Determination of Surface Coverage of Catalysts: Temperature Programmed Experiments on Platinum and Iridium Sponge Catalysts after Low Temperature Ammonia Oxidation

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The activity of iridium and platinum sponge catalysts was studied in the low temperature gas phase oxidation of ammonia with oxygen. Under the reaction conditions used, iridium was found to be more active and more selective to nitrogen than platinum. Furthermore it was established from activity measurements that both catalysts lose activity as a function of time on stream due to inhibition of the surface by reaction intermediates. The used catalysts were studied with XPS and temperature programmed techniques. It was found that the surface of the catalysts had a high coverage of NH and OH and some additional NH_2. It seems most likely that the reaction mechanism proceeds through a stepwise dehydrogenation of the ammonia molecule. It appears that the last dehydrogenation step (NH by OH to N and water) is the rate determining step. The high selectivity of iridium to nitrogen can be explained by the higher activity of iridium in dissociating NO. © 1999 Academic Press

INTRODUCTION

Selective oxidation of ammonia with oxygen to nitrogen and water could be a solution to several ammonia emissions, caused by various sources like the selective catalytic reduction of NO_x (SCR process), soda production, or agriculture (1). The temperature at which the catalytic oxidation of the ammonia has to take place depends on the process that causes the ammonia emission (2). At low temperatures (<800 K) nitrogen is the favored product of the reaction for most catalyst systems:

$$2\,NH_3 + 1\tfrac{1}{2}\,O_2 \rightarrow N_2 + 3\,H_2O. \qquad [1]$$
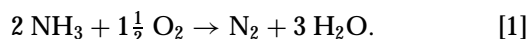
However, the formation of N_2O is often seen as a byproduct at these temperatures:

$$2\,NH_3 + 2\,O_2 \rightarrow N_2O + 3\,H_2O. \qquad [2]$$
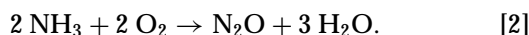
At higher temperatures NO can be produced:

$$2\,NH_3 + 2\tfrac{1}{2}\,O_2 \rightarrow 2\,NO + 3\,H_2O. \qquad [3]$$
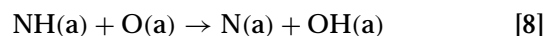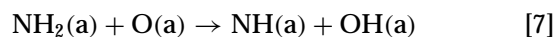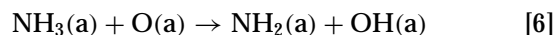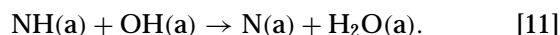
Various catalysts of different types have been tested for the ammonia oxidation reaction: biological catalysts (3), metal oxide catalysts (4), ion-exchanged zeolites (4–6), and metallic catalysts (1, 2, 7, 8). At a low reaction temperature (<473 K) metallic catalysts are the only catalysts that combine a high activity and selectivity to nitrogen (1, 2, 7–9). Of the various metals, platinum (7–9) and iridium (9) are found to be the most active catalysts. Furthermore it was established (10, 11) that larger metal particles are more active in the oxidation of ammonia than smaller metal particles. Also it was found that the metal catalysts lose a large portion of their activity as a function of time on stream (10–14). This loss of activity of the platinum catalysts was attributed to oxidation of the platinum surface (11) or to blocking of the surface with nitrogen containing intermediates (13, 14).

Information on mechanistic aspects of the ammonia oxidation reaction is available for platinum catalysts from surface science (15–18), electrochemical (13, 14), and theoretical studies (19). The reaction mechanism was described in studies on the Pt(100) surface (15) or the Pt(111) surface (17, 18) or platinized platinum electrode (13, 14). The mechanism starts with the adsorption of the reactants on different sites (denoted s for adsorption through a N atom and * for adsorption through an O atom) on the surface:

$$NH_3 + s \rightarrow NH_3(a) \qquad [4]$$

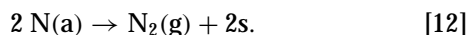$$O_2 + 2^* \rightarrow 2\,O(a). \qquad [5]$$
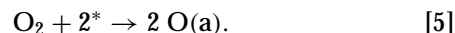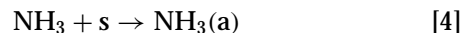
After adsorption the NH_3 molecule can react with O, as in Eqs. [6]–[8] or with OH (after it has been formed) as in Eqs. [9]–[11]:

$$NH_3(a) + O(a) \rightarrow NH_2(a) + OH(a) \qquad [6]$$

$$NH_2(a) + O(a) \rightarrow NH(a) + OH(a) \qquad [7]$$

$$NH(a) + O(a) \rightarrow N(a) + OH(a) \qquad [8]$$

$$NH_3(a) + OH(a) \rightarrow NH_2(a) + H_2O(a) \qquad [9]$$

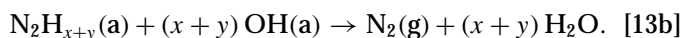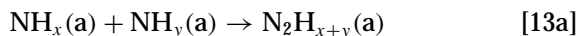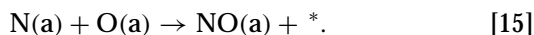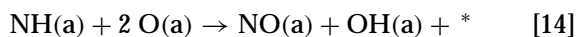$$NH_2(a) + OH(a) \rightarrow NH(a) + H_2O(a) \qquad [10]$$

$$NH(a) + OH(a) \rightarrow N(a) + H_2O(a). \qquad [11]$$

Thereafter N_2 can be formed (15, 17):

$$2\,N(a) \rightarrow N_2(g) + 2s. \qquad [12]$$

Alternatively (13, 14), N_2 can be formed from $NH_x(a)$ ($x = 1$ or 2) via a N_2H_x ($x = 2$ to 4):

$$NH_x(a) + NH_y(a) \rightarrow N_2H_{x+y}(a) \qquad [13a]$$

$$N_2H_{x+y}(a) + (x + y)\,OH(a) \rightarrow N_2(g) + (x + y)\,H_2O. \qquad [13b]$$

Different mechanisms are presented in the literature on the formation of NO at low temperature. Two reactions are reported (15, 17):

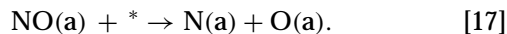$$NH(a) + 2\,O(a) \rightarrow NO(a) + OH(a) + {}^{*} \qquad [14]$$

$$N(a) + O(a) \rightarrow NO(a) + {}^{*}. \qquad [15]$$

The onset of NO desorption from the platinum surface,

$$NO(a) \rightarrow NO(g) + s, \qquad [16]$$
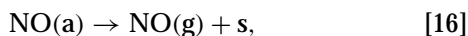
was observed in various studies starting at a temperature of 300 K (17), 400 K (15), or 550 K (18).

Also, on the Pt(100) surface it is possible at temperatures higher than 350 K to dissociate NO (15):

$$NO(a) + {}^{*} \rightarrow N(a) + O(a). \qquad [17]$$

On the Pt(111) or Pt(110) surface it is more difficult to dissociate NO (20).

In this study platinum and iridium sponge catalysts were tested in the low temperature (<373 K) gas phase ammonia oxidation reaction. In order to determine the cause of the time on stream behavior, used catalysts were studied with XPS and temperature programmed experiments.

METHODS

Sample Preparation

The platinum and iridium sponge samples were acquired from Johnson Matthey. The sponge samples were of >99.9% purity. The size of the sponges was between 250 and 350 μm for the platinum sample and <841 μm for the iridium sample. In the reaction setup particles were used with a particle size between 125 and 425 μm; if necessary, samples of the catalyst were pelleted, crushed, and sieved to acquire the appropriate particle size. A diluted sample was made by mixing a sample of the sponge with γ-alumina particles of the same particle size. All catalysts were reduced in the reaction setup in a dried hydrogen flow to a temperature of 573 K.

Electron Microscopy Measurements

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) measurements were done on a Jeol 840 electron microscope. Both reduced and used platinum and iridium sponge samples were measured.

Krypton BET Measurements

Krypton BET measurements were done on a Micromeritics ASAP 2000 setup, using a standard procedure without any pretreatment of the sample. Krypton was used as an adsorbent because of the low surface area of the metal sponge samples. The average metal particle size was determined from the surface area, assuming cubic close packed symmetry for both metals.

Experimental Setup

Catalytic and temperature programmed tests were done in a fixed bed reaction setup equipped with a gas chromatograph (ATI UNICAM 610, spec 2790) and a quadrupole mass spectrometer (Balzers QMG-420) for on-line analysis of the reactants and products. The gas chromatograph was capable of analyzing NH_3, O_2, H_2O, N_2, and N_2O quantitatively. The mass spectrometer was used to check the results of the gas chromatograph and for the detection of NO and NO_2. A quartz tube with an internal diameter of 4 mm was used as the reactor.

Steady State Catalytic Tests

For the steady state catalytic tests the reactor was filled with the metal sponge (12.2 mg for Ir, 92.8 mg for Pt) diluted with about 130 mg of γ-alumina. The reactor was assumed to be differential at low conversion, using calculated estimations of diffusion and heat transfer. The catalyst was diluted with γ-alumina in order to satisfy plug flow requirements. It was determined experimentally that γ-alumina is not active for oxidation of ammonia at the conditions used in this study. Catalytic tests were done with a reaction mixture consisting of 2.0 vol% of ammonia and 1.5 vol% of oxygen in helium with a total flow of 48.8 cm^3/min (STP). The reaction temperature was adjusted to keep conversion below 10%. Steady state experiments were done using the gas chromatograph after at least 12 h on stream. Reaction orders were determined by lowering the concentration of one of the reactants at a fixed concentration of the other reactant. For the platinum catalysts reaction orders were determined at a temperature of 433 K. For the iridium catalysts reaction orders were determined at a temperature of 403 K. Activation energies were determined by varying the temperature (for the platinum catalysts in the range 413–443 K, for the iridium catalysts in the range 413–383 K). Used catalysts were regenerated by reduction in a dried hydrogen flow at

573 K. The regenerated catalyst showed exactly the same behavior as the fresh catalysts.

Time on Stream (TOS) Experiments

For the time on stream (TOS) and the temperature programmed experiments a sample of 1.0 g of pure sponge was used as the catalytic bed. In the TOS experiments a flow with the reactants was switched to a reduced catalyst at time zero. The concentrations of the reactants and products were measured using the mass spectrometer for at least 2 h on stream. A flow consisting of 2.0 vol% of ammonia and 1.5 vol% of oxygen in helium with a total flow of 48.8 cm^3/min (STP) was used. The experiment was done at a temperature of 323 K for the iridium sponge catalyst and at 373 K for the platinum sponge catalyst.

XPS Experiments

XPS experiments were done on a VG Scientific XP spectrometer, Al $K\alpha$ photon radiation was used. The measurements were corrected for charging by using the Ir 4f signal at 60.9 eV or the Pt 4f signal at 71.2 eV as a reference. XP spectra were taken of freshly reduced platinum and iridium sponge samples as well as of samples that were used in a TOS experiment. The samples were taken out of the reactor and transported in air to be fitted on an iron stub carrying an indium foil. Because of interference of an InO$_2$ layer on the indium foil it was not possible to get a clear O 1s signal for oxygen on platinum or iridium.

Temperature Programmed Experiments

Two different experiments were done to examine the adsorbed species on the catalyst: temperature programmed desorption (TPD) followed by reduction and temperature programmed reduction (TPR). In the TPD and reduction experiment, a TOS experiment is done first with the catalyst for 2 h. Then the catalyst was flushed with a helium flow of 10.2 cm^3/min (STP) for 1 h at the reaction temperature. Subsequently, in the TPD experiment, the temperature was raised at 10 K per minute to a temperature of 773 K. After 30 min at 773 K, the reduction experiment was carried out by switching the helium flow to a 20 vol% H$_2$ in helium mixture, with a flow rate of 10.2 cm^3/min (STP). After 1 h at 773 K the temperature was lowered to the reaction temperature and the flow was switched back to pure helium. The catalyst was found to be regenerated by the TPD and reduction experiment and was used in the next experiment. In the TPR experiment a TOS experiment is first done with the catalyst for 2 h. Then the catalyst was flushed with a helium flow of 10.2 cm^3/min (STP) for 1 h at the reaction temperature. Subsequently, the TPR experiment was started. The reactor flow was switched to a 20 vol% H$_2$ in helium mixture with a flow rate of 10.2 cm^3/min (STP). First the temperature is kept at the reaction temperature;

this is the isothermal part of the TPR. After 1 h the temperature programmed part of the TPR was started, in which the temperature was raised at 10 K per minute to 773 K. After 30 min at 773 K the temperature was lowered to the reaction temperature and the flow was switched to pure helium. Like in the TPD and reduction experiment, the catalyst was found to be regenerated by the TPR experiment and was used in the next experiment. Both the TPD and reduction experiment and the TPR experiment were repeated using D$_2$ instead of H$_2$. The experiments with H$_2$ made it possible to distinguish between NH$_3$ and H$_2$O (mass 17 and 18, respectively). The results of the D$_2$ experiments gave information about the occurrence of the various deuterated forms: ND$_3$ and D$_2$O (mass 20), ND$_2$H and HDO (mass 19), NDH$_2$ and H$_2$O (mass 18), and NH$_3$ (mass 17). However, in the calculation of concentrations from these data the experimental error was enhanced largely by interference of fragmentation ions of the different deuterated species. As a consequence it was not possible to distinguish between the various deuterated species.

RESULTS

Particle Size Determination

The results of the particle size determination are given in Table 1. The particle sizes determined with krypton BET agree with the particle sizes that were determined with SEM. From SEM it can be deduced that the sponges consist of small nonporous particles that are clustered together in much larger sponge-like structures. From EDS it was found that no significant impurities are present in the sponges.

Steady State Catalytic Tests

The results of the steady state catalytic tests are summarized in Table 2. The iridium catalyst was found to be more active than the platinum catalyst. Furthermore the selectivity to nitrogen was also higher for the iridium catalyst. The reaction orders that were determined are all low, the order in O$_2$ is lower for iridium than for platinum, whereas the order in NH$_3$ is higher for iridium than for platinum. The activation energy was found to be somewhat higher for the iridium catalyst.

TABLE 1

Metal Particle Size Determination

Catalyst	BET		SEM size[a] (μm)
	Area (m^2/g)	Size (μm)	
Ir sponge	0.567	0.50	0.2–3.0
Pt sponge	0.099	3.0	1.0–5.0

[a] Size of the small nonporous particles.

TABLE 2

Steady State Activity, Selectivity, Reaction Orders, and Activation Energy

Catalyst	TOF (h^{-1})	Selectivity to N_2	Order in O_2	Order in NH_3	E_{act} (kJ/mol)
Ir sponge	640 ± 9^a	97^a	-0.3 ± 0.1^b	0.24 ± 0.05^b	126 ± 3^c
Pt sponge	72 ± 7^a	80^a	0.3 ± 0.1^d	-0.1 ± 0.2^d	108 ± 3^e

Note. Error margins are 95% confidence intervals.
[a] Determined at 413 K.
[b] Determined at 403 K.
[c] Determined from 383 to 413 K.
[d] Determined at 433 K.
[e] Determined from 413 to 443 K.

Time on Stream (TOS) Experiments

As can be seen in Figs. 1 and 2, both iridium and platinum catalysts showed a severe loss of activity after the catalyst was exposed to the reaction mixture. The resultant steady state activity per surface site was the same order of magnitude for both catalysts, but it must be noted that the iridium catalyst was tested at 323 K, whereas the platinum catalyst was tested at 373 K. The iridium sponge catalyst first becomes more activate at the start of the reaction and then becomes less active. Figure 1 clearly shows that maximum activity was reached in 20 s; thereafter the activity decreased to 10% of the maximum activity in 60 s. Finally after 1200 s (not shown) the activity is stable at 2% of the maximum activity. The selectivity to N_2 is 100% at the start of the reaction, dropping to 95% during some TOS, the remainder being N_2O. The platinum sponge catalyst is also found to become more active at the start and subsequently become less active. As shown in Fig. 2, the activity increases during the first 12 s on stream, and then it decreases. The activity decreased to 10% of the initial activity in just 60 s. After 1200 s on stream (not shown) the activity is stable at 2% of the maximum activity. As can be clearly seen in
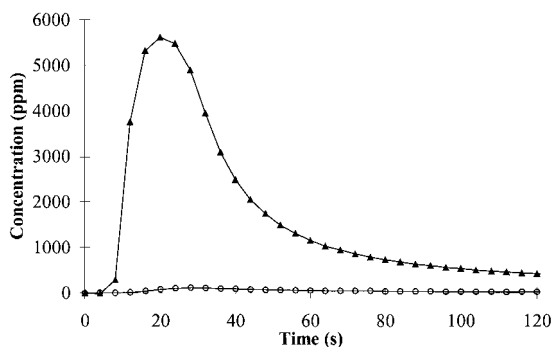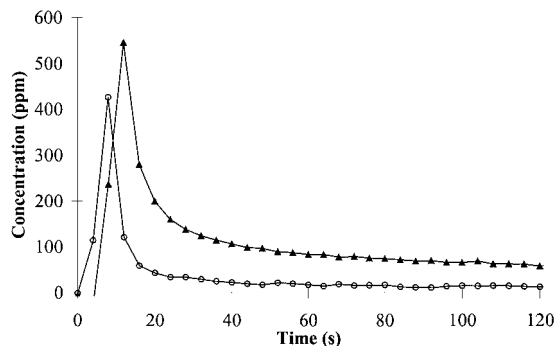

FIG. 2. Initiation of reaction with a stoichiometric reaction mixture with a platinum sponge catalyst. ▲, N_2; ○, N_2O; ammonia concentration, 2.0 vol%; oxygen concentration, 1.5 vol%; GHSV, 3000.

Fig. 2, immediately at the start of the reaction mostly N_2O is produced, with the production decreasing rapidly after 8 s on stream. Thereafter a large increase in N_2 production is seen, with the production rapidly decreasing after 12 s on stream. At steady state the selectivity to N_2 is constant at 75%, with the remainder being N_2O.

XPS Experiments

The XP spectra around the binding energy of N $1s$ of both reduced and deactivated iridium sponge are shown in Fig. 3. The broad N $1s$ peak centered around 399 eV can be observed only in the used sample. From literature (21, 22) it is known that the N $1s$ signal of NH_x ($x = 0$–3) has a binding energy below 400 eV, whereas the N $1s$ signals of NO_x, N_2H_x, and NH_4^+ have a binding energy above 400 eV. Therefore, the measured N $1s$ signal must be due to an adsorbed NH_x ($x = 0$–2) species, excluding NH_3 since it would already be desorbed at the temperature used in this experiment. The broad nature of the peak suggests that a mixture of NH_x ($x = 0$–2) species are present on the surface of the used iridium catalyst.

The XP spectra around the binding energy of N $1s$ of both reduced and deactivated platinum sponge are shown in Fig. 4. The N $1s$ peak centered around 398 eV can be

FIG. 1. Initiation of reaction with a stoichiometric reaction mixture with an iridium sponge catalyst. ▲, N_2; ○, N_2O; ammonia concentration, 2.0 vol%; oxygen concentration, 1.5 vol%; GHSV, 3000.
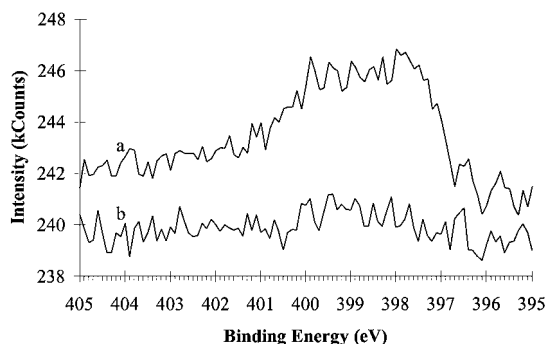

FIG. 3. XP-spectra for N $1s$ of used (a) or reduced (b) iridium sponge.
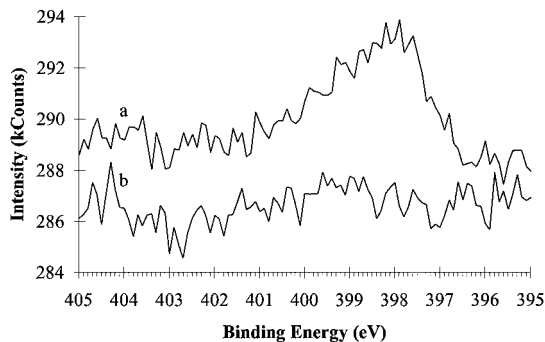
FIG. 4. XP-spectra for N 1*s* of used (a) or reduced (b) platinum sponge.

TABLE 3

Amounts of Desorbed Species in the TPD and Reduction Experiments for Iridium Sponge, Variation of Reactant Concentration

Reactant concentration		Desorbed species per surface site						
		TPD			Reduction			
NH_3	O_2	N_2	N_2O	NH_3	H_2O	N_2	NH_3	H_2O
2.0	0.8	0.128^a	0.010^a	0.025^a	0.24^b	0.003^a	0.010^a	0.00^b
2.0	1.5	0.122^a	0.011^a	0.021^a	0.24^b	0.003^a	0.001^a	0.01^b
1.0	1.5	0.104^a	0.011^a	0.019^a	0.23^b	0.003^a	0.002^a	0.02^b

[a] 95% Confidence interval is ± 0.003 for N_2, N_2O, and NH_3.
[b] 95% Confidence interval is ± 0.01 for H_2O.

observed only in the used sample. Since the peak is similar to the that of the iridium sample it must also be due to adsorbed NH_x ($x = 0$–2) species. This is in agreement with an XPS study (23) which showed that on Pt(111) NH_3 and NH_x ($x = 1$ or 2) give rise to N 1*s* peaks at 399.8 and 397.5 eV, respectively. Different values are reported in literature for the peak position of N_{ads} on Pt. In a study of NO adsorption on Pt(100) and Pt(310) (20) it was found that N_{ads} gives rise to a N 1*s* peak and 399.5 eV, whereas in a study of ammonia oxidation on Pt(111) (24) the N 1*s* peak was found at 397.6 eV. Since the N 1*s* measured in this study is very broad we cannot exclude the contribution of N_{ads} on the basis of any of the literature values.

Temperature Programmed Experiments on Iridium Sponge

The result of the TPD experiment on iridium sponge is shown in Fig. 5 and summarized in Table 3. In Fig. 5, the desorption of N_2 and H_2O can be seen clearly together with smaller amounts of N_2O and NH_3. The peaks of N_2 and N_2O are relatively sharp and are centered around a temperature of 410 K, whereas NH_3 and H_2O show broad peaks centered around a temperature of 430 K. This difference is probably caused by a stronger adsorption of NH_3 and H_2O in the reaction system. The peaks of N_2 and NH_3 also appear to have
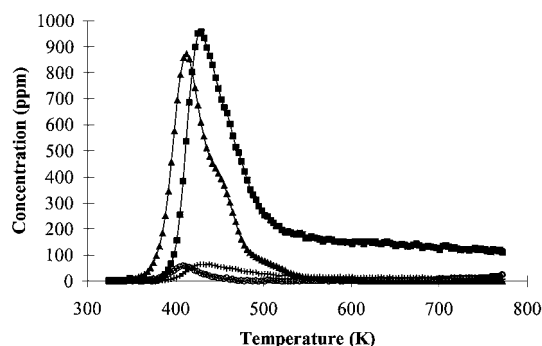
two shoulders at 450 and 510 K, respectively. In the subsequent reduction with H_2, also listed in Table 3, only small amounts of H_2O, N_2, and NH_3 were observed. In the D_2 reduction (not shown) no signal for mass 20 (D_2O or ND_3) was detected. The results of the TPR experiment with H_2 are shown in Fig. 6 (isothermal part) and Fig. 7 (temperature programmed part). In the isothermal part of the TPR experiment the immediate formation of N_2, followed by the subsequent production of NH_3 and H_2O can be clearly seen. In the temperature programmed part NH_3 and H_2O are observed in two peaks at 410 and 480 K, respectively. The first peak consist of mainly H_2O, whereas the latter is observed in both H_2O and NH_3. In the TPR experiment with D_2 (not shown) no signal for mass 20 (D_2O or ND_3) was detected.

The results of the TPD experiment after ammonia oxidation with various reactant concentrations are shown in Fig. 8 and also summarized in Table 3. From the results it appears that when the catalyst is exposed to a lower concentration of NH_3, less N_2 and H_2O are formed in the TPD experiment. When the catalyst is exposed to a lower concentration of O_2, the amounts of N_2 and H_2O formed in the TPD are about the same as after exposure to
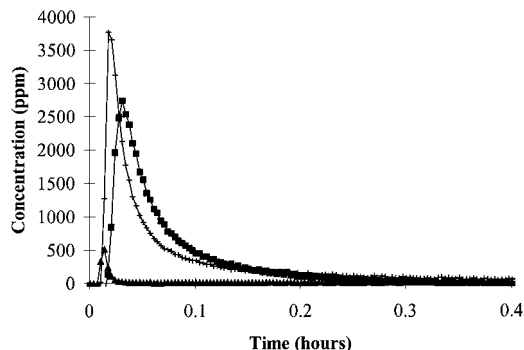

FIG. 5. TPD experiment on iridium sponge after reaction at 323 K. ▲, N_2; ■, H_2O; ○, N_2O; +, NH_3.

FIG. 6. Isothermal part of TPR experiment on iridium sponge after reaction at 323 K. ▲, N_2; ■, H_2O, +, NH_3.

FIG. 7. Temperature programmed part of TPR experiment on iridium sponge after reaction at 323 K. ▲, N_2; ■, H_2O, +, NH_3.
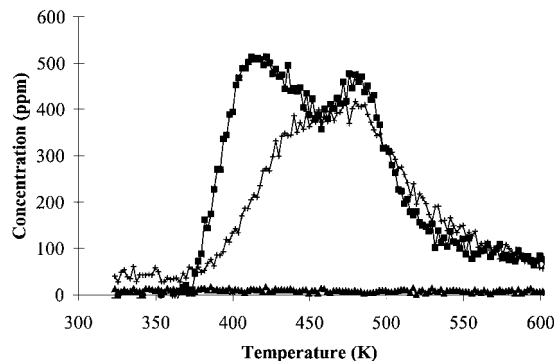
FIG. 9. TPD experiment on platinum sponge after reaction at 373 K. ▲, N_2; ■, H_2O; ○, N_2O; +, NH_3.

stoichiometric concentrations. However, after exposure to a lower concentration of O_2 the first peak in the TPD is lower and the second peak in the TPD is higher than in the TPD after exposure to stoichiometric concentrations. The subsequent reduction with H_2 is also listed in Table 3. It was found that after ammonia oxidation with a lower amount of O_2, less H_2O and more NH_3 were produced in the reduction, whereas after ammonia oxidation with

a lower amount of NH_3, more H_2O was produced in the reduction. In the D_2 reduction (not shown) no signal for mass 20 (D_2O or ND_3) was detected.

Temperature Programmed Experiments on Platinum Sponge

The result of the TPD experiment on platinum sponge is shown in Fig. 9 and summarized in Table 4. In Fig. 9, the desorption of N_2, H_2O, N_2O, and NH_3 can be seen clearly; all signals show broad peaks. The peaks of N_2 and N_2O are centered around a temperature of 490 K, whereas the NH_3 and H_2O peaks are centered around a temperature of 510 K. Similar to the case of the iridium experiments, this difference in temperature is probably caused by a stronger adsorption of NH_3 and H_2O in the reaction system. In the subsequent reduction with H_2, also listed in Table 4, a significant amount of H_2O together with small amounts of N_2 and NH_3 were observed. In the D_2 reduction (not shown) no signal for mass 20 (D_2O or ND_3) was detected. The results of the TPR experiment with H_2 are shown in Figs. 10 (isothermal part) and 11 (temperature programmed part). In the isothermal part of the TPR experiment only the production of H_2O can be seen. In the temperature programmed
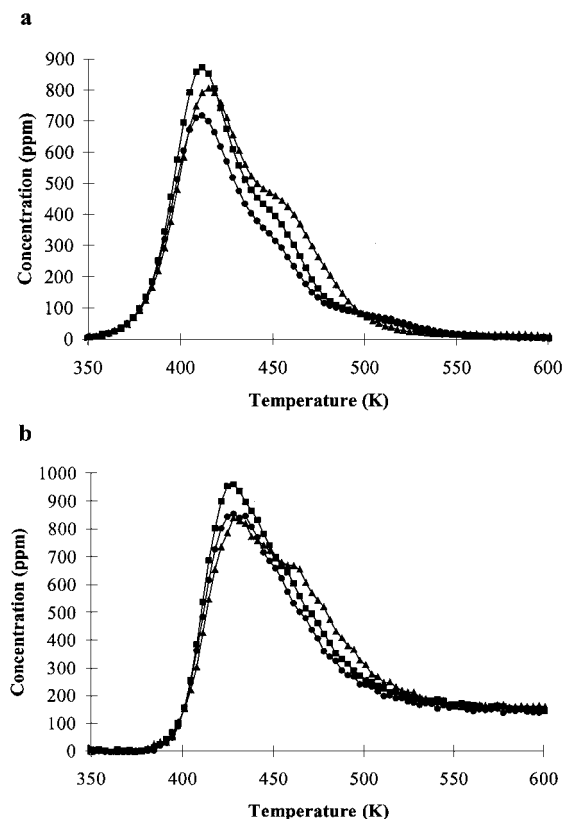

FIG. 8. Experiments after reaction of iridium sponge with various reactant concentrations. (a) N_2 signal of TPD; (b) H_2O signal of TPD. Reaction conditions: ▲, excess NH_3; ■, stoichiometric; ●, excess O_2.

TABLE 4

Amounts of Desorbed Species in the TPD and Reduction Experiments for Platinum Sponge, Variation of Reactant Concentration

Reactant concentration		Desorbed species per surface site						
		TPD			Reduction			
NH_3	O_2	N_2	N_2O	NH_3	H_2O	N_2	NH_3	H_2O
2.0	0.8	0.14^a	0.01^b	0.05^b	0.26^c	0.01^a	0.02^b	0.06^c
2.0	1.5	0.09^a	0.03^b	0.06^b	0.24^c	0.01^a	0.00^b	0.01^c
1.0	1.5	0.15^a	0.01^b	0.04^b	0.27^c	0.01^a	0.00^b	0.14^c

^{a} 95% Confidence interval is ±0.01 for N_2.
^{b} 95% Confidence interval is ±0.02 for N_2O and NH_3.
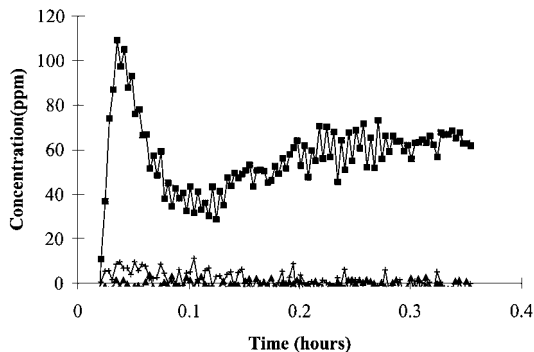^{c} 95% Confidence interval is ±0.03 for H_2O.

FIG. 10. Isothermal part of TPR experiment on platinum sponge after reaction at 373 K. ▲, N_2; ■, H_2O; +, NH_3.

part a small amount of NH_3 can be seen at temperatures above 480 K together with a larger amount of H_2O peaking at the same temperature. In the TPR experiment with D_2 (not shown) no signal for mass 20 (D_2O or ND_3) was detected.

The results of the TPD experiment after reaction with various reactant concentrations are shown in Fig. 12 and also summarized in Table 4. From the results it appears that when the catalyst is exposed to reactant concentrations other than stoichiometric, more N_2 and H_2O and less N_2O and NH_3 are formed. The subsequent reduction with H_2 is also listed in Table 4. It was found that after ammonia oxidation with a lower amount of O_2, less H_2O and more NH_3 were produced in the reduction. Whereas after ammonia oxidation with a lower amount of NH_3, more H_2O was produced in the reduction. In the D_2 reduction (not shown) no signal for mass 20 (D_2O or ND_3) was detected.

DISCUSSION

Iridium Sponge

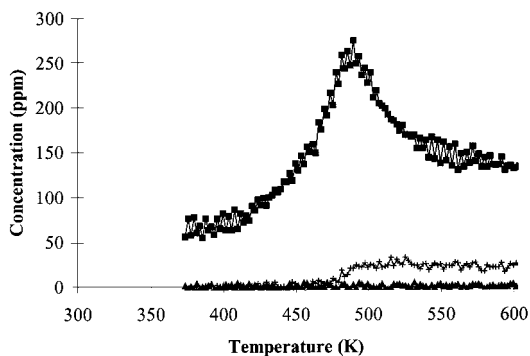In the TOS experiment shown in Fig. 1 it appeared that the iridium sponge catalyst becomes less active after an ini-

FIG. 11. Temperature programmed part of TPR experiment on platinum sponge after reaction at 373 K. ▲, N_2; ■, H_2O; +, NH_3.
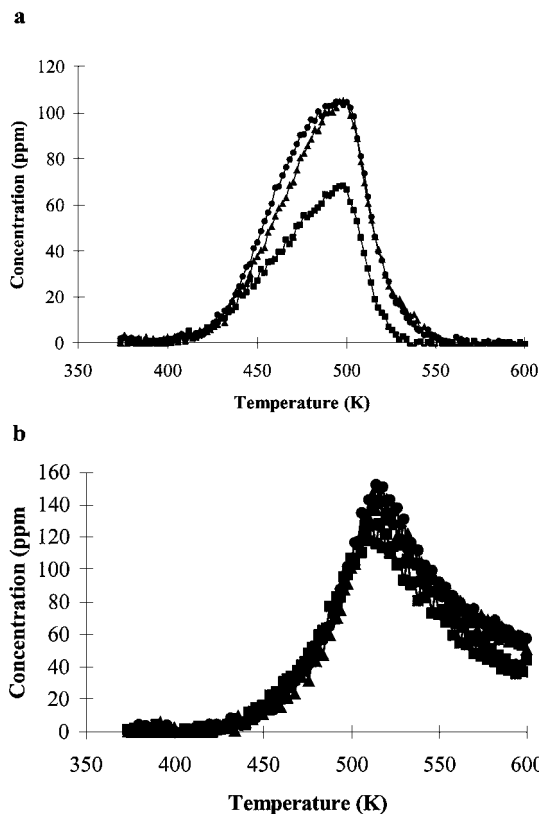

FIG. 12. Experiments after reaction of platinum sponge with various reactant concentrations. (a) N_2 signal of TPD; (b) H_2O signal of TPD. Reaction conditions: ▲, excess NH_3; ■, stoichiometric; ●, excess O_2.

tial increase in activity. In the steady state measurements shown in Table 2 it was found that the reaction orders were low, which is an indication of a highly covered catalyst surface. Therefore it is likely that the loss of activity is caused by intermediate species adsorbed on the catalyst surface.

In order to determine the nature of the surface species on the deactivated catalyst it must be first noted that the catalyst is flushed with helium at the reaction temperature (323 K) before the start of the TPD experiment; therefore any reaction product on the surface will desorb at this stage of the experiment. This is consistent with literature findings on the desorption of molecularly adsorbed N_2 (25), N_2O (25), and H_2O (26) on iridium surfaces. Molecularly adsorbed O_2, however, can be expected to remain adsorbed on the surface at this temperature (25), whereas molecularly adsorbed NH_3 will desorb (27). From the results of the XPS study on the deactivated catalyst sample it was concluded that the only N containing species on the surface can be N, NH, and NH_2. From the results of the reduction and TPR experiment with deuterium it was found that no ND_3 or D_2O was produced. From this result it can be concluded that there is no O_{ads} or $O_{2,ads}$ on the surface, since D_2O would be produced if O_{ads} or $O_{2,ads}$ would react with D_{ads}. Furthermore it can be deduced from this result that

TABLE 5

Calculated Surface Composition of Deactivated Catalysts

Reactant concentration		Iridium sponge			Platinum sponge		
NH_3	O_2	Θ NH	Θ NH$_2$	Θ OH	Θ NH	Θ NH$_2$	Θ OH
2.0	0.8	0.32[a]	0.00[a]	0.25[a]	0.35[b]	0.03[b]	0.33[b]
2.0	1.5	0.29[a]	0.00[a]	0.26[a]	0.25[b]	0.07[b]	0.038[b]
1.0	1.5	0.24[a]	0.02[a]	0.26[a]	0.35[b]	0.01[b]	0.43[b]

[a] 95% Confidence interval is ± 0.02 for iridium.
[b] 95% Confidence interval is ± 0.06 for platinum.

there is no N_{ads} on the surface. In the TPR experiment with H_2 the production of NH_3 is observed. Furthermore, it is known that the hydrogenation of NH_2 is the rate determining step in the production of NH_3 over Rh(111) (28). Therefore, there should be some ND_3 formed in the TPR experiment if there is N_{ads} present on the surface. Since no ND_3 is observed it can be concluded that there is no N_{ads} on the surface. The only surface species on the deactivated iridium sponge catalyst can therefore only be OH, NH, and NH_2. The composition of the iridium surface after the TOS experiment can now be calculated from the results of the TPD and reduction experiments. The results are shown in Table 5, together with the results for the platinum sponge catalyst. The values for NH and NH_2, however, must be treated with some care. Since the desorption of H_2O and NH_3 is broad it is possible that some signal is missed which would result in a larger value for NH_2 and a lower value for NH. However, obviously there is more NH than NH_2 on the surface.

The results in Table 3 also show that in the TPD after reaction with a stoichiometric reaction mixture almost all NH_x and OH reacts to form products. Only a small amount of OH and NH_x remains on the surface and reacts with H_2 in the subsequent reduction experiment. Furthermore, the results show that variation of the reactant concentrations varies the surface composition of the used catalyst. Compared to reaction with a stoichiometric reaction mixture, it would be expected that reaction with a lower concentration of oxygen gives rise to a larger amount of NH_x and a smaller amount of OH on the surface. This is indeed found in the combined TPD and reduction experiments. In the TPD experiment more N_2 and NH_3 and less H_2O are produced. After the TPD experiment only some NH_x remains on the surface. Therefore, in the subsequent reduction, only some NH_3 is produced. Compared to reaction with a stoichiometric reaction mixture, it would be expected that reaction with a lower concentration of ammonia gives rise to a larger amount of OH and a smaller amount of NH_x on the surface. This is indeed found in the combined TPD and reduction experiments. In the TPD experiment less N_2, NH_3, and H_2O are produced. After the TPD experiment a larger amount

of OH and some NH_x remain on the surface. Therefore, in the subsequent reduction, H_2O together with some NH_3 is produced.

Platinum Sponge

In the TOS experiment shown in Fig. 2 it appeared that activity of the platinum sponge catalyst decreases strongly after an initial increase in activity. Furthermore the selectivity to nitrogen and nitrous oxide changes strongly in the initial period. In the steady state measurements shown in Table 2 it was found that the reaction orders were low, which is an indication of a highly covered catalyst surface. Similar to the case of iridium, it is therefore likely that the loss of activity is caused by intermediate species adsorbed on the catalyst surface. Furthermore the change in selectivity is a strong indication of a change in surface coverage; the reactions forming N_2 and N_2O are apparently dependent on surface coverage in the case of platinum.

Similar to the iridium case discussed above, the catalyst was flushed with helium at the reaction temperature (373 K) before the start of the TPD experiment; therefore any molecularly adsorbed reactant and reaction product on the surface would desorb at this stage of the experiment. This is consistent with literature findings on the desorption of molecularly adsorbed N_2 (29), N_2O (30), H_2O (31), O_2 (32), and NH_3 (23, 33) on platinum surfaces. From the results of the XPS study on the used catalyst sample it was concluded that the only N containing species on the surface can be N, NH, and NH_2. In the results of the reduction and TPR experiment with deuterium it was found that no ND_3 or D_2O was produced. As discussed above for the iridium catalyst it can be concluded from this result that there is no O_{ads} or N_{ads} on the surface. The only surface species on the deactivated platinum sponge catalyst can therefore only be OH, NH, and NH_2. Therefore in contrast with electrochemical studies on platinum (13, 14) it can be excluded in this study that the loss of activity is due to N_{ads}. The composition of the platinum surface the TOS experiment can now be calculated from the results of the TPD and reduction experiments. The results are shown in Table 5, together with the results for the iridium sponge catalyst. The values for NH and NH_2, however, must be treated with some care. Since the desorption of H_2O and NH_3 is broad it is possible that some signal is missed which would result in a larger value for NH_2 and a lower value for NH. However, obviously there is more NH than NH_2 on the surface.

The results in Table 4 also show that in the TPD almost all NH_x reacts to form products, whereas some OH remains on the surface. This OH is reduced with H_2 in the subsequent reduction experiment. Furthermore the results show that variation of the reactant concentrations in the reaction varies the surface composition. Compared to reaction with a stoichiometric reaction mixture, it would be expected that reaction with a lower concentration of oxygen gives rise to

a larger amount of NH_x and a smaller amount of OH on the surface. This is indeed found in the combined TPD and reduction experiments. In the TPD experiment, however, a larger amount of H_2O is produced. This indicates that the reactions forming N_2 and N_2O are coupled to the reaction forming H_2O. Because of the larger amount of NH_x on the surface, besides N_2 and N_2O also a larger amount of H_2O is produced in the TPD experiment. After the TPD experiment less OH remains on the surface together with some NH_x. Therefore, in the subsequent reduction, less H_2O and even some NH_3 is produced. Compared to reaction with a stoichiometric reaction mixture, it would be expected that reaction with a lower concentration of ammonia gives rise to a larger amount of OH and a smaller amount of NH_x on the surface. However, this is not found. From the combined TPD and reduction experiments both a higher NH_x as well as a higher OH coverage is found. Apparently the surface with a higher OH coverage can contain more NH_x, while the value of x is lower.

Comparison of Iridium and Platinum Sponges

At steady state, after the initial loss of activity the iridium catalyst showed to be almost 10 times more active than the platinum catalyst. Furthermore the selectivity to nitrogen is significantly enhanced on the iridium catalyst. Therefore iridium is a more suitable catalyst than platinum for the low temperature selective oxidation of ammonia under the conditions used in this study. Since the reaction orders that were found are different for iridium and platinum, other reaction conditions may change the difference in performance. Both the used platinum and the iridium have surfaces covered with NH, NH_2, and OH species. It appears that there is somewhat more NH_2 and OH on the platinum surface than on the iridium surface. The largest difference in behavior between iridium and platinum can be seen in the TPD experiments: the products desorb from the surface at much lower temperatures in the case of the iridium catalyst.

Time on Stream (TOS) Behavior and Reaction Mechanism

Iridium is known to form stronger interactions with adsorbed species than platinum, for example with oxygen and nitrogen adatoms (34, 35). Therefore iridium catalysts are more active than platinum catalysts in reactions in which bond breaking is rate determining. This is the reason that iridium is more active than platinum in the decomposition of ammonia (36), but not in the decomposition of hydrazine (37, 38). Iridium catalyst are less active than platinum in reactions in which desorption of the products is the rate determining step. Because of the stronger interaction with the adsorbed oxygen atoms the reaction rate of iridium is lower than that of platinum in the hydrogen and carbon monoxide oxidation (39). Since in this study it was found that iridium is

much more active in than platinum in the low temperature ammonia oxidation reaction it appears that bond breaking will be the rate determining step in this reaction. Therefore the reaction producing N_2 will not proceed through a N_2H_x intermediate (Eq. [13]). In that case platinum would be expected to be the most active catalyst. It was shown that there is no N_2H_x intermediate on the surface. Furthermore no hydrazine is seen as a product of the reaction. Therefore the formation of the N_2H_x intermediate would have to be the rate determining step. Since this is a N–N bond forming step it would be expected that platinum would be more active than iridium. The other route for forming N_2 is the associative desorption of N_{ads} (Eq. [12]). This reaction is known in surface science to occur at higher temperatures (400 K for Pt (40), 500 K for Ir (35)) than the reaction temperatures used in this study. However, nitrogen is seen as a reaction product. Since there is no N_{ads} found on the surface all N_{ads} that was on the surface must be desorbed during the flushing with helium. Possibly the high surface coverage during reaction makes the desorption of N_2 possible at this low temperature. This could also be the explanation of the increasing activity at the start of the reaction; the desorption of nitrogen is only possible at a high surface coverage. Since the associative desorption of N_2 would be expected to be faster on platinum this step cannot be the rate determining step in a steady state reaction. Furthermore the surface would be covered with N_{ads} if this step would be rate determining. Therefore it seems more likely that the stepwise dehydrogenation of NH_3 (Eqs. [6]–[8]) is rate determining. In that case iridium would be expected to be more active than platinum, since N–H bonds are broken in these steps. Since the surfaces of both platinum and iridium are covered with mainly NH and OH it appears that the reactions using this NH are the slowest step (Eqs. [8] and [11]). Since there is no O on the surface the main reaction therefore is the reaction of NH with OH (Eq. [11]). From computational chemistry it is known that this surface reaction is endothermic (19). Therefore this path will be much slower than the path via the reaction of NH with O (Eq. [8]). The loss of activity is therefore caused by inhibition of active sites with NH and OH. The TPD experiments provide evidence for this mechanism. The production of water from hydroxyl groups on platinum or iridium should occur at temperatures below the reaction temperature used in this study (26, 31). However, during the TPD production of water is observed. This water therefore must be produced by the reaction of NH_x with OH (Eqs. [10] and [11]).

The reaction forming N_2O must proceed via a NO intermediate. Since no NO is seen as a reaction product or on the surface of the deactivated catalyst the reaction forming N_2O must be fast. The lower production of N_2O on iridium can be explained by the higher activity of iridium to dissociate NO (35), therefore reducing the lifetime of NO on the iridium surface to react with N to form N_2O.

CONCLUSIONS

In this study it was shown that, under the reaction condition used, iridium is a more active and selective catalyst than platinum for the low temperature (<373 K) oxidation of ammonia with oxygen to nitrogen. Furthermore it was established that both catalysts lose activity with time on stream due to inhibition of the surface with reaction intermediates. The used catalysts were found to contain a high coverage with NH and OH and some additional NH_2. Since iridium is more active than platinum the reaction mechanism must proceed through a stepwise dehydrogenation of the ammonia molecule. Since most of the nitrogen on the surface is NH it appears that the last dehydrogenation step (NH with OH to N and water) is the rate determining step. The high selectivity of iridium to nitrogen can be explained by the stronger interaction of iridium with reaction intermediates.

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