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LOW TEMPERATURE ISOTOPIC EXCHANGE OF MOLECULAR OXYGEN VIA THE REACTION OF NO, NH_3 AND O_2 OVER SUPPORTED VANADIA AND MOLYBDENA CATALYSTS

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This study describes the behaviour of NO, NH_3 and $^{18}O_2$ over supported molybdena and vanadia catalysts. The study was carried out using differential scanning calorimetry. The catalysts show different behaviour with respect to the reaction of NO, NH_3 and O_2 and similar behaviour with respect to the formation of water.

1. Introduction

Selective catalytic reduction is one of the techniques of removing NOx from flue gas. Supported catalysts such as V_2O_5 on TiO_2 [1]; V_2O_5 on TiO_2/SiO_2 [2] and MoO_3 on TiO_2 [3] are used for the selective catalytic reduction of NO with NH_3 and O_2. NO, NH_3 and O_2 react over these catalysts to produce N_2 and H_2O. The reaction over supported vanadia catalysts may be described by the overall stoichiometry:

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O.$$

The high activity and selectivity of NH_3 for the reaction with NO, combined with the enhanced reaction rate in the presence of oxygen, makes NH_3 the preferred reducing agent.

Over MoO_3 on SiO_2 catalysts containing MoO_3 loadings of 15% (wt) and higher, NH_3 is oxidised to N_2 and H_2O and the conversion of NO is very low [4], whereas NH_3, NO and O_2 react over V_2O_5 on SiO_2 resulting in NO, N_2, N_2O and H_2O [4].

This study describes the reduction and oxidation behaviour of silica supported molybdena and titania supported vanadia catalysts. The reduction was carried out using NH_3 and the oxidation using either O_2 or NO. The heat effects during the respective reactions and the gas composition of the gas mixture, were monitored using differential scanning calorimetry (DSC) and mass spectrometry respectively. The aim of this paper is to show that molecular (labeled) oxygen may be introduced into the oxide lattice of supported vanadia and molybdena catalysts via the oxidation of NH_3 at 673 K. Moreover, the method of inserting oxygen into supported vanadia and molybdena catalysts below 673 K has been discussed both in a qualitative and quantitative sense.

2. Experimental

The experimental set-up used for the experiments with labeled molecules has been described previously [5,6]. Some of the details and procedures will be mentioned briefly. The reaction system used consists of a gas mixing system, a conventional fixed-bed reactor and a mass spectrometer. In some experiments the fixed-bed reactor was placed into a differential scanning heat-flow calorimeter [7,8]. The DSC and its calibration procedures have been described recently [7,8].

For determining of the product distribution over the catalyst, labeled molecules such as ^{15}NO and $^{18}O_2$ were used.

The V_2O_5 on TiO_2 catalyst was kindly provided by Julian Ross's group from the University of Twente whereas the V_2O_5 on TiO_2/SiO_2 and the MoO_3 on SiO_2 catalysts were prepared by John Geus's group from the University of Utrecht (the Netherlands).

The catalysts studied are shown in table 1.

The V_2O_5 on TiO_2 catalyst was prepared by monolayer adsorption of vanadyl acetylacetonate onto TiO_2 (68% Anatase, 32% Rutile).

The V_2O_3 on TiO_2/SiO_2 catalyst was prepared using homogeneous deposition precipitation [2]. The active material V^{5+} was electrochemically reduced to V^{3+} at pH 1 and precipitated by raising the pH slowly. The MoO_3 on SiO_2 catalyst was prepared by incipient wetness impregnation of SiO_2 from an aqueous solution of Mo^{3+}. After filtration and drying, the products were calcined at 673 K for more than 24 hours.

3. Procedures

The catalysts were introduced into a quartz reactor (inner diameter 4.7 mm) which was placed in the sample compartment of the DSC. The reference quartz

Table 1
Catalysts used in this study

Catalyst	V or Mo content (wt%)	S_{BET} (m^2g^{-1})
V_2O_5/TiO_2	1.1	45
$V_2O_5/TiO_2/SiO_2$ [1]	3.4	235
MoO_3/SiO_2	6.7	100

[1] Ti content is 19.6% (wt).

reactor contained about 50 mg quartz powder. Prior to the experiments the catalyst samples were calcined at 673 K in situ in a helium flow containing 25% $^{16}O_2$. The experiments were carried out using 50 mg catalyst. The particle size of the catalysts varied from 0.25 to 0.5 mm.

Four distinct types of experiments have been carried out.

In the first type of experiment the reaction of NO, NH_3 and $^{18}O_2$ over the V_2O_5 on TiO_2 and MoO_3 on SiO_2 catalysts was carried out at 673 K. At time = 0 NO, NH_3 and $^{18}O_2$ were introduced to the fresh calcined catalyst. $^{18}O_2$ was replaced by $^{16}O_2$ when the concentration of water was at steady state. This procedure was repeated for the V_2O_5 on TiO_2 catalyst.

In the second type of experiment, the catalyst was reduced in a flow of NH_3 (500 ppm in He) under isothermal conditions at 673 or 723 K for the supported molybdena catalyst, and for the vanadia on TiO_2/SiO_2 catalyst until the evolution of heat became constant. The pre-reduced catalyst was flushed with helium for about 15 minutes in order to remove adsorbed ammonia from the walls of the tubing and other parts of the system, and then exposed to molecular oxygen.

In the third type of experiment, the ammonia reduction of the oxidised catalyst was repeated and the pre-reduced catalyst exposed to nitric oxide at 673 K, while in the fourth type of experiment, the reaction of NH_3 and O_2 over the prereduced catalyst was examined. After each step in the experiments the catalyst was flushed with helium until the heat effect measured using the DSC was constant. The evolution of heat during the reactions was measured by means of DSC, and the amount of reactants and products by means of the mass spectrometer.

To completely remove NH_3 from the system after carrying out the reduction of the catalyst it has to be flushed with helium for about 15 minutes. However, all the gas mixtures used contain traces of oxygen in concentrations of less than 1 ppm. Moreover, it is inevitable that the leak valves are not completely gas tight. This implies that the reduced catalyst surface, unreacted NH_3 and chemisorbed NH_3 can react with traces of oxygen present in helium which is passed to the catalyst. Those traces of oxygen of less than 10 ppm can produce a heat effect of less than 0.6 mW during the reduction of the catalyst with ammonia and during the removal of ammonia after reduction. These heat effects seriously affect the quantification of the heat evolved. Therefore, the time of flushing should be kept as short as possible.

4. Results

The conversion of NH_3 and oxygen over the V_2O_5 on TiO_2/SiO_2 and the MoO_3 on SiO_2 catalyst is 30% and 90% respectively at a temperature of 673 K. The selectivity to nitrogen (N_2) is 100% for the vanadia catalyst and about 90% for the molybdena catalyst.

Table 2
Reaction heats of various reactions (673 K)

No	Reaction	$-dH$ (kJ)
1	$4NO+4NH_3+O_2 = 4N_2+6H_2O+$	1625
2	$6NO+4NH_3 = 5N_2+6H_2O+$	1806
3	$4NH_3+3O_2 = 2N_2+6H_2O+$	1263
4	$3MoO_3+2NH_3 = 3MoO_2+N_2+3H_2O+$	164
5	$2MoO_2+O_2 = 2MoO_3 +$	312
6	$2MoO_2+2NO = 2MoO_3+N_2+$	486
7	$3V_2O_5+2NH_3 = 3V_2O_4+N_2+3H_2O+$	328
8	$2V_2O_4+O_2 = 2V_2O_5 +$	202
9	$2V_2O_4+2NO = 2V_2O_5+N_2 +$	386

In the presence of ^{15}NO, NH_3 and O_2 minor amounts of $N^{15}NO$ and $N^{15}N$ produced by the reaction of equimolar amounts of ^{15}NO and NH_3, and minor amounts of N_2O and NO produced by the oxidation of NH_3 were found over the MoO_3 on SiO_2 catalyst. However, NO, NH_3 and O_2 react over the V_2O_5 on TiO_2/SiO_2 catalyst according to reaction 1 (table 2). Figure 1 shows the concentration levels of $H_2^{18}O$ as a function of time over 50 mg of the V_2O_5 on TiO_2 catalyst at a temperature of 673 K. The feed consists of NO, NH_3 and $^{18}O_2$ or $^{16}O_2$. After 220, 450 and 700 minutes the isotopic composition of oxygen in the feed was abruptly changed. This causes a rapid change of the concentration of $H_2^{18}O$. During the reaction H_2O and $H_2^{18}O$ are formed. The labeled oxygen is mainly found in the product water. The areas under the curves of increasing $H_2^{18}O$ concentration are identical and equivalent to about 225 μmol of $H_2^{18}O$.

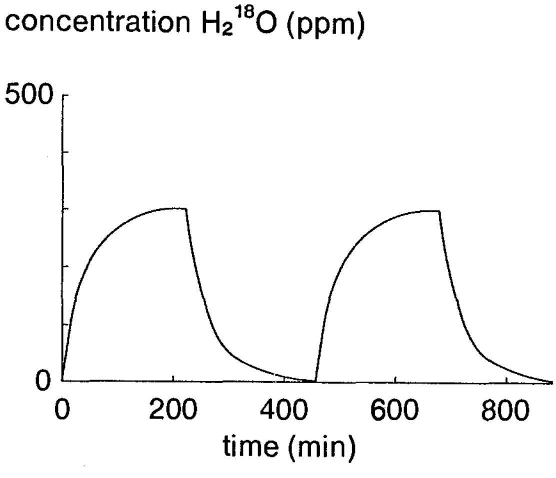

Fig. 1. Concentration profile of $H_2^{18}O$ over the catalyst V_2O_5 on TiO_2 (50 mg) at 673 K. $[NO]_1 = [NH_3]_1 = 500$ ppm; $[^{18}O_2]_1 = 495$ ppm; $[^{16}O_2]_1 = 637$ ppm. After 220, 450 and 700 minutes the isotopic composition was abruptly changed from $^{18}O_2$ to $^{16}O_2$ and vice versa; conversion of NO and NH_3 is about 80%; flow 100 cm^3/min.

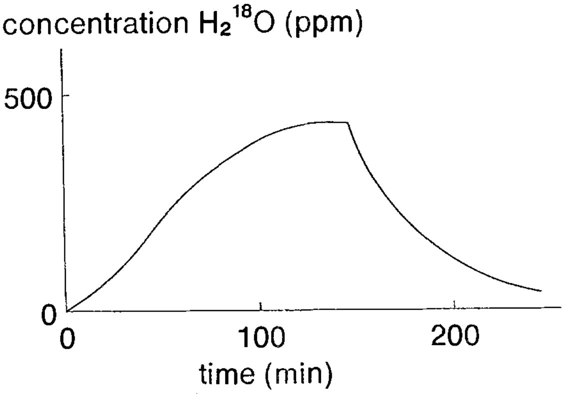

Fig. 2. The reaction of NH_3 and $^{18}O_2$ over MoO_3 on SiO_2 catalyst (50 mg) at 673 K; $[NH_3]_1 = 500$ ppm; $[^{18}O_2]_1 = [^{16}O_2]_1 = 500$ ppm; [NO] = 500 ppm during the first 120 minutes and 180 ppm after this period of time; conversion of NH_3 is about 100%; flow 100 cm^3/min.

Similar $H_2^{18}O$ profiles were obtained using the V_2O_5 on TiO_2/SiO_2 catalyst. When the experiment is carried out with a mixture of NO, NH_3 and $^{16}O_2$, the concentration of water and nitrogen is at steady state within 10 minutes. And thus, these concentration profiles differ strongly from those of $H_2^{18}O$. Moreover, in contrast to the concentration of $H_2^{18}O$ the reaction heat is at steady state within 10 minutes. In fig. 2 the concentration profiles of $H_2^{18}O$ are shown for the molybdena catalyst. The area under the curve of increasing $H_2^{18}O$ corresponds to 164 μmol $H_2^{18}O$. The form of the curves in figs. 1 and 2 is the same, but the time lapses after which steady state is obtained are different. The areas under the curves of decreasing $H_2^{18}O$ concentration are proportional to 48 and 82 μmol respectively. These amounts correspond to the amounts of ^{18}O present in the oxidic lattices of V_2O_5 and MoO_3 at steady state.

Figure 3 gives the relationship between the heat produced over the molybdena catalyst, and time. This is an example of the experiment of type four as described in the experimental section. The heat produced during reduction with ammonia passes a maximum and reaches steady state after about 15 minutes. The heat produced remains constant and below 0.6 mW during the flushing step, which was carried out with helium. Extra heat is produced when NH_3 and O_2 are admitted to the catalyst. The area under the overshoot in fig. 3 represents the heat evolved caused by oxidation of the reduced catalyst. The same results were obtained with the V_2O_5 on TiO_2/SiO_2 catalyst. The oxidation/reduction behaviour of both catalysts is reversible.

Figure 4 shows the relationship between the relative heat produced over the catalysts and the pretreatment of the catalyst. It is assumed that Mo^{6+} and V^{5+} are reduced to Mo^{4+} and V^{4+} respectively and not to other valence states and therefore, to calculate the relative heat produced during the reduction and oxidation of the V_2O_5 on TiO_2/SiO_2 catalyst the heat of reaction of reactions 7

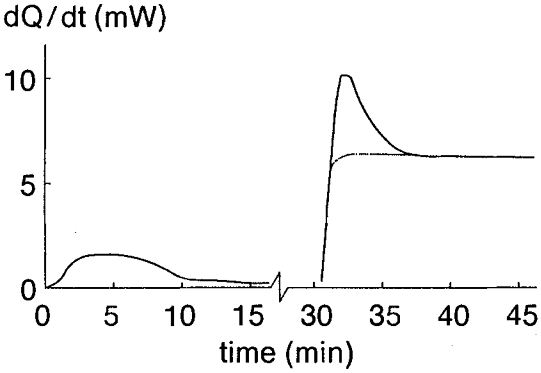

Fig. 3. The heat evolved as a function of time for the reduction with NH_3 (0–15 minutes), flushing with helium (15–30 minutes) and reaction of NH_3 and O_2 over the MoO_3 on SiO_2 catalyst (30–45 minutes); amount of catalyst 50 mg; $[NH_3]_1 = 500$ ppm; $[O_2]_1 = 320$ ppm; flow 100 cm^3/min; temperature 673 K.

and 8 (table 2) was used and for the MoO_3 on SiO_2 the heat of reaction of reactions 4 and 5. From fig. 4 it appears that about 30% (mol%) and 60% (the average) of the MoO_3 content is reduced to MoO_2 at 673 and 723 K respectively. The vanadia catalyst shows a value of 46% at 673 K and 723 K (not shown in fig. 4). NO oxidises the pre-reduced catalysts to the same extent as oxygen does but at a much lower rate.

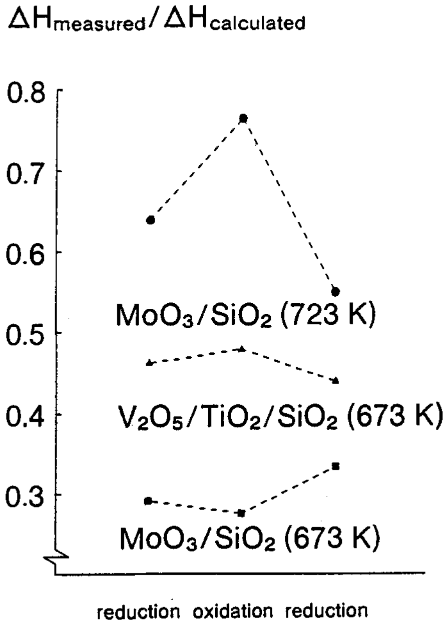

Fig. 4. The relative heat produced after reduction and subsequent oxidation and reduction with ammonia (330 ppm in helium) and oxygen (172 ppm in helium). Amount of catalyst is 48 mg and the gas flow is 60 cm^3/min.

5. Discussion

In two previous papers [5,9] the role of oxygen in the selective catalytic reduction of nitric oxide with ammonia over V_2O_5 on TiO_2 and the formation of water during the reaction was described. Two 'types' of water are formed: (i) that originating from the reaction of gaseous NO with chemisorbed ammonia species, and (ii) that formed as a result of dehydration of OH groups present on the surface of the catalyst. The first 'type' of water is formed almost instantaneously whereas the formation of the second 'type' shows a delay. Furthermore, it was shown that gaseous oxygen could be exchanged with the lattice oxygen of the catalyst during the reaction at 673 K and that O_2 is adsorbed by the catalyst as molecular oxygen.

The observed transients are not caused by pore diffusion effects because in the experiment in which NO, NH_3 and O_2 was used, both the concentration of H_2O and N_2, and the heat evolved are at steady state within 10 minutes. From the similarity between figs. 1 and 2 it is assumed that the mechanism of dehydration of the surface of the supported vanadia as previously proposed [5,9] is the same as that of dehydration of the surface of the molybdena catalyst. On the contrary, the behaviour of the compounds NH_3 and NO over the vanadia catalyst is different from that over the molybdena catalyst. NO and NH_3 react over the V_2O_5 on TiO_2/SiO_2 catalyst mainly according to overall reaction 1 (table 2) [2], while reaction 3 dominates over the molybdena catalyst [4]. The reason for the difference in behaviour of the two catalysts is not yet clear. In a previous paper it was concluded that NO from the gas phase reacts with NH_2 species present on the vanadia catalyst [5]. However, no N_2 is formed from NO and NH_3 over the molybdena catalyst. We suppose therefore, that the nitrogen containing species is present on the molybdena catalyst as =NH species, which is not able to react with NO from the gas phase.

After treating the catalyst with ammonia at 673 K part of the Mo^{6+} and V^{5+} is reduced to a lower valence state. The measured heat minus the heat produced by the reactions of NH_3 and O_2 (low concentrations) is proportional to the reduced amount of Mo and V (fig. 3). For the calculation of these amounts reactions 4 and 7 (table 2) were applied respectively. From the heat measured (which is proportional to the area under the overshoot curve) during the oxidation of the reduced catalyst the amount of oxidised Mo or V can be calculated using reactions 5 and 8. It turns out then that the reduced amounts of Mo or V, and their respective amounts of oxidised Mo or V are equal which suggests that Mo^{4+} and V^{5+} are present in the reduced catalysts. This is consistent with the data presented in fig. 4. From these considerations and the results presented in fig. 3 it is concluded that most of the molybdenum and vanadium is in the highest valence state when the reaction of ammonia and oxygen is at steady state.

The vanadia material contains only one type of reducible species below 723 K, whereas the molybdena catalyst contains two reducible species below 723 K (see fig. 4). The last remark agrees with the work of Barbaux et al. [10]. They observed, on catalysts containing amounts of molybdenum between 5 and 10%, the presence of polymolybdate species on top of a layer of silicomolybdic acid. We will report on these phenomena in a forthcoming paper.

During the reaction of NH_3 and $^{18}O_2$ over the surface of the catalysts, oxygen from the surface layer is replaced by ^{18}O. Theoretically, for 50 mg of the V_2O_5 on TiO_2 and MoO_3 on SiO_2 catalyst about 27 and 105 μmol O respectively is available for oxygen exchange, assuming that species such as V_2O_5 and MoO_3 are present on the surface of the catalysts. However, it can be calculated from figs. 1 and 2 that about 50 and 80 μmol of ^{18}O is present in the surface layer of the catalyst. This means that more ^{18}O was consumed by the V_2O_5 on TiO_2 catalyst and less by the MoO_3 on SiO_2 catalyst than expected. This supports the supposition that part of the molybdenum is present as MoO_3 and that this species is isolated from the support, whereas vanadium shows a strong interaction with the support. This means that oxygen can enter the support of the vanadia catalyst via a compound on the surface which contains vanadium, titanium and oxygen. This surface compound is chemically bonded to the support. Another possible mechanism for the introduction of oxygen in the support is via spillover.

6. Conclusions

The dehydration of the molybdena catalyst during the oxidation of ammonia occurs according to the same mechanism as for the vanadia catalyst. The same remarks are true for the insertion of oxygen into the lattice of the active material.

Oxygen atoms of MoO_3 are almost completely (80%) exchanged during the reaction of NH_3 and O_2.

The MoO_3 on SiO_2 catalyst contains two reducible species, occurring at two temperatures, in contrast with the V_2O_5 on TiO_2/SiO_2 catalyst which shows only one reducible species below 723 K.

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