

Water-promoted ammonia oxidation by a platinum amine complex in zeolite HZSM-5 catalyst

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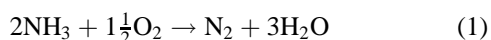
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In this study it was found that $[\text{Pt}(\text{NH}_3)_4]\text{HZSM-5}$ is an active catalyst for the oxidation of ammonia at low temperature that, in contrast with other catalysts, becomes more active in the presence of water. Furthermore, the selectivity to nitrogen was found to increase when water is present.

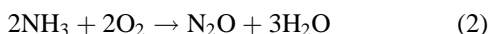
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1. Introduction

Selective oxidation of ammonia with oxygen to nitrogen and water could be a solution to several ammonia emissions, caused by various sources like: the SCR process, soda production, or agricultural sources [1]. Usually the concentration of ammonia in the emission is low ($<1\%$), therefore the process should use a catalyst that is active at a low concentration [1] or the ammonia should be concentrated by adsorption in water and subsequent desorption [2]. Various catalysts of different types have been tested for the ammonia oxidation reaction; biological catalysts [3], metal oxide catalysts [4,5], ion-exchanged zeolites [4–6] and metallic catalysts [5,7,8]. The most active catalysts at low temperature are the precious metal (Pt, Pd, Ir) catalysts [5,7,8]. At low temperature, the product of the reaction is nitrogen, as shown in equation (1).



The formation of nitrous oxide is often seen as a by-product, following equation (2).



Since nitrous oxide is an unacceptable environmental emission, an effective catalyst should have a high selectivity towards nitrogen [9]. A recent study [9] showed that ion-exchanged $[\text{Pt}(\text{NH}_3)_4]^{2+}$, Rh^{3+} , and Pd^{2+} in zeolite NaZSM-5 are active in the oxidation of ammonia at temperatures from 473 K. Although reduction of the metal ions increased the activity, the unreduced complexes were also active. The activity of these catalysts was found to be suppressed by the addition of water. In a recent study [10] on the decomposition of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ion-exchanged in zeolite HZSM-5, it was shown that the partial decomposition of this complex in 2.4% O_2/He is already possible at a temperature of 473 K. However, it was found that at that

temperature this reaction is only possible in the presence of water. This suggests that water might be expected to have a positive effect if $[\text{Pt}(\text{NH}_3)_4]^{2+}$ in zeolite HZSM-5 is used as a catalyst for the oxidation of ammonia at a temperature of 473 K. This would be remarkable since water usually decreases the activity of catalysts [8,9]. Therefore, in this study the activity of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ in zeolite HZSM-5 was studied in the oxidation of ammonia at 473 K. The reaction was carried out both with a reaction mixture containing water and a reaction mixture which was dry.

2. Methods

2.1. Sample preparation

A batch of 10 g of NaZSM-5 (Exxon, AT281/78962, $\text{Si}/\text{Al} \approx 40$) was calcined up to a temperature of 550 °C in order to remove the template. HZSM-5 was prepared from the calcined NaZSM-5 by triple exchange with 1 M NH_4NO_3 followed by calcination in dry air up to 500 °C. $[\text{Pt}(\text{NH}_3)_4]\text{HZSM-5}$ was prepared by ion exchange, following literature methods [10,11]. A dilute solution of $[\text{Pt}(\text{NH}_3)_4](\text{OH})_2$ (Strem Chemicals, lot no. 132413-S4) was added dropwise to a stirred HZSM-5 slurry (200 ml doubly deionized water per gram of zeolite); after 24 h of stirring at room temperature, the slurry was filtered and washed twice with 100 ml doubly deionized water. During the exchange, the pH of the solution was found to be 7. A UV/VIS measurement of the filtrate showed that the ion exchange was complete. The platinum loading of the sample was 0.50 wt%, which is equivalent to a Pt/Al ratio of 15.8. In the reaction setup particles were used with a particle size between 125 and 425 μm ; samples of the catalyst were pelletized, crushed, and sieved to acquire the appropriate particle size.

2.2. Measurement of catalytic activity

Catalytic 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 quadrupole mass spectrometer was used for the detection of NH_3 , O_2 , H_2O , N_2 , and N_2O quantitatively and for detection of the presence of NO and NO_2 . In order to measure accurately, the mass spectrometer was calibrated for each experiment with the gas chromatograph using the reaction mixture. A quartz tube with an internal diameter of 4 mm was used as the reactor. An amount of 150 mg of the catalyst was used in the reactor ($\text{GHSV} \approx 6000$). A reaction mixture consisting of 1.3% of ammonia and 1.0% of oxygen in helium was used as a standard reaction mixture; if water was added a concentration of 1.7% was used. The total flow was 30.7 Nml/min for all experiments.

3. Results

In figure 1 the results for the production of nitrous oxide are shown as a function of time in the oxidation of ammonia over $[\text{Pt}(\text{NH}_3)_4]\text{HZSM-5}$ as a catalyst with and without water in the reaction mixture. From figure 1 it can be clearly seen that at the start of the reaction much nitrous oxide is produced, but the production rate drops rapidly. This drop in activity occurs at the moment that ammonia gas is first

measured (breakthrough of ammonia). Furthermore, it is obvious that at the initial state of the reaction slightly more nitrous oxide is produced in the dry case than in the case with water in the reaction mixture. After the drop in production rate, however, it appears that the production rate of nitrous oxide is somewhat larger in the case when water is present in the reaction mixture than in the dry case. However, due to the noise at this low concentration the difference is not significant. In figure 2 the results for the production of nitrogen are shown as a function of time in the oxidation of ammonia over $[\text{Pt}(\text{NH}_3)_4]\text{HZSM-5}$ as a catalyst with and without water in the reaction mixture. From figure 2 it can be clearly seen that at the start of the experiment not much nitrogen is produced, but the production rate increases rapidly after the breakthrough of ammonia. Furthermore, it is obvious that the production rate is much larger when there is water in the reaction mixture: after the rapid increase the rate increases further slowly when there is water in the reaction mixture, whereas it decreases rapidly when there is no water. Also it must be noted that at the start of the experiment the production of nitrogen can be seen immediately when water is present, whereas the production of nitrogen starts after some time when there is no water in the reaction mixture. The turnover frequency (TOF) that can be derived from the combined production of nitrogen and nitrous oxide is calculated to be 2.2 mole of NH_3 converted per mole of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ per hour in the case with water and 0.7 mole of NH_3 converted per mole of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ per hour in the dry case after 2 h on stream.

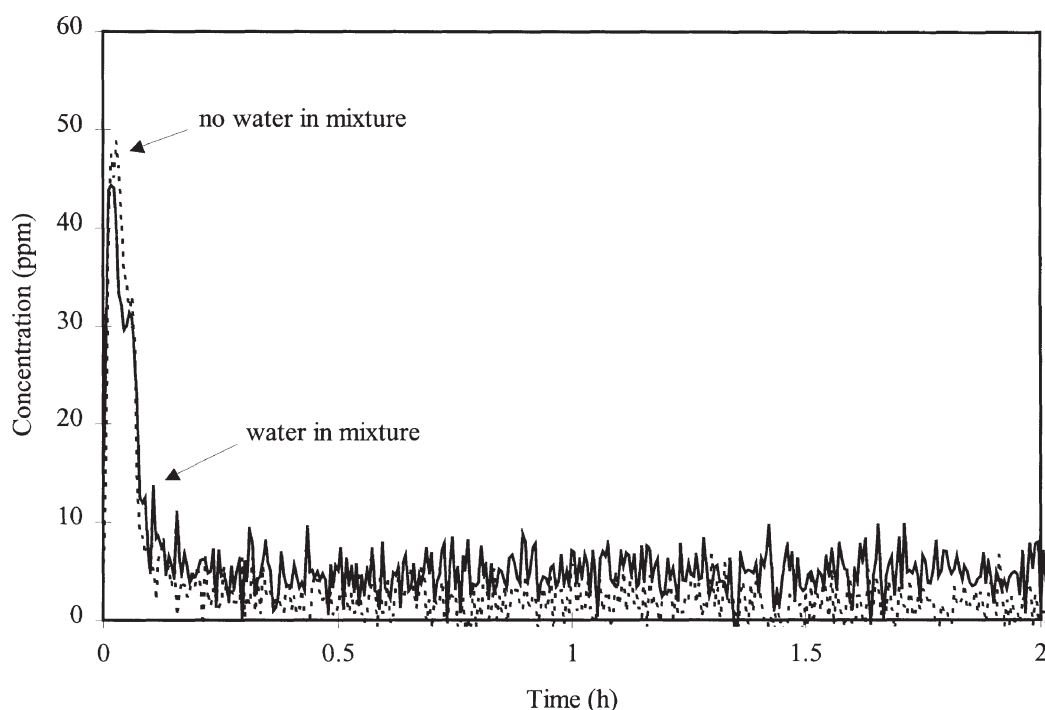


Figure 1. Production of nitrous oxide in the oxidation of ammonia over $[\text{Pt}(\text{NH}_3)_4]\text{HZSM-5}$ at 473 K. Reaction mixture: without water – dotted line; with water – solid line.

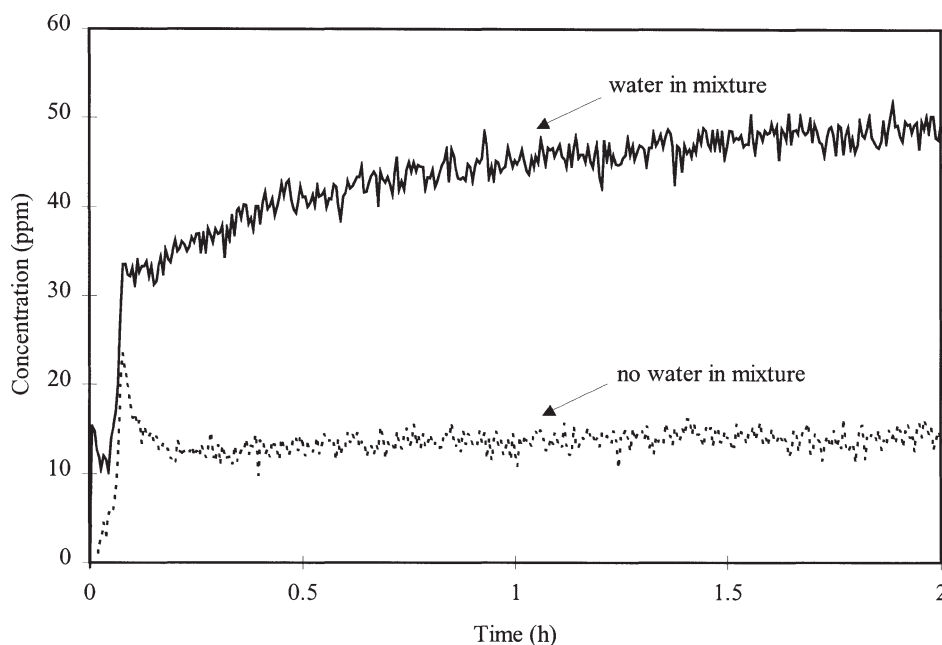


Figure 2. Production of nitrogen in the oxidation of ammonia over $[\text{Pt}(\text{NH}_3)_4]\text{HZSM-5}$ at 473 K. Reaction mixture: without water – dotted line; with water – solid line.

4. Discussion

From the results of the experiments, two periods in the reaction can be seen: before and after the breakthrough of ammonia gas. Since the experiment was performed with and without water four different reaction states can be distinguished, as shown in table 1.

The reaction of ammonia with oxygen over $[\text{Pt}(\text{NH}_3)_4]^{2+}$ in zeolite HZSM-5 is sensitive to the ammonia concentration at the catalyst. Since ammonia is adsorbed by the acid sites of the zeolite, at the start of the reaction the ammonia concentration is low and the acid sites are available; but after some time the zeolite acid sites are fully covered with ammonia and the ammonia concentration at the $[\text{Pt}(\text{NH}_3)_4]^{2+}$ site will be the same as in the gas phase. In table 1 it can be clearly seen that before the breakthrough of ammonia the product of the reaction is mostly nitrous oxide, whereas the favored product is nitrogen after the breakthrough of ammonia. Therefore, the reaction forming nitrous oxide must be either enabled by the acid sites or suppressed by ammonia gas. In contrast, the reaction forming nitrogen must be either enabled by ammonium sites or ammonia gas or suppressed by the acid sites. Furthermore, it can be seen in table 1 that the presence of water also influences the reaction product ratio. Addition of water only influences the reaction producing nitrogen: more nitrogen is produced when water is present. Possibly nitrogen can be produced only by a reaction involving water. That there is some production of nitrogen when there was no water in the reaction mixture does not necessarily disagree with this theory. There will be water present in this case since it was produced in the oxidation reaction producing nitrous oxide. That the production of nitrogen starts later in the experiment without water is a support for this theory: the

Table 1
Products in various reaction states.

	Before breakthrough of NH_3	After breakthrough of NH_3
Without H_2O	N_2O	(N_2)
With H_2O	N_2O (N_2)	N_2

production of nitrogen can only start after some water is available. Also, the small peak observed in the dry case at the moment of ammonia breakthrough agrees with this view: because of the higher ammonia concentration water is released by the zeolite. Once the reaction producing nitrogen is running it could produce the water to sustain itself.

Possibly the reaction proceeds through a mechanism similar to that of the oxidation of coordinated ammonia on Ru amine complexes [12,13] in a basic solution and the reaction of NO with Ru and Os amine complexes [14–16]. This would involve the formation of a complex with a nitrosyl and a hydride ligand. This nitrosyl ligand could be oxidized further by oxygen to form a nitrate ligand. Subsequently, the nitrate ligand can react with an ammonia and the hydride to form ammonium nitrate which decomposes to nitrous oxide and water. Alternatively, the nitrosyl ligand could react with water to form a nitrite ligand. Similar to the nitrate, the nitrite ligand can react with an ammonia and the hydride to form ammonium nitrite which decomposes to nitrogen and water. A reaction mechanism involving the reactions described above would explain the unusual behaviour of this catalyst towards water. The explanation of the behavior of the catalyst before and after the breakthrough of ammonia would be that the complex can be activated to form a nitrosyl complex by either the extraction of an ammonia ligand by an acid site or the exchange of an ammonia

ligand with water. The nitrosyl complex formed by action of an acid site would eventually yield nitrous oxide. This complex cannot be formed anymore after the breakthrough of ammonia since then there are no acid sites available anymore. The nitrosyl complex formed by the action of water would eventually yield nitrogen. This complex can still be formed after breakthrough of ammonia and the rate forming nitrogen will be higher, since the ammonia concentration is raised and more active sites are available for this path since the other reaction path is not reactive anymore. Although this reaction mechanism can explain the results observed in this study there is no direct evidence for the occurrence of the intermediates yet. However, platinum(II) amine complexes with a hydride ligand [17] or nitrosyl, nitrite, or nitrate ligands [18] are known in literature.

Part of the products will be produced from the decomposition of the $[\text{Pt}(\text{NH}_3)_4]^{2+}$ complex. It is not possible from the experiments described in this study to discriminate between the products of the decomposition of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ and the reaction of ammonia with oxygen. Total turnover numbers of 4.5 mole of NH_3 per mole of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ (experiment with water) and 1.5 mole of NH_3 per mole of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ (experiment without water) were measured in 2 h on stream. The catalytic turnovers are calculated to be 3.5 mole of NH_3 per mole of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ (experiment with water) and 1.5 mole of NH_3 per mole of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ (experiment without water), since it is known that only one of the four amine ligands is decomposed at 473 K when water is present and none when no water is present [10]. Most of the products are therefore formed by catalysis. The slow increase in production of nitrogen in time (0.1–2.0 h on stream) that can be observed in figure 2 indicates that the formation of the active species is being completed during this time. However, only experiments with labeled molecules can provide information about the part of the products that can be attributed to the catalytic reaction at a certain time on stream.

In order to compare the activity of the $[\text{Pt}(\text{NH}_3)_4]^{2+}$ in HZSM-5 catalyst with the metallic catalyst the activity of a reduced Pt/HZSM-5 catalyst has to be known. Since these platinum catalysts are known to show light-off behavior around 473 K [19], the activity cannot be determined directly. Therefore, the comparison has to be made with an activity that is determined at somewhat deviating conditions (NH_3 concentration 2.0%, O_2 concentration 1.5%, no water, 50 Nml/min flow) is known to be 0.91 mole of NH_3 converted per mole of surface Pt per hour at 443 K [8]. Using the activation energy of 72 kJ/mole which was determined for this catalyst, the activity at 473 K without light-off is expected to be approximately 3.1 mole of NH_3 converted per mole of surface Pt per hour. Since the activity of metallic catalysts is known to decrease under the influence of water [8,9] it appears that the activity of the $[\text{Pt}(\text{NH}_3)_4]^{2+}$ in HZSM-5 catalyst is similar (2.2 mole of NH_3 converted per mole of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ per hour) to that of the metallic catalyst. For practical purposes, however, it must be noted that a strong particle size effect gives rise to

an enhanced activity of catalysts that contain larger metal particles [8,9].

5. Conclusions

In this study it was found that $[\text{Pt}(\text{NH}_3)_4]\text{HZSM-5}$ is an active catalyst for the oxidation of ammonia at low temperature that, in contrast with other catalysts, becomes more active in the presence of water. Furthermore, the selectivity to nitrogen was found to increase when water is present. At the start of the reaction nitrous oxide was found to be the main product. However, nitrogen became the main product after the breakthrough of ammonia; the nitrous oxide production was largely decreased. It appears that water enables the reaction path to nitrogen, since the reaction rate for this path was much higher if water was present in the reaction mixture. Probably water takes part in the reaction that leads to the production of nitrogen. The activity of this catalyst is approximately the same as the activity of small metallic platinum particles in zeolite HZSM-5.

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