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Activity and selectivity of pure manganese oxides in the selective catalytic reduction of nitric oxide with ammonia

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Abstract

Manganese oxides of different crystallinity, oxidation state and specific surface area have been used in the selective catalytic reduction (SCR) of nitric oxide with ammonia between 385 and 575 K MnO_2 appears to exhibit the highest activity per unit surface area, followed by Mn_5O_8, Mn_2O_3, Mn_3O_4 and MnO, in that order This SCR activity correlates with the onset of reduction in temperature-programmed reduction (TPR) experiments, indicating a relation between the SCR process and active surface oxygen Mn_2O_3 is preferred in SCR since its selectivity towards nitrogen formation during this process is the highest In all cases the selectivity decreases with increasing temperature The oxidation state of the manganese, the crystallinity and the specific surface area are decisive for the performance of the oxides The specific surface area correlates well with the nitric oxide reduction activity The nitrous oxide originates from a reaction between nitric oxide and ammonia below 475 K and from oxidation of ammonia at higher temperatures, proven by using $^{15}NH_3$ Participation of the bulk oxygen of the manganese oxides can be excluded, since TPR reveals that the bulk oxidation state remains unchanged during SCR, except for MnO, which is transformed into Mn_3O_4 under the applied conditions In the oxidation of ammonia the degree of oxidation of the nitrogen containing products (N_2, N_2O, NO) increases with increasing temperature and with increasing oxidation state of the manganese A reaction model is proposed to account for the observed phenomena

Key words ammonia oxidation, manganese oxides, selective catalytic reduction

INTRODUCTION

Manganese oxides are well known for their activity in oxidation reactions [1–4] This activity is ascribed to the ease by which they undergo changes in

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oxidation state. Recently, it was reported that supported manganese oxides are highly active for the selective catalytic reduction of nitric oxide with ammonia [SCR, eqn (1)], in the low temperature range of 380–570 K [5,6]

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

This activity has been reported before for pure MnO_2 by Markvart and Pour [7].

Several oxides of manganese are known, viz MnO_2, Mn_5O_8, Mn_2O_3, Mn_3O_4 and MnO, which are all stable at ambient conditions. The thermodynamic stability of these oxides increases in the given order with increasing temperature and decreasing partial pressure [8], a fact which can be made use of while preparing the different oxides

A recent study [5] with alumina supported manganese oxide, prepared from nitrate and from acetate precursors, revealed significant differences with respect to their SCR performance.

For these alumina supported catalysts two types of oxides were identified, one with an average stoichiometry of Mn_2O_3, prepared from manganese acetate, and the other with a stoichiometry approaching that of MnO_2, prepared from manganese nitrate Apart from nitrogen also nitrous oxide was observed as a product, especially at temperatures above 470 K

$$S = \frac{[N_2]}{[N_2] + [N_2O]} \times 100\% \quad (2)$$

The nitrogen selectivity, defined in eqn (2), decreased continuously with increasing loading for the ex-acetate catalyst, whereas the selectivity remained constant above 3 wt -% Mn loading for the ex-nitrate catalyst The results of these studies [5,9] indicated that the SCR activity and selectivity was related to the degree of dispersion and oxidation state of the manganese. This prompted us to investigate the behaviour of the different pure manganese oxides for the low-temperature SCR. The pure oxides turned out to have good activities for SCR, partly due to the fact that they can be prepared with significant specific surface areas, which makes them fairly unique model systems to investigate Several aspects, like the activity, the effect of oxygen on the nitric oxide conversion, the selectivity towards nitrogen formation, the ammonia oxidation, together with the characterization by temperature-programmed reduction (TPR) and X-ray diffraction (XRD) have been investigated in order to establish whether correlations exist with the oxidation state of the manganese and other factors like the crystallinity and the specific surface area

EXPERIMENTAL

Gases

0 40 vol.-% NO/He, 0.40 $^{15}NH_3$/He, 0 42 vol -% NH_3/He, O_2 (2.6) and He (4 6) were used during the study (UCAR) The oxygen was dried before use with molecular sieves (5 A, Janssen Chimica)

Catalysts

The unsupported manganese oxides, used as catalysts, were prepared in different ways, using three different precursors: manganese acetate tetrahydrate ($Mn(CH_3CO_2)_2 \cdot 4H_2O$, Aldrich), manganese nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$, Merck) and manganese carbonate ($MnCO_3$, Aldrich). In Table 1 the preparation methods are given for the model compounds used, as well as their specific surface area, determined by nitrogen adsorption at 77 K (BET method) The letter between brackets indicates whether the precursor used was manganese acetate (A), manganese nitrate (N) or manganese carbonate (C) MnO_2 (M), purchased from Merck, was also used

Mn_5O_8 was prepared from manganese citrate [12] by calcining it in oxygen for 8 h at 600 K. It could also be prepared by oxidation of Mn_3O_4 [8,15], but in this case the specific surface area was well below 1 m^2/g and it could not be used in this comparative study.

Activity measurements

The nitric oxide reduction measurements were carried out in an experimental set-up, described in more detail elsewhere [16]. The standard conditions of the activity measurements are given in Table 2.

Activity comparisons between the different unsupported manganese oxides have been carried out by dilution with γ-Al_2O_3 (Ketjen 000-1 5E CK 300, $S_{BET} = 200\ m^2\ g^{-1}$, $V_p = 0.5\ cm^3\ g^{-1}$, $d_p = 210\text{–}250\ \mu m$) and by keeping the total BET (N_2) area of the manganese oxide sample in the reactor constant (0 28

TABLE 1

Model compounds used in this study, their preparation method and XRD identification

		S_{BET} ($m^2\ g^{-1}$)	XRD ref (JCPDS)
MnO_2(C)	Treatment of $MnCO_3$ in O_2 up to 675 K [10]	82	24-735
MnO_2(N)	Treatment of manganese nitrate in O_2 up to 675 K [11]	10	12-141
MnO_2(M)	Purchased from Merck	12	24-735
Mn_5O_8	Calcination manganese citrate in O_2 up to 600 K [12]	52	39-1218
Mn_2O_3(C)	Treatment of $MnCO_3$ in air up to 825 K [10]	51	24-508
Mn_2O_3(A)	Calcination of manganese acetate in O_2 up to 675 K [13]	5	6-540
Mn_3O_4(C)	Treatment of $MnCO_3$ in Ar up to 925 K, followed by a treatment in air till 675 K [10]	3	24-734
MnO(C)	Treatment of $MnCO_3$ in Ar up to 925 K [14]	1	7-230

TABLE 2

Standard experimental conditions of the activity measurements

Nitric oxide	500 ppm
Ammonia	550 ppm
Oxygen	2 vol -%
Helium	balance
Temperature	385-575 K
Pressure	10^5 Pa
Flow-rate	50 cm^3(STP) min^{-1} (34 μmol s^{-1})

m^2) Dilution was applied to maintain a packed bed length of about 4 cm in the reactor

Before each temperature-programmed experiment the activity was measured isothermally at 425 K during at least 15 h to ensure that a constant activity and steady-state conditions had been reached, after which the temperature was decreased to 385 K to start the temperature-programmed nitric oxide reduction. After having measured the activity at 385 K, the temperature was increased stepwise at a rate of 4 K min^{-1} to 400 K, 425 K, 450 K, 475 K, 525 K and finally to 575 K At each reaction temperature the catalytic activity was monitored for at least 2 h This temperature sequence was at least 4 times repeated. Except for MnO, only during the first sequence the activity differed somewhat from that in the following sequences, during which the activity remained the same. Other runs with new samples yielded the same results, indicating the reproducibility of the experiments

Some activity measurements were carried out with $^{15}NH_3$ to trace the origin of both nitrogen atoms in the nitrogen containing reaction products (nitrogen and nitrous oxide)

The effect of oxygen was investigated by simply shutting off the oxygen flow after a measurement in the presence of oxygen

The oxidation of ammonia was studied separately by using a standard reaction mixture without nitric oxide in the temperature range between 385 and 575 K

Characterization

Temperature-programmed reduction

In TPR a gas mixture containing 67 vol.-% H_2 and Ar as balance was used at a flow-rate of 8.8 μmol s^{-1}, 10 mg of manganese oxide and a heating rate of 10 K min^{-1} The TPR was carried out up to 1275 K, followed by a 1 h isothermal period A detailed description of the TPR equipment can be found elsewhere [17] The apparatus was equipped with a thermal conductivity detector

(TCD) to determine the hydrogen consumption during the reduction and a flame ionization detector (FID) to correct for methane production Calibration of the TCD signal was accomplished by reduction of V_2O_5 (Ventron)

X-ray diffraction

XRD was carried out on a Philips diffractometer 1710 with Cu Kα radiation A Ni filter was used to remove the Cu Kβ radiation

RESULTS

In Fig. 1a the nitric oxide conversion as a function of the temperature is shown for the different oxides with the highest specific surface area

Apparently, γ-Al_2O_3 hardly exhibits any activity Hence, the nitric oxide reduction activity can be completely ascribed to the manganese oxide itself Up to about 450 K the activity order per unit surface area is· $MnO_2(C) > Mn_5O_8 > Mn_2O_3(C) > Mn_3O_4(C)$ Above 475 K the activity of

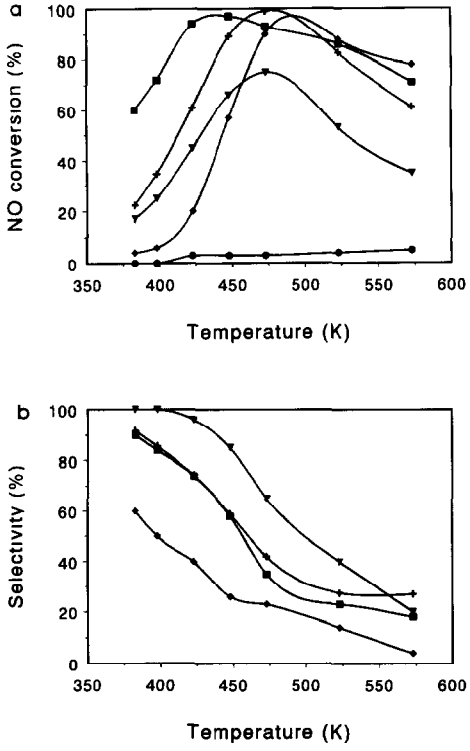


Fig 1 Nitric oxide conversion (a) and nitrogen selectivity (b) as a function of temperature for different manganese oxides (550 ppm NO, 550 ppm NH_3, 2 vol -% O_2 and helium balance) (■) $MnO_2(C)$, (+) Mn_5O_8, (▼) $Mn_2O_3(C)$, (◆) $Mn_3O_4(C)$, (●) γ-Al_2O_3

Mn_3O_4(C) increased considerably and showed an activity, comparable to that of MnO_2 The nitric oxide conversion passed through a maximum in all cases and decreased considerably above 500 K.

A complete conversion of ammonia was observed above 525 K, while nitric oxide was still present in the product mixture

The results of MnO(C) have not been included, since it had been gradually converted during the SCR experiment into Mn_3O_4, as was revealed by TPR

During the SCR reaction, the formation of nitrous oxide is regarded as undesired In Fig 1b the nitrogen selectivity (S) is given as a function of the temperature for the activity measurements of Fig 1a

Based on equal surface areas Mn_2O_3(C) exhibits the highest selectivity towards nitrogen formation, whereas with Mn_3O_4(C) the lowest selectivity was achieved in the temperature region measured. Those of MnO_2 and Mn_5O_8 are intermediate All selectivities decreased monotonically as a function of the temperature. Moreover, at constant temperature and using different amounts of oxide the selectivity decreased with increasing nitric oxide conversion

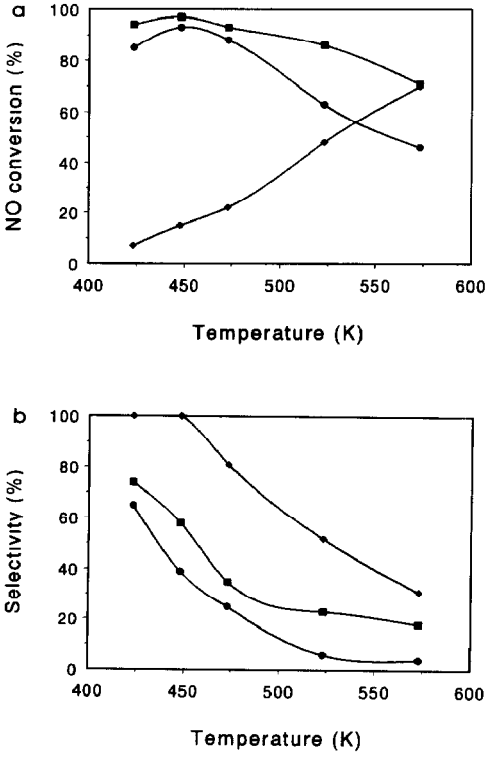


Fig 2 Comparison of nitric oxide conversion (a) and nitrogen selectivity (b) as a function of temperature (550 ppm NO, 550 ppm NH_3, 2 vol -% O_2 and helium balance) for different MnO_2 samples (●) MnO_2(N), (■) MnO_2(C), (◆) MnO_2(M)

A comparison of the activities of MnO_2(C), MnO_2(N) and MnO_2(M) based on equal total BET surface areas is given in Fig 2a, while in Fig. 2b the corresponding selectivities are shown Evidently, MnO_2(M) showed the lowest activity in the lower temperature range. MnO_2(C) yielded higher nitric oxide conversions than MnO_2(N); especially above 475 K a pronounced difference can be observed. MnO_2(M) exhibited the highest selectivity, followed by MnO_2(C) and finally by MnO_2(N). Again, all selectivities decreased with increasing temperature.

Comparing Mn_2O_3(C) and Mn_2O_3(A), based on equal total surface areas (Fig 3a), it appears that below 460 K Mn_2O_3(C) shows somewhat higher nitric oxide conversion than Mn_2O_3(A), whereas above this temperature the reverse occurs. The temperature dependency of both activity curves is comparable: the nitric oxide conversion increases with temperature and passes through a maximum around 480–500 K. With respect to the selectivity of these two compounds, Fig. 3b, it is clear that over the temperature range measured, Mn_2O_3(A) exhibits a lower selectivity than Mn_2O_3(C).

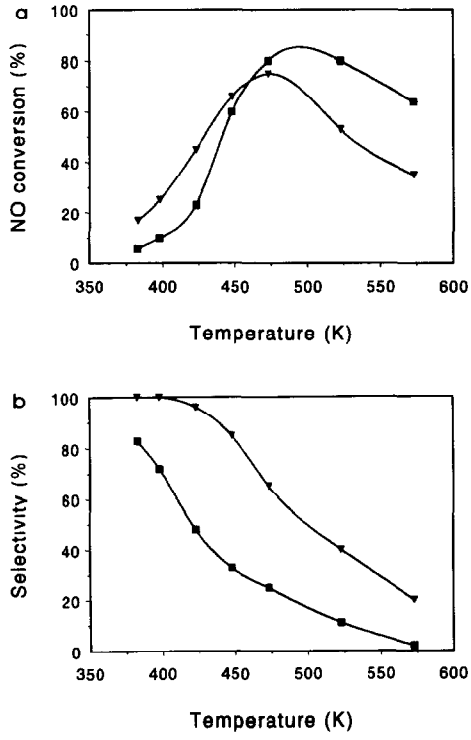


Fig 3 Comparison of nitric oxide conversion (a) and nitrogen selectivity (b) as a function of temperature (550 ppm NO, 550 ppm NH_3, 2 vol -% O_2 and helium balance) for different Mn_2O_3 samples (■) Mn_2O_3(A), (▼) Mn_2O_3(C)

By using $^{15}NH_3$ the origin of the nitrogen atoms in the formed nitrogen and nitrous oxide can be traced. Nitrogen consists either of NN ($m/e=28$), ^{15}NN ($m/e=29$) or $^{15}N^{15}N$ ($m/e=30$). Nitrous oxide can show analogous mass differences: NNO ($m/e=44$), ^{15}NNO or $N^{15}NO$ ($m/e=45$) and $^{15}N^{15}NO$ ($m/e=46$). A detailed description of the MS data interpretation, concerning the results of the experiments with $^{15}NH_3$, has been given elsewhere [6]

$^{15}NH_3$ was used in the experiments with Mn_2O_3(C), Mn_3O_4(C) and MnO_2(N). The experiments with $^{15}NH_3$ reveal that for both Mn_2O_3(C) and Mn_3O_4(C) up to 475 K the nitrogen containing reaction products mainly consist of ^{15}NN and ^{15}NNO. Above this temperature still ^{15}NN is observed together with ^{15}NO, ^{15}NNO and $^{15}N_2O$. The amount of ^{15}NNO is lower, compared to that below 475 K. The presence of ^{15}NO and $^{15}N_2O$ indicates the oxidation of $^{15}NH_3$. Similar results were obtained for MnO_2(N), however, the ammonia oxidation products were only above 525 K observed

The effect of interrupting the oxygen flow, followed by the reverse after a short period on the nitric oxide conversion of Mn_2O_3(C), is shown in Fig. 4 Interrupting the oxygen supply results in an instantaneous decrease of the activity from 35% to 4% within 1 min Subsequently, upon reintroduction of the oxygen the original activity is restored within 4 min The other samples exhibited the same behaviour, without oxygen the activity dropped to a very low level. Oxygen is essential for the reaction to proceed

The oxidation of ammonia was carried out at equal total surface areas for all the oxides prepared from manganese carbonate, except for MnO (Fig. 5) MnO_2(C) and Mn_2O_3(C) show more or less the same activity for ammonia oxidation, while Mn_3O_4(C) has a lower activity. Clear differences are observed in the products formed, depending on the temperature The product distributions for the three samples at three temperatures are given in Fig 6 With MnO_2(C) up to 425 K only nitrous oxide is formed, whereas above this temperature nitric oxide and nitrogen are formed as well The major product is

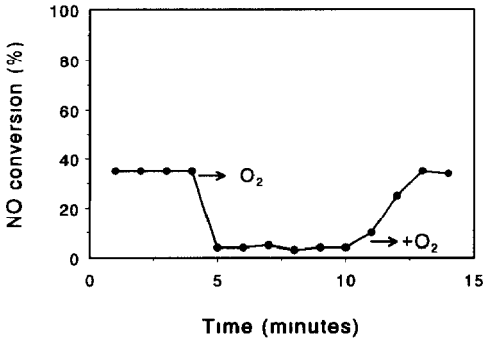


Fig 4 Nitric oxide conversion as a function of time upon removal and reintroduction of oxygen at standard experimental conditions for Mn_2O_3(C) at 425 K

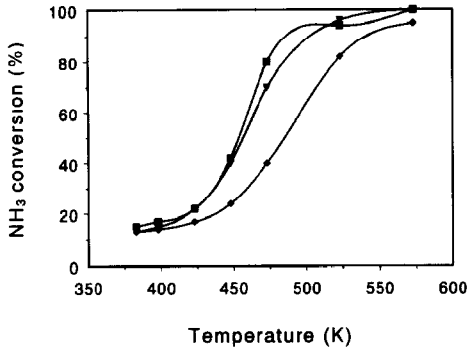


Fig 5 Ammonia conversion as a function of the temperature (550 ppm NH_3, 2 vol -% O_2 and balance helium) (■) MnO_2(C), (▼) Mn_2O_3(C), (♦) Mn_3O_4(C)

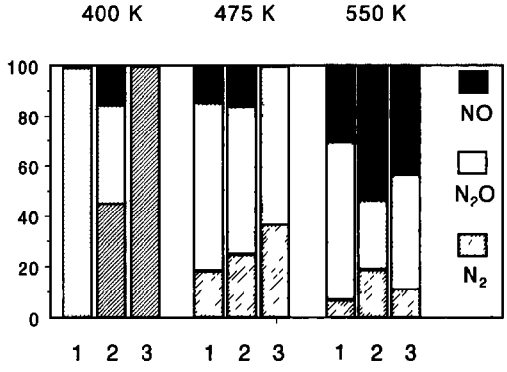


Fig 6 Product distribution during the ammonia oxidation at 400 K, 475 K and 550 K (1) MnO_2(C), (2) Mn_2O_3(C), (3) Mn_3O_4(C)

nitrous oxide In the case of Mn_2O_3(C) these three compounds are formed over the entire investigated temperature range At 475 K mainly nitrous oxide and above 525 K mainly nitric oxide is formed. For Mn_3O_4(C) only nitrogen is formed up to 425 K. Nitrogen and nitrous oxide are observed between 425 K and 525 K, and above this temperature also nitric oxide is detected

The TPR patterns of the oxides, mentioned in Table 1, are shown in Fig 7, except for MnO. The total amount of hydrogen consumption during the TPR experiments of all samples is in accordance with the indicated stoichiometry of the manganese oxides, assuming that MnO is the final state after the reduction Mn_3O_4(C) shows one reduction peak with T_{max} = 740 K

The reduction of Mn_2O_3(C) results in two peaks with T_{max} = 590 K and 675 K

A similar reduction pattern is obtained for Mn_2O_3(A), but the T_{max} has shifted slightly: T_{max} = 580 K and 695 K. In both cases the ratio between the

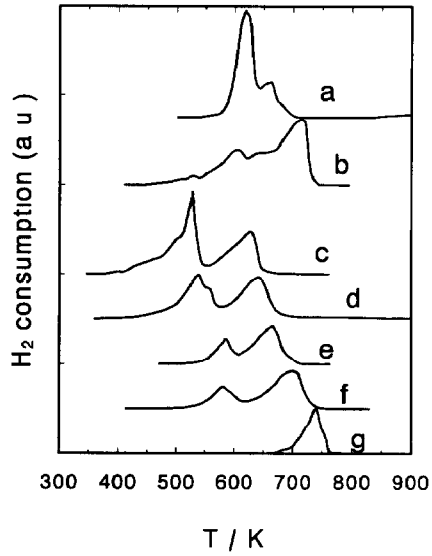


Fig 7 TPR patterns of (β=10 K min^{-1}) the various manganeses oxides (a) MnO_2(M), (b) MnO_2(N), (c) MnO_2(C), (d) Mn_5O_8, (e) Mn_2O_3(C), (f) Mn_2O_3(A), (g) Mn_3O_4(C)

hydrogen consumption during the first reduction and the second one, 1 2, is consistent with the successive reduction of Mn_2O_3 into Mn_3O_4, followed by a final reduction to MnO The same holds for the globally two step reductions of Mn_5O_8 and MnO_2(C), with hydrogen consumption ratios of 4 5 and 2 1, respectively. The first reduction step of Mn_5O_8 exhibits a distinct shoulder, suggesting a convolution of two peaks

MnO_2(C) shows two major peaks with T_{max}=530 K and 635 K. The first peak exhibits two shoulders on the leading edge The reduction of MnO_2(N) proceeds with more difficulty; the highest T_{max} being observed at as high as 715 K. Two reduction peaks, with T_{max} at 620 K and 665 K, are measured for MnO_2(M), the first peak being much larger than the second one.

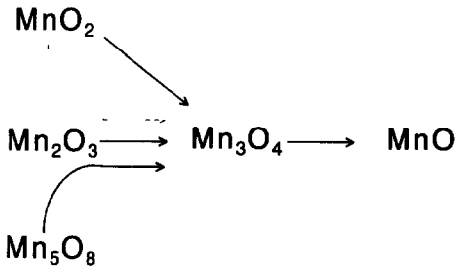
TPR experiments were also carried out with the oxides that had been used in the SCR experiments and of which the results have been presented in Fig 1 This revealed that during the SCR reaction only MnO was transformed into Mn_3O_4, whereas the other manganese oxides retained their original average bulk oxidation state This explains the observation that the activity of the MnO sample increases slowly during the successive temperature sequences, whereas those of the other samples remain constant after the first sequence It must be noted that due to the transfer of the samples in air some reoxidation cannot be excluded

The XRD patterns of the oxides could all be identified with the JCPDS references [18], which are indicated in Table 1 It is clear that the crystalline structure of MnO_2 and Mn_2O_3 depends on the precursor and preparation

method used. The samples with increasing specific surface areas exhibit broader and less intense XRD peaks, reflecting smaller particles and more amorphous structures. The pattern of Mn_3O_4(C) indicates that some MnO is present in the sample

DISCUSSION

The reduction process of the manganese oxides studied can be generalised in the following way:



No clear distinguishable reduction peak for an intermediate transformation of MnO_2 into Mn_2O_3 was observed during the reduction, although some irregularities can be perceived on the leading edge of the first reduction step So, if formed at all, the Mn_2O_3 reduces readily further to Mn_3O_4 Mn_5O_8 ($MnO_2 \cdot 2Mn_2O_3$) exhibits a clear shoulder on the first reduction peak, suggesting that an intermediate transformation into Mn_2O_3 takes place, readily followed by a further reduction to Mn_3O_4.

The low specific area of Mn_3O_4(C) might explain the relatively high T_{max} compared to that of Mn_3O_4 formed in situ during the reduction of MnO_2, Mn_5O_8 and Mn_2O_3. In these latter cases a higher specific surface area of the Mn_3O_4 contributes to a lower T_{max}, since the starting material also has a higher specific area. The same phenomenon is also observed when comparing the reduction profiles of the other MnO_2 compounds MnO_2(N) and MnO_2(M) give higher T_{max} values than MnO_2(C), and have much lower specific surface areas

It is clear that the oxides prepared from manganese carbonate have a lower specific surface area as the oxidation state of the manganese decreases During reduction of the oxide the structure collapses, resulting in lower specific surface areas, as was indicated by unsuccessful attempts to prepare Mn_3O_4 samples with high surface areas by a slow reduction

Comparing the various oxides it appears that the temperature of the onset of reduction is the lowest for the highest oxide, increasing with decreasing oxidation state of the manganese. Specific surface area and crystallinity have an additional effect on this trend.

The TPR results also reveal that the SCR reaction has been carried out with manganese oxides of the indicated average stoichiometry Except for MnO,

converted into Mn_3O_4 during SCR, the other oxides seem to retain their original oxidation state, although reoxidation during the transfer of the reactor tube to the TPR equipment cannot be excluded. These TPR data suggest, however, that the bulk oxygen does not participate in the SCR reaction, which is also proven by the quick response in activity level during the in-situ removal and reintroduction of the oxygen in the feed.

Due to the fact that MnO is oxidized during the SCR reaction, this oxide has not been studied as extensive as the other model compounds

Since γ-Al_2O_3 shows hardly any activity, the nitric oxide reduction activity during the SCR experiments can be completely ascribed to the activity of the corresponding model oxides. The formation of ^{15}NN in the SCR experiments with $^{15}NH_3$ confirm that eqn. (1) applies where nitric oxide and ammonia react with each other in a 1 1 ratio

SCR experiments with equal total surface areas, Fig 1a, reveal that below 460 K the activity decreases with decreasing average oxidation state This correlates with the onset of reduction in TPR, which strongly suggests that the most active oxygen, which is removed first in TPR, determines the nitric oxide removal activity

The selectivity decreases, but, in a different order $Mn_2O_3(C) > MnO_2(C) \approx Mn_5O_8 > Mn_3O_4(C)$ The fact that $Mn_3O_4(C)$ has an nitric oxide reduction activity comparable to that of $MnO_2(C)$ above 475 K, whereas the selectivity is lower than that of $MnO_2(C)$ in this temperature region, indicates that $Mn_3O_4(C)$ produced much more nitrous oxide It should be noted that reaction selectivities are only properly compared at similar conversion levels. Therefore, here mainly the temperature dependency of the selectivity of an individual oxide can be considered. Comparison of the different oxides can only be made if the nitric oxide conversion levels are taken into account From experiments with other sample amounts [6], resulting in comparable conversion levels, it is evident that the selectivity order given above still holds

The general observation that the selectivity decreases with increasing nitric oxide conversion at constant temperature suggests that the nitrogen and the nitrous oxide have a different dependency on the partial pressures of the reactants. It can also indicate that a series reaction mechanism is involved at the catalyst surface, whereby nitrogen is a first and nitrous oxide is a second nitrogen containing product. This model is further substantiated later on

Comparing the MnO_2 samples prepared from different precursors, it appears that there is also a pronounced activity difference between the samples with a low specific surface area. $MnO_2(N)$ exhibits a higher activity than $MnO_2(M)$ in the lower temperature range in spite of the equal total surface area (Fig 2a). Upon comparing the selectivities, $MnO_2(M)$ should not be taken into account due to its much lower nitric oxide conversion. It is striking that the sample with the lowest specific surface area, $MnO_2(N)$, has the lowest selec-

tivity over the entire investigated temperature range. These data suggest that a relatively well-ordered MnO_2, i.e. a lower specific surface area and a better developed XRD pattern, leads to more nitrous oxide formation than a more disordered structure, like that of MnO_2(C)

For the Mn_2O_3 samples [(A) and (C)] the same conclusion can be drawn as for MnO_2 Using the same total surface area the nitric oxide reduction activities are comparable up to 475 K. The ex-carbonate sample even has a slightly higher activity and a considerably higher selectivity The ex-acetate sample, having the lowest specific surface area, produces much more nitrous oxide Apparently, the nitrous oxide formation correlates with low specific surface areas and better crystalline ordering This is in agreement with results for alumina supported manganese oxides [5], for supported V_2O_5 [19] and for Cr_2O_3 [20,21]. In these latter studies it was proposed that crystalline V_2O_5 and Cr_2O_3 are responsible for the nitrous oxide formation.

The nitrous oxide formation can arise from the oxidation of ammonia, which has been studied separately for that reason. Based on equal total surface area the same order in activity is observed as in the SCR reaction and in TPR: $MnO_2(C) \geqslant Mn_2O_3(C) > Mn_3O_4(C)$. However, the composition of the products formed differs. In the case of MnO_2(C) only nitrous oxide has been detected up to 425 K and above this temperature nitrous oxide together with nitric oxide and nitrogen are formed. With Mn_2O_3(C) all the three nitrogen containing compounds are formed: the average oxygen content of the products increases with the temperature and above 525 K mainly nitric oxide is formed. Mn_3O_4(C) forms only nitrogen up to 425 K and up to 525 K both nitrogen and nitrous oxide are formed. Moreover, above 525 K nitric oxide is also formed The oxidation of ammonia, resulting in N_2, NO and N_2O, can be represented by the following overall reactions:

$$NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad (3)$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \quad (4)$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad (5)$$

In the lower temperature range Mn_3O_4 has a selectivity towards nitrogen, MnO_2 towards nitrous oxide, whereas Mn_2O_3 takes an intermediate position Moving to higher temperatures, preferences shift to the higher oxides of nitrogen, indicating that for a specific oxide sample the apparent activation energy increases: $E_a(3) < E_a(4) < E_a(5)$. The increasing oxidation state of the manganese oxides correlates with the increasing formation of more oxidized products: $N_2 < N_2O < NO$. Il'Chenko and Golodets [3,4], who studied the oxidation of ammonia over MnO_2 amongst other transition metal oxides, ascribed the increasing apparent activation energy for the formation of more oxidized products to the increasing number of surface-oxygen bonds, that have to be broken. If applied to the different manganese oxides, this means that the sur-

face-oxygen bond strength increases with decreasing oxidation state of the manganese, which is in excellent agreement with the TPR results. The reduction of MnO_2(C) occurs at the lowest temperature, followed by Mn_5O_8, Mn_2O_3(C), while Mn_3O_4 reduces at the highest temperature, similarly as the Mn_3O_4 formed in situ during the reduction of MnO_2, Mn_5O_8 and Mn_2O_3

The observed nitrogen formation at higher temperatures for the MnO_2 sample (Fig. 6) is ascribed to a consecutive reaction of nitric oxide, formed through ammonia oxidation, with unconverted ammonia according to the SCR reaction [eqn. (1)]. In this case it might not be a prerequisite for nitric oxide, formed at the surface, to desorb first. All reaction steps may occur on the surface of the oxide. The formation of nitrogen, together with nitric oxide and nitrous oxide, has been observed also by Il'Chenko and Golodets for MnO_2 [3,4]. This was not interpreted as the result of an SCR reaction (not yet recognized at that time), but they used the model of Zawadsky [2], where imine and nitroxyl groups are proposed.

The ammonia oxidation is clearly the reason for the maximum in the nitric oxide conversion curves during the SCR experiments: the higher the activity is, the lower is the temperature of this maximum At higher temperatures a part of the ammonia is no longer available for SCR and can even be converted into nitric oxide, both resulting in a decrease of the apparent nitric oxide conversion In the presence of nitric oxide, however, the oxidation of ammonia is shifted to temperatures higher than 475 K, due to the selectivity for the SCR reaction at lower temperatures, as was also observed for alumina supported manganese oxides [5].

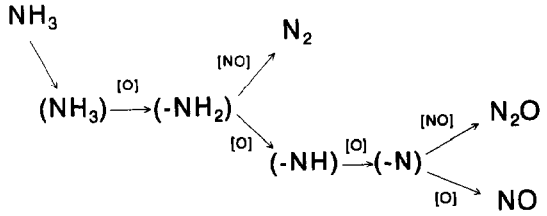
The labelling studies also revealed that nitrous oxide is not only formed by ammonia oxidation, which occurs at higher temperatures, but also through a reaction between NO and $^{15}NH_3$ in a ratio of 1 1, resulting in ^{15}NNO [eqn. (6)]

$$4NO + 4NH_3 + 3O_2 \rightarrow 4N_2O + 6H_2O \quad (6)$$

This suggests that the oxygen remains bonded to the nitrogen in the nitric oxide molecule. So, considerations with regard to the selectivity of the manganese oxides towards nitrogen or nitrous oxide formation, taking into account only reaction (1) or (6), respectively, are valid up to 475 K, where the ammonia oxidation can be neglected. These reactions occur simultaneously on the oxide surfaces. The possibility of a series reaction for the SCR process with nitrous oxide as intermediate is excluded, since nitrous oxide is not reduced over this system [5]. In the present day view on the SCR mechanism nitric oxide (or NO_x) reacts with surface ($-NH_3$) or ($-NH_2$) species to yield directly nitrogen and water [22–26]. In view of the correlation between the ease of reduction of the manganese oxides and their SCR activity, it is probable that the first step in SCR is an oxidative abstraction of an hydrogen from adsorbed ammonia, yielding a surface amine species that reacts further with nitric oxide

to nitrogen and water. The nitrous oxide formation in eqn. (6) is explained by an oxidative abstraction of more than one hydrogen from ammonia. The resulting (–NH) or (–N) species are unable to react with the nitric oxide to nitrogen and can only leave the surface as nitrous oxide. This implies that reactive surface-oxygen must be present to achieve this hydrogen abstraction proceeding too far Recently, Curry-Hyde et al. [20] compared crystalline and amorphous Cr_2O_3 in relation to SCR. Amorphous chromia exhibited a good selectivity towards nitrogen whereas with crystalline chromia considerable amounts of nitrous oxide are produced. They found by TPRD experiments (temperature programmed reaction and desorption) that some surface-oxygen on crystalline chromia is more reactive ("labile") than on amorphous chromia, supporting the ideas stated here and suggesting that the same holds for MnO_2 and Mn_2O_3

These indications imply that the products of the interaction of NO, NH_3 and O_2 over manganese oxides can be explained by a model where the ammonia is successively dehydrogenated by surface oxygen, forming nitric oxide in the limit The intermediate surface species ($-NH_2$) can react with nitric oxide to form nitrogen, according to an SCR mechanism, while (–NH) or (–N) species can only react with nitric oxide to nitrous oxide or with surface oxygen to nitric oxide. This nitric oxide formed by the ammonia oxidation can also enter the scheme and produce nitrogen or nitrous oxide. This model is depicted in the following scheme.



In this model, the product distribution is determined by the concentration of reactive surface oxygen and by nitric oxide, since both affect the relative distribution of the surface species. A high surface oxygen concentration facilitates the ($-NH_2$) formation. The further reaction route is a competition between the SCR route with nitric oxide and a further hydrogen abstraction leading to nitrous oxide or nitric oxide Their rates are proportional to the nitric oxide concentration and to the surface oxygen concentration, respectively, which process determines the reaction selectivity. At sufficiently high partial pressure the nitric oxide can effectively intercept this ($-NH_2$) intermediate to result in SCR, preventing it from being dehydrogenated further, which would result in a decreased SCR selectivity.

So, the lower selectivity of MnO_2 in SCR is ascribed to the presence of a relatively high concentration of active surface oxygen that causes a too far

enhanced hydrogen abstraction from the ammonia. The lower selectivity of Mn_3O_4 is due to the presence of the reactive oxygen on the more crystalline structure, with a similar result as for MnO_2. Also the decrease in selectivity with increasing nitric oxide conversion is accounted for. At higher conversion levels the amount of nitric oxide available decreased, slowing down the SCR reaction path and, hence, increasing the probability that the hydrogen abstraction proceeds further, leading to more nitrous oxide formation The decreased ammonia concentration has no effect since its reaction order is zero [27] For the adsorption of ammonia coordinatively unsaturated sites are needed, so it is not surprising that samples with high specific surface areas, thus having many structural defects, exhibit the highest activities.

Apparently, Mn_2O_3 is the preferred oxide for SCR since it has the highest selectivity, which probably originates from an optimal balance between the oxidative abstraction activity and the SCR path in the model Therefore, from the point of view of a supported catalyst, the most desired system for a good activity and a high selectivity is a highly dispersed amorphous Mn_2O_3 phase

The model proposed here still remains speculative, although it can account for the observed activities and selectivities Further research will be necessary to demonstrate short living intermediate complexes which can support this model. For vanadia catalysts short living NH_2NO species are claimed to have been demonstrated [28] Pulse reactor studies, employing labelled molecules seem an excellent tool to tackle this problem and are subject of current activities

CONCLUSIONS

The SCR activity and selectivity for nitrogen of unsupported manganese oxides is determined by the oxidation state, the degree of crystallinity and the specific surface area

Per unit of surface area the highest SCR activity is exhibited by MnO_2, followed by Mn_5O_8, Mn_2O_3 and Mn_3O_4, in that order. This activity correlates with the onset of reduction in TPR, suggesting that the most active oxygen is involved in the SCR process. Mn_2O_3 exhibits the highest selectivity for nitrogen and Mn_3O_4 the lowest The nitrous oxide formed during SCR originates from the reaction between nitric oxide and ammonia in a ratio of 1 1 at lower temperatures and from the oxidation of ammonia at higher temperatures The nitrous oxide formation occurs preferentially on crystalline material

The bulk oxygen of the manganese oxides does not participate in the SCR reaction, so the manganese oxides retain their pristine oxidation state, except for MnO, which is gradually converted into Mn_3O_4 under SCR conditions

In the oxidation of ammonia the average degree of oxidation of the nitrogen containing products (N_2, N_2O and NO) increases with increasing temperature and increasing oxidation state of the manganese So, below 400 K Mn_3O_4 pro-

duces only nitrogen and MnO_2 only nitrous oxide, whereas above 500 K significant amounts of nitric oxide are formed

A model is proposed that can account for the observed SCR and ammonia oxidation behaviour

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