TEMPERATURE PROGRAMMED REDUCTION OF UNSUPPORTED MOLYBDENA AND VANADIA CATALYSTS BY AMMONIA AND HYDROGEN

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Temperature-programmed reduction (TPR) is a valuable tool for the characterisation of catalysts. The reductant mostly used is hydrogen. Hydrogen reduces the catalyst by producing water. The amount of hydrogen reacted is measured by menas of a thermal conductivity detector. In this paper the temperature-programmed reduction of vanadia and molybdena catalysts by ammonia is emphasized. During the temperature-programmed reduction ammonia is consumed. The compounds formed in this process are detected by means of a mass spectrometer. It was found that almost exclusively N_2, H_2O and H_2 were formed. Hydrogen formed by the decomposition of ammonia over vanadia and molybdena above 600° produces hydroxyl groups, which are a source for the formation of water at temperatures above 600°.

NH_3–TPR gives more relevant information than H_2–TPR for processes in which ammonia is used as a reactant.

In KEMA laboratories catalysts for the selective catalytic reduction of NO_x by ammonia over vanadia catalysts and the oxidation of ammonia over molybdena catalysts have been studied over the past seven years [1-3].

One of the steps in the catalytic reaction is the reduction of the catalyst by chemisorption of ammonia [4]. For the case of vanadia catalysts NO_x reacts with the chemisorbed nitrogen-hydrogen species forming N_2 and H_2O and molecular oxygen oxidizes the reduced oxide.

The molybdena catalysts are reduced by ammonia, producing nitrogen and water; again the reduced material is oxidized by gas phase oxygen. Therefore, in order to characterize catalysts for their ability in the reduction

of the catalyst it is very useful to study the reduction step by means of temperature-programmed reduction (TPR).

This technique has become one of the most widely used physicochemical techniques for the characterization of heterogeneous catalysts [5, 6]. It has been used to study the rate and extent of hydrogen uptake. TPR is a convenient technique for following the evolution of a catalyst system as a function of the preparation of the precursor and the calcination conditions.

During the reduction of an oxide the following overall reaction occurs

$$M_xO_y + H_2 \quad \rightarrow \quad H_2O + M_xO_{y-1} + a \text{ kJ} \tag{1}$$
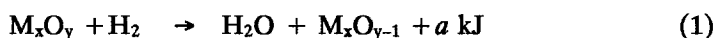
Reduction of an oxide means that oxygen ions are removed from the lattice leaving behind oxygen vacancies. At a certain stage of reduction the disturbed lattice of the oxide rearranges and a more stable lattice is formed.

At equilibrium the Gibbs free energy must be at minimum, that is, μ_o in the equation $\mu_i = \mu_o + RT \ln(K)$ must be negatively balanced by the $\ln(K)$ term. For most oxides, however, the absolute value of μ_o is larger than that of the term $RT \ln(K)$. During temperature-programmed reduction the activity of hydrogen is constant, while the activity of water decreases because water is removed by the flowing gas atmosphere. Therefore, reaction (1) proceeds in such a way that the oxide is reduced into a lower oxide.

Most of the users of TPR apply hydrogen as a reductant. Because the reduction of the catalyst by ammonia is an important step in the mechanism of the reaction over V_2O_5 and MoO_3 catalysts, ammonia is used as a reductant instead of hydrogen. Using ammonia as a reductant, a number of overall reactions can occur. Ammonia can be oxidized by the metal oxides into N_2, NO, N_2O, or it may decompose into nitrogen and H_2O.

For analysis of the reaction products a mass spectrometer is used instead of a thermal conductivity detector.

The present paper describes an investigation of the reduction of unsupported catalysts by hydrogen or ammonia. Qualitative aspects of the use of hydrogen and ammonia are discussed.

Experimental

The amount of unsupported V_2O_5 and MoO_3 catalysts used in this study are summarized in Table 1. Two commercial available well annealed catalysts are compared with catalysts prepared in our laboratories. Well annealed V_2O_5(a) and MoO_3(a) were purchased from Cerac (The Nether-

lands). V_2O_5(d) was prepared by thermal decomposition of ammonium vanadate at 400° for 16 h. MoO_3(p) was prepared according to the homogeneous deposition precipitation method developed by Geus [7].

Table 1 Catalysts used for the reduction experiments and the positions of the peak maxima in the TPR spectra

| Catalyst | H2–TPR | | NH3–TPR | |
| | Weight, | Peak maxima | Weight, | Peak maxima |
	mg		mg	
V2O5 (a)	14.8	675(s)*; 712(s); 780	14.6	370; 405(s); 482(s); 640(s)
V2O5 (d)	18.0	672(s); 704(s); 788; 818	51.8	383; 427(s); 494(s); 714(s)
MoO3(a)	20.4	763(s)	20	510(s)
MoO3(p)	22.8	685(s); 700(s)	21	431(s); 449(s); 695(s)

* (s) means strong peak

Results were obtained by modification of the existing TPR instrumentation [2]. The cold traps were removed and the thermal conductivity detector replaced by a sector mass spectrometer (MS). All mass spectra were checked for the presence m/z 30 (NO) and m/z 44 (N_2O). These compounds might be formed from the oxidation of ammonia. During programmed heating mass spectra were acquired from m/z =14 to m/z =60 at 30 s intervals. The mass peaks at m/z 17, 18 and 28 were assigned to NH_3, H_2O and N_2 respectively. The ion current at m/z 17 was corrected for the contribution as a result of the fragmentation of H_2O into OH^+.

The ion current plots for all emitted compounds were obtained. Hydrogen in argon (5%) and ammonia in helium (5%) were used as reduction agents. The gas flow was 65 $cm^3 \cdot s^{-1}$. The heating rate was 5 $deg \cdot min^{-1}$ and the temperature varied from 100 to 900°.

Results and discussion

In Table 1 and Figs 1-4 the results are shown of the reduction by hydrogen or by ammonia of the unsupported materials.

In Table 1 the temperatures for the maximum reduction rate in the TPR spectra are given for both H_2–TPR and NH_3–TPR. The H_2–TPR spectrum of V_2O_5(a) resembles that of V_2O_5(d).

The H_2–TPR spectrum of MoO_3(a) and MoO_3(d) shows one and two peaks respectively.

When the reduction is carried out with NH_3 instead of H_2 the temperatures for the peak maxima shift to lower temperatures.

Figure 1 shows the NH_3–TPR spectrum of V_2O_5(d). The ion currents of NH_3, H_2O and N_2 are plotted as a function of temperature. Neither N_2O nor NO were formed during the reduction of the catalyst by ammonia.
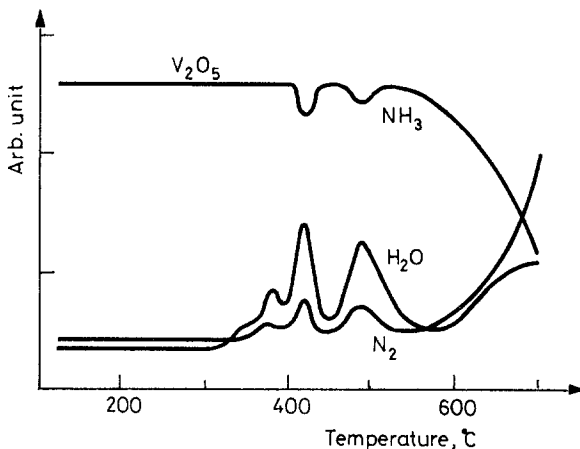

Fig. 1 NH_3–TPR of unsupported V_2O_5(d). Heating rate $dT/dt = 5$ deg·min^{-1}, amount of V_2O_5 is 51.8 mg, [NH_3] is 5% (vol.) in helium
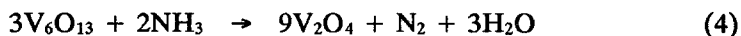
As can be seen from Fig. 1 the form of the curves of H_2O and N_2 for temperatures ranging from 200 to 600° resemble each other. Another feature is that the ratio of the corresponding peak heights is about 3. This can be explained by assuming that NH_3 is oxidised into N_2 and H_2O.

The following subtle differences may be observed. The form of the three peaks of the signals for m/z 18 and 28 is identical whereas for m/z 17 only two peaks corresponds with two peaks of the water and nitrogen signals.

The shoulder at about 380° may be explained as follows. As a result of the reduction of the top layer of the vanadium particles hydroxyl groups are formed. The surface may be dehydrated producing H_2O. The two larger peaks may be assigned as a result of the following reaction sequence which was proposed by Bosch et al. [8]

$$V_2O_5 \quad \rightarrow \quad 1/3\ V_6O_{13} \quad \rightarrow \quad V_2O_4 \qquad (2)$$

Thus, the peaks at 427 and 494° may be ascribed to the following consecutive overall reactions,

$$9V_2O_5 + 4NH_3 \rightarrow 3V_6O_{13} + 2N_2 + 6H_2O \qquad (3)$$

$$3V_6O_{13} + 2NH_3 \rightarrow 9V_2O_4 + N_2 + 3H_2O \qquad (4)$$

Above 600° ammonia is decomposed into nitrogen and hydrogen. Above 600° hydrogen acts as a reducing agent forming hydroxyl groups on V_2O_4. The broad peak is probably due to water which is a result of dehydration of V_2O_4. At 800° V_2O_5 is completly reduced to V_2O_3. Comparing the NH_3–TPR spectra of V_2O_5(a) and V_2O_5(d) with the H_2–TPR spectra it can be seen from Table 1 that the strongest peaks are shifted to higher temperatures. Figures 2 and 3 show the NH_3–TPR profiles of well–annealed MoO_3(a) and MoO_3(p) respectively. Over those oxides NH_3 is exclusively oxidised into N_2 and H_2O in the temperature range of 400 to 600°. The peak assigned to the production of water is somewhat enlarged in order to give more detailed information about the form of the peak. The two peaks occurring at 431 and 449° shown in Fig. 3 are ascribed to the reduction of MoO_3 via non-stoichiometric molybdenum oxides into MoO_2 [9]. Comparing Figs 2 and 3 it is observed that the peaks of the ammonia and water signals for MoO_3(p) occur at a lower temperature than that for MoO_3(a). This may be explained by the fact that the specific surface area of MoO_3(a) is smaller
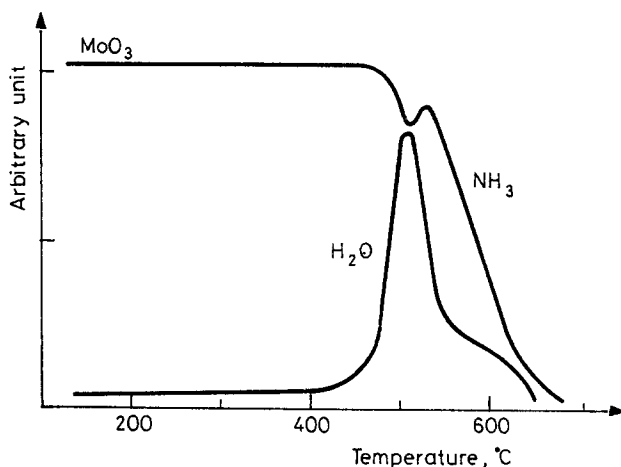

Fig. 2 NH_3–TPR of MoO_3(a), amount of catalyst is 20 mg. For other experimental conditions see Fig. 1

than that of $MoO_3(p)$. Moreover, $MoO_3(p)$ contains more surface defects which enables reduction at lower temperatures. As for V_2O_5, at temperatures above $600°$ the concentrations of N_2 (not shown in Fig. 2) increases and NH_3 decreases simultaneously whereas the concentration of H_2O shows a maximum. Again, the same explanation as for V_2O_5 may be given. Figure 4 is composed from two H_2–TPR spectra for the two types of MoO_3. The form of the peaks is comparable to those of Figs 2 and 3. However, the values for the peak maximum are shifted to higher temperatures. The temperature difference between the two 'water peaks' is about $80°$.
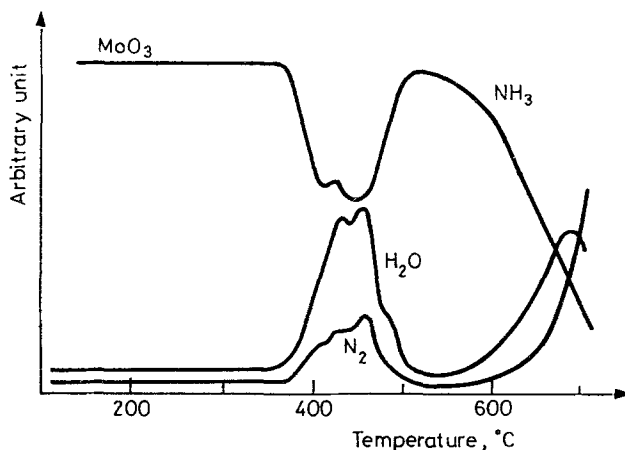

Fig. 3 NH_3–TPR of $MoO_3(p)$, amount of catalyst is 21 mg. For other experimental conditions see Fig. 1

So far the reduction of vanadia and molybdena have been described. More research needs to be done, such as the study of the influence of the amount of material used, the concentration of the reduction agent, the heating rate and the gas flow rate on the reduction profile. In a forthcoming paper the results using supported materials will be presented.

Conclusions

Ammonia reduces the catalysts V_2O_5 and MoO_3 forming almost exclusively water and nitrogen.

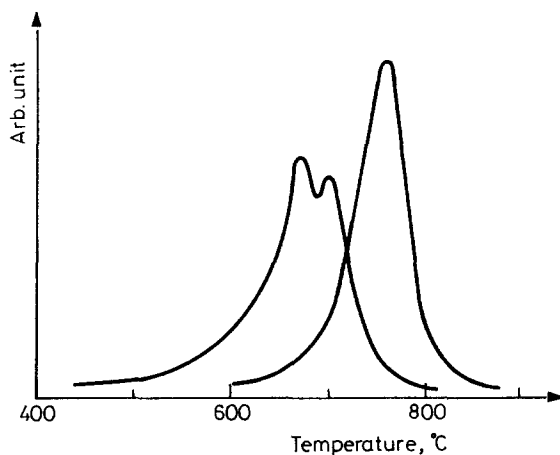The molybdena materials show a different reduction behaviour from that of vanadia.

Fig. 4 H_2–TPR of well annealed MoO_3(a) (peak at the right) and MoO_3(p) (peak at the left). Amount of catalyst is 20.4 and 22.8 mg respectively, dT/dt is 5 deg·min^{-1}, 5% (vol.) H_2 in helium

Both catalysts are reduced below 600° by ammonia whereas above that temperature ammonia is decomposed into hydrogen and nitrogen. Above 600° water is produced which is attributed to the dehydroxylation of the surface of the materials.

The maximum of mass peaks of water shifts to higher temperatures if hydrogen is used as reductant instead of ammonia.

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References

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Zusammenfassung — Temperaturprogrammierte Reduktion (TPR) ist ein wertvolles Mittel zur Charakterisierung von Katalysatoren. Das am häufigsten Benutzte Reduktionsmittel ist Wasserstoff. Wasserstoff reduziert den Katalysator, wobei Wasser entsteht. Die Menge des in der Reaktion verbrauchten Wasserstoffes wird mit Hilfe eines Wärmeleitfähigkeitsdetektors bestimmt. In vorliegender Arbeit wird die temperaturprogrammierte Reduktion von Vanadium- und Molybdänkatalysatoren durch Ammoniak näher erläutert. Ammoniak wird bei der temperaturprogrammierten Reduktion verbraucht. Die dabei gebildeten Verbindungen wurden mittels Massenspektrometrie nachgewiesen. Man fand, daß fast ausschließlich N_2, H_2O und H_2 gebildet werden. Der bei der Zersetzung von Ammoniak entstehende Wasserstoff erzeugt an Vanadium und Molybdän oberhalb 600°C Hydroxylgruppen, die die Quelle für die Bildung von Wasser bei einer Temperatur über 600°C darstellen.