts almost completely to N₂ and desorbs as such in the presence of adsorbed ammonia. As a result of the excess ammonia on the surface [25], the N₂ profile in Fig. 9 represents the amount of adsorbed nitric oxide during reaction conditions quite well (oxidation of ammonia to N₂ is negligible up to 600 K [3]). Moreover, previous results have shown [24] that the nitric oxide species desorbing at high temperature (peak at 615 K in Fig. 6),

Table 2

Amounts of desorbed water, ammonia and nitrogen during TPD after abruptly stopping the SCR reaction at 423 K; 2 wt.-% Mn/Al₂O₃ catalyst

TPD	desorption 'dry' sample ($\times 10^{-6}$ mol m ⁻²)	desorption deactivated sample ($\times 10^{-6}$ mol m ⁻²)	desorption inhibited sample ($\times 10^{-6}$ mol m ⁻²)
H ₂ O	10.4	14.2	15.4
NH ₃	2.05	1.75	1.07
NO 350–500 K	0.17	0.15	0.03
NO 500–700 K	0.29	0.24	0.24
NO total	0.46	0.39	0.27

reacts with adsorbed ammonia to form N_2 at a considerably lower temperature (500–550 K). During TPD the total amount of desorbed N_2 is low compared to the amount of desorbed ammonia (Table 2), showing the excess ammonia present on the surface during SCR reaction conditions. The desorption profile of the deactivated sample does not differ significantly from the profile of the ‘dry’ sample. In contrast, the desorption profile of the inhibited sample shows hardly any N_2 formed from the reaction between weakly bound nitric oxide (low temperature peak in Fig. 6, i.e., completely desorbed at 500 K) and adsorbed ammonia. The amount of nitric oxide adsorbed in this form is reduced by about 82% by the presence of water. All evidence presented up to here point to the conclusion that under SCR conditions at 423 K the adsorption of both reactants is strongly inhibited by the presence of gas phase water.

Influence of water on the reaction kinetics

It is not possible to determine at this stage whether inhibition of nitric oxide or ammonia adsorption by water is responsible for the reversible decrease in activity shown in Fig. 1 and Fig. 2. Therefore reaction kinetics were determined on a 2 wt.-% Mn/ Al_2O_3 over a wide concentration range at 423 K. Samples in stage I, II and III (Fig. 1) were compared. The reaction rate can be expressed in the form of a power rate law:

$$r_{NO} = k p_{NO}^{\alpha} p_{NH_3}^{\beta} p_{O_2}^{\gamma} p_{H_2O}^{\delta} \quad (4)$$

The fractional orders α , β , γ and δ were determined by combining a Simplex and a Levenberg–Marquardt algorithm and are presented in Table 3. As expected, the reaction order in water is strongly negative. The reaction order with respect to ammonia is approximately zero, which can be explained by an excess of adsorbed ammonia present on the surface. Despite the significant inhibition of the ammonia adsorption by water (Fig. 8) the reaction rate is not affected by the reduced ammonia coverage: the reaction order in ammonia remains zero in the presence of water, whereas the reaction order in nitric oxide increases significantly in the presence of water. The inhibition of the weak nitric oxide adsorption, as shown in Fig. 9, seems to be relevant for the inhibiting effect of water on the SCR reaction rate. Moreover, the reaction order in nitric oxide increases in the presence of water indicating adsorbed nitric oxide as a likely intermediate in the SCR reaction. To validate this, a more detailed kinetic study is in preparation.

Table 3

Reaction orders according to power rate (Eq. (4)) of a 2 wt.-% Mn/ Al_2O_3 catalyst; T = 423 K

Sample	α	β	γ	δ
‘dry’	0.79 (± 0.028)	−0.04 (± 0.03)	0.51 (± 0.043)	
deactivated	0.81 (± 0.041)	−0.05 (± 0.03)	0.53 (± 0.060)	
inhibited	1.07 (± 0.076)	−0.05 (± 0.03)	0.62 (± 0.113)	−0.86 (± 0.157)

3.4. Deactivation by water

According to the above mentioned results the deactivation by water on $\text{MnO}_x/\text{Al}_2\text{O}_3$ catalysts can be ascribed to the formation of (additional) surface hydroxyls that do not leave the surface at temperatures below approximately 523 K. The impact of the additionally formed surface hydroxyls on the reaction kinetics can be evaluated from the results presented in Table 3 and Fig. 4. From the kinetic results reported in Table 3, it is clear that the fractional reaction orders with respect to the SCR reactants do not differ before and after water addition. The activation energies under these conditions were compared by constructing the Arrhenius plots from the measured reaction rates as a function of temperature (Fig. 4). The activation energy does not change after removing water from the gas stream, whereas the pre-exponential factor decreases slightly. These features can be explained assuming that a part of the active sites for SCR is irreversibly blocked by the formed hydroxyls, whereas others function in the same way as before.

Deactivation merely occurs during the first cycle of water addition (Fig. 1). Cyclic supply and removal of water from the gas stream does not result in further deactivation. Moreover, the degree of deactivation by water seems to be independent on the water pressure in the gas stream (Fig. 2). These observations indicate that the degree of deactivation is limited to a quickly reached maximum value. By consequence, the amount of surface hydroxyls that can be present on the catalyst surface should be limited. It is assumed that during water addition surface hydroxyls will be formed first; as soon as the surface is saturated, molecularly adsorbed water starts to build up. This pattern of water uptake on the surface was observed on $\alpha\text{-Al}_2\text{O}_3$ [16], TiO_2 [17,34] and SnO_2 [18]. To verify this hypothesis TGA profiles of a 15 wt.-% $\text{Mn}/\text{Al}_2\text{O}_3$ catalyst after water addition at 323 K during different exposure times were compared; see Fig. 10. Dry samples did not show weight loss during the TGA desorption experiments; hence, all weight loss from the water saturated samples is due to water desorption. Surface hydroxyls, desorbing in the temperature range 525–775 K, are formed during the first 30 min of water addition. Subsequently, only molecularly adsorbed water is taken up, as can be seen from the progressively growing peak at about 400 K at increasing periods of water addition. These features correspond fairly well with the above stated hypothesis. Catalysts at lower MnO_x -loadings and the $\gamma\text{-Al}_2\text{O}_3$ support itself exhibit similar adsorptive behaviour of water as a function of time.

Up to now the relative OH-distribution on the Al_2O_3 -sites and MnO_x -sites as a consequence of the dissociative adsorption of gas phase water is not clear. Therefore, the formation of surface hydroxyls was compared with samples with different MnO_x -loadings. Table 4 shows the quantities of surface hydroxyls desorbing (between 525 and 775 K) from the different samples after saturation with water at 323 K. The desorbed amount from $\gamma\text{-Al}_2\text{O}_3$ is comparable to a number of literature studies reviewed in [15]. Both $\gamma\text{-Al}_2\text{O}_3$ and unsupported Mn_2O_3 are able to adsorb water dissociatively to form surface hydroxyls. However, the amount of hydroxyls

Fig. 10. Differential weight loss as a function of temperature; TGA after adsorption 1.15 vol.-% H_2O at 323 K during 10 min (·····), 18 min (-----), 30 min (-.-.-) and 2 h (—) exposure time; 15 wt.-% $\text{Mn}/\text{Al}_2\text{O}_3$.

formed per unit surface area is (slightly) higher on $\gamma\text{-Al}_2\text{O}_3$ than on Mn_2O_3 . Alumina supported manganese oxides form intermediate amounts of hydroxyls. This experiment can not distinguish between surface hydroxyls formed on MnO_x -centres and Al_2O_3 -sites; it can only be stated that the amount of hydroxyls is reduced at increasing MnO_x -loading. An effect of the structure of the MnO_x -particles as a function of loading can not be excluded. As surface hydroxyls are presumed to be responsible for the deactivation by water one may expect a (slightly) higher deactivation at lower loadings. In Table 4 the normalized reaction rate constant after the removal of water from the gas stream is compared with catalysts with different Mn-loadings; it should be mentioned that the absolute reaction rates [i.e., per weight of Mn; see Eq. (3)] of these samples differ considerably. As expected, the degree of deactivation by water decreases as the amount of MnO_x on the surface increases.

Table 4

Amount of surface hydroxyls desorbed in temperature range 525–775 K after H_2O addition at 323 K and normalized reaction rate constant at 423 K after supply 2 vol.-% H_2O ; Mn-loading varied

Sample	Moles OH m^{-2} ($\times 10^{-6}$)	k'/k'_{ref}
Al_2O_3	5.75	
1 wt.-% $\text{Mn}/\text{Al}_2\text{O}_3$		0.75
2 wt.-% $\text{Mn}/\text{Al}_2\text{O}_3$	5.14	0.79
6 wt.-% $\text{Mn}/\text{Al}_2\text{O}_3$		0.85
15 wt.-% $\text{Mn}/\text{Al}_2\text{O}_3$	3.96	
Mn_2O_3	4.02	0.95

Whereas these results are in good agreement, the nature of the deactivating surface hydroxyls remains unclear. Catalytic activity is associated to MnO_x -centres (probably to coordinatively unsaturated sites [19]), so the enhanced formation of surface hydroxyls on Al_2O_3 -sites can not explain the stronger degree of deactivation by water on low loaded catalysts. Previously reported [29] IR spectra show that three types of (isolated) surface hydroxyls are present after activation at 623 K. However, under reaction conditions water is formed and a broad band of H-bridged hydroxyls determines the spectrum [29], obscuring the bands of the isolated hydroxyls. Addition and subsequent removal of gas phase water will further increase the amount of hydroxyls, which will disappear in the broad H-bridged OH-band in the spectrum. So, IR can not elucidate the nature of the additionally formed hydroxyls.

The difference between the surface hydroxyls formed by the dissociative adsorption of gas phase water and the surface hydroxyls already present on the surface (mainly as a result of the SCR reaction) has not been clarified. At stage I in Fig. 1 a steady state surface hydroxyl concentration and water vapour pressure have already been reached. At stage II, after one cycle of water addition/removal, leaving additional hydroxyls on the surface, a new steady state is reached. If the surface hydroxyls formed by the dissociative adsorption of gas phase water would be of the same type as the hydroxyls already present on the surface at stage I, stage II could not be stable. Apparently, stage II represents a stable situation, suggesting that the surface hydroxyls formed from gas phase water are different from those formed by the SCR reaction. The nature of isolated and hydrogen-bridged surface hydroxyls on $\gamma\text{-Al}_2\text{O}_3$ differing in acid-base properties has been reviewed extensively [15]. However, the deactivation caused by the additionally formed surface hydroxyls during exposure to water vapour can not be explained simply in terms of these properties.

3.5. Effect water on selectivity towards nitrogen production

Low loaded $\text{MnO}_x/\text{Al}_2\text{O}_3$ catalysts exhibit almost complete selectivity towards nitrogen production at 423 K [3]. The selectivity is determined from the concentrations at the reactor exit and is defined as:

$$S = \frac{[\text{N}_2]}{[\text{N}_2] + [\text{N}_2\text{O}]} \quad (5)$$

To determine the influence of water on the selectivity, experiments were carried out at a temperature (598 K) where selectivity is comparatively low (80% in the absence of water). Unsupported Mn_2O_3 shows a considerably lower selectivity at 423 K [35]; therefore the influence of water on the selectivity can be clearly observed at this temperature. The results are shown in Fig. 11. Clearly, water exhibits a reversible, positive effect on the selectivity, as was reported on other oxidic catalysts [7,12,13,32,36] too. The inhibition of the ammonia oxidation and

Fig. 11. Selectivity as a function of time before, during and after supply 2 vol.-% H₂O; 2 wt.-% Mn/Al₂O₃ at 598 K (□) and Mn₂O₃ at 423 K (○).

the non-selective catalytic reduction of nitric oxide appears to be stronger than the inhibition of the SCR reaction.

4. Conclusions

The effect of water on the reaction rate of the selective catalytic reduction of nitric oxide with ammonia over alumina supported manganese oxides at temperatures below 473 K is two fold: water exhibits both a reversible, inhibiting effect and an irreversible, deactivating effect.

Inhibition is caused by molecular adsorption of water. Both the adsorption of nitric oxide and of ammonia is inhibited by the presence of gas phase water. However, even in the presence of water an excess of adsorbed ammonia remains on the catalyst surface, as demonstrated by kinetic data. The decreased rate of the SCR reaction in the presence of water is due to reduced adsorption of weakly bound nitric oxide. Moreover, the fact that the presence of gas phase water results in a higher reaction order in nitric oxide suggests adsorbed nitric oxide to be a likely intermediate in the SCR reaction.

Deactivation by water is probably caused by the dissociative adsorption of water to surface hydroxyls. These surface hydroxyls do not leave the catalyst surface upon water removal from the gas stream at temperatures below 523 K. The amount of surface hydroxyls that can be formed is limited to a saturation concentration on

the surface. Consequently, the deactivation by gas phase water is limited too. On surfaces with higher MnO_x -loading less surface hydroxyls per unit surface area are formed; consequently deactivation decreases slightly at increasing MnO_x -loading. Possible chemical differences between the surface hydroxyls formed during water addition and the surface hydroxyls formed in the SCR reaction have not been elucidated yet.

The presence of gas phase water increases the selectivity of the SCR reaction to the production of N_2 . Apparently, non-selective reduction as well as ammonia oxidation is inhibited more strongly than selective reduction of nitric oxide.

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