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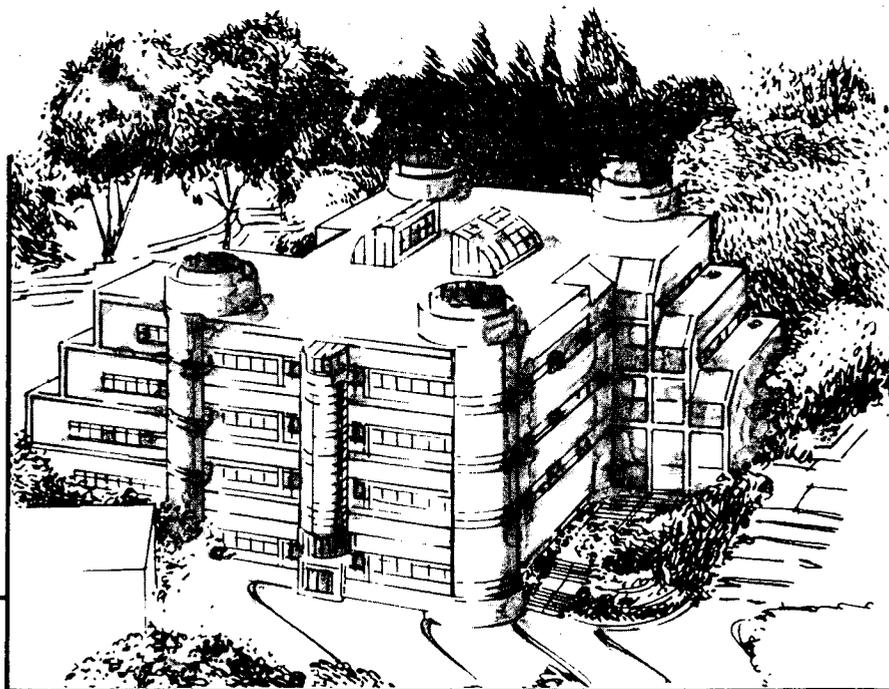
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## AES and TDS Study of the Adsorption of $\text{NH}_3$ and $\text{NO}$ on $\text{V}_2\text{O}_5$ and $\text{TiO}_2$ Surfaces: Mechanistic Implications

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AES and TDS Study of the Adsorption of  $\text{NH}_3$  and  $\text{NO}$   
On  $\text{V}_2\text{O}_5$  and  $\text{TiO}_2$  Surfaces. Mechanistic Implications

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## ABSTRACT

The adsorption of  $\text{NH}_3$  and  $\text{NO}$  on pure  $\text{V}_2\text{O}_5$  and on  $\text{TiO}_2$  samples at pressures (ca. 25 Torr) and temperatures (room temperature to 675K) close to those used in industry with  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts has been studied by Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS), using an UHV chamber equipped with a built-in high pressure cell (up to 1 atm.).

$\text{NH}_3$  adsorption takes place over the whole range of temperatures studied on  $\text{TiO}_2$  and on both  $\text{V}_2\text{O}_5$  as well as on reduced  $\text{V}_2\text{O}_5$  surfaces while  $\text{NO}$  adsorption occurs on  $\text{TiO}_2$  and on reduced  $\text{V}_2\text{O}_5$  but not on oxidized  $\text{V}_2\text{O}_5$  surfaces. It is shown that  $\text{NH}_3$  reduces the vanadium pentoxide surface resulting in the production of  $\text{N}_2\text{O}$ . The presence of  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{O}_2$  results in the reoxidation of the vanadium surface with the nitrogen oxides being converted into  $\text{N}_2$ . No evidence for the  $\text{NO}+\text{NH}_3$  reaction has been obtained on the  $\text{TiO}_2$  surface. However,  $\text{NO}$  adsorption on  $\text{TiO}_2$  appears to be a main factor for the catalyst effectiveness in  $\text{V}_2\text{O}_5/\text{TiO}_2$  samples since it may provide a source of  $\text{NO}$  at the interface of vanadia islands on  $\text{TiO}_2$  in the actual catalyst.

Finally, from TDS and AES data a reaction mechanism is hypothesized that may explain the reduction of  $\text{NO}$  to  $\text{N}_2$  as well as the side reaction responsible for the production of  $\text{N}_2\text{O}$ .

## INTRODUCTION

Interest in air quality and emission control has resulted in a considerable amount of research dealing with the selective reduction of nitrogen oxides. An extensive review of this subject has been recently published [1]. Among the catalysts tested supported vanadium oxides seem to be preferred for catalysing the  $\text{NO}_x+\text{NH}_3+\text{O}_2$  reaction. Although

$\text{NO}_x$  can be reduced to  $\text{N}_2$  with the use of reducing gases such as  $\text{CH}_4$ ,  $\text{H}_2$ , and  $\text{CO}$ , ammonia is preferred since the other gases are readily consumed by reaction with  $\text{O}_2$ . The characterization of the supported vanadium species by different techniques, such as extended x-ray absorption fine structure (EXAFS) [2,3], high resolution electron microscopy (HREM) [4], x-ray photoelectron spectroscopy (XPS) [5-8], laser Raman spectroscopy [9,10] and electron spin resonance (ESR) [11,13], has been reported. Kinetic studies directed towards the elucidation of the reaction mechanism [14,27], in some cases supported by theoretical approaches [28], have been undertaken and the preparation of titania-supported  $\text{V}_2\text{O}_5$  with improved redox properties [29] has been described.

Although surface sensitive electron spectroscopies are excellent tools for studying the catalyst surfaces, not much has been reported on the use of surface science techniques for studying the adsorption of  $\text{NH}_3$  and  $\text{NO}$  on  $\text{V}_2\text{O}_5$  and on  $\text{V}_2\text{O}_5/\text{TiO}_2$  surfaces. Only Tsai et al. [30,31] have reported an AES study of the surface of supported group VIII metals for the  $\text{NH}_3+\text{NO}$  reaction after  $\text{SO}_2$  poisoning. Most papers assume that reduction of supported  $\text{V}_2\text{O}_5$  occurs during the  $\text{NO}+\text{NH}_3$  reaction, but the mechanism through which the reduction takes place is still speculative.

The aim of the present work was to study the adsorption of  $\text{NO}$  and  $\text{NH}_3$  on pure  $\text{V}_2\text{O}_5$  and on  $\text{TiO}_2$  by means of Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS). Based on our findings, elementary steps are proposed for the  $\text{NO}+\text{NH}_3+\text{O}_2$  reaction on  $\text{V}_2\text{O}_5$  and  $\text{TiO}_2/\text{V}_2\text{O}_5$ . As will be shown later,  $\text{NO}$  cannot adsorb on fully oxidized  $\text{V}_2\text{O}_5$  surfaces. The experimental setup of this work allowed us to demonstrate the reduction of the vanadium oxide catalyst in the presence of  $\text{NH}_3$ , which in turn is oxidized to  $\text{N}_2\text{O}$ . In addition, the role of oxygen in the reactant mixture has been established mainly as a counterpart in the  $\text{NO}$  and  $\text{NH}_3$  competition for the reduced surface sites improving the catalyst life.

## EXPERIMENTAL

In this study a powdered vanadium oxide catalyst ( $V_2O_5$ ) from Aldrich Chemical Co. 99.999% pure was employed. High purity gases,  $NH_3$ ,  $NO$ , and  $O_2$ , were obtained from Matheson and used without further purification.

The apparatus used for the Auger Electron Spectroscopy (AES) and Thermal Desorption Spectroscopy (TDS) studies has been previously described [32]. It consists of a stainless steel bell-jar, evacuated to pressures below  $5 \times 10^{-9}$  Torr by a Varian VHS6 diffusion pump, backed by a rotary pump. A built-in high pressure cell isolates the sample from the UHV environment accounting for sample treatments in different atmospheres up to 1 atm. [32].

The sample holder is part of the high pressure cell. When it is open, the cell exposes the sample to ultra-high vacuum (UHV), for AES and/or TDS analysis, and when it is closed, it becomes a part of the reactor used for sample treatments. The sample is pressed against a gold coated stainless steel grid, and it is in intimate contact with a chromel-alumel thermocouple. The grid is held against a gold foil by two lateral flaps. By passing current through the foil, the sample can be heated to the desired temperature.

The Auger electrons were detected by a double-pass cylindrical mirror analyzer (CMA) equipped with a coaxial electron gun (Physical electronics 15-255G). A 6eV peak-to-peak modulation and a response time of 20 ms were selected. The electron gun was always operated at 1kV and 0.8 mA at normal incidence.

For TDS studies, the adsorbate was introduced into the high pressure cell at pressures close to the ones usually achieved under actual industrial conditions (ca. 25 Torr), allowing it to circulate at the temperature chosen (room temperature to 675k) for 15 minutes. After

that the sample was cooled in the adsorbate atmosphere and outgassed in the UHV chamber, at the adsorption temperature, until the system base pressure was achieved. The sample was then heated, under UHV conditions, at a constant heating rate ( $15\text{K}\cdot\text{s}^{-1}$ ). A mass spectrometer (UTI 100C) monitors the gas evolution of a given mass, and a plot of the signal intensity versus temperature was generated on an XY recorder (Hewlett-Packard 7044B). Alternatively, the sample was exposed to the reactant gases in an UHV environment in which case the gases were introduced into the UHV chamber through a leak valve at pressures below  $1\cdot 10^{-6}$  Torr.

## RESULTS

### a) Studies on $\text{V}_2\text{O}_5$

The adsorption of  $\text{NH}_3$  and  $\text{NO}$  on  $\text{V}_2\text{O}_5$  has been studied by AES and TDS. The presence of carbon contamination on  $\text{V}_2\text{O}_5$  has been described as responsible for the reactivity of thin films of  $\text{V}_2\text{O}_5$  on gold foils [33]. The formation of  $\text{CO}$  and/or  $\text{CO}_2$  that desorbs at ca. 675K might be responsible for the generation of oxygen vacancies on the  $\text{V}_2\text{O}_5$  surface leaving exposed  $\text{V}^{4+}$  species that can then react with the adsorbates [3,33]. To avoid any interference from coadsorbed species we carried out an oxidation treatment that would leave a clean  $\text{V}_2\text{O}_5$  surface, before adsorbing  $\text{NH}_3$  and/or  $\text{NO}$ . Figure 1 shows the AES spectrum of the vanadia sample after oxidizing it in 40 Torr of  $\text{O}_2$  at 675K for 15 minutes followed by heating at the same temperature for 10 minutes in the UHV chamber; this results in a clean  $\text{V}_2\text{O}_5$  sample characterized by the presence of the  $\text{V}(\text{L}_3\text{M}_{23}\text{M}_{23})$  and  $\text{V}(\text{L}_3\text{M}_{23}\text{M}_{45})$  transitions at 430 and 469 eV, respectively, and at 510eV for the  $\text{O}(\text{KLL})$  transition.

Unfortunately the oxidation state of the vanadium species is not unequivocally obtainable by AES. Even at low peak-to-peak modulation (2eV), the intensity ratio between the  $\text{O}(\text{KLL})$  and  $\text{V}(\text{L}_3\text{M}_{23}\text{M}_{23})$  lines

is the same, 2.4, for the oxidized and reduced vanadia samples. Considering the cross sections for oxygen and vanadium [34], this value represents an oxygen to vanadium atomic ratio equal to the stoichiometric one, 2.5. Although Szalkowski and Somorjai [35] drew some conclusions from the relative intensity of these lines, they were using oxidized vanadium films which means that only with a very thin film of oxide is it possible to obtain information about sample stoichiometry. Another approach to determine the oxidation state of 3d metals by AES has been described by Rao et al. [36,37]. They state that changes of the oxidation state of the 3d metal alters the population of the valence band and that is reflected in the relative intensities of the  $L_{3M_{23}M_{23}}$  and  $L_{3M_{23}M_{45}}$  lines in the Auger spectrum. Again this study, confirmed in this laboratory by Lewis et al. [33], has been carried out on thin oxide films. In our case the relative intensity of the vanadium lines is always equal to 0.95, Fig. 1. If we consider that the mean free path for the electrons having kinetic energies around 450 eV is ca. 10 Å, we would have to reduce much of the  $V_2O_5$  sample to notice a substantial change in the AES spectrum. As this is not the general case in catalysis, where only a small concentration of the surface sites undergoes changes, statements about a surface oxidation state on the basis of AES are not meaningful. Thus, information concerning the oxidation state of surface vanadium species has to be obtained, indirectly, from TDS experiments.

Both the adsorption of  $NH_3$  and NO has been carried out as a function of temperature. Figure 2 curve A displays the AES spectrum of  $V_2O_5$  after adsorption of 25 Torr of  $NH_3$  at room temperature. The presence of a new peak at 377 eV, with respect to the pure  $V_2O_5$  spectrum, is now noticeable; this peak can be assigned to the N(KLL) transition indicating that  $NH_3$  can be adsorbed at room temperature. After heating the sample to 775K the nitrogen peak disappears. On this presumably reduced vanadium surface, the adsorption of  $NH_3$  also occurs, Figure 2 curve B, although no conclusions can be drawn about the nature of the resulting ammonia species on the basis of the AES spectrum.

Evidence for the reduction of the  $V_2O_5$  surface is obtained from TDS experiments. One of the proposed mechanisms for the  $NH_3+NO$  reaction is the redox mechanism, which implies the oxidation of  $NH_3$  to  $N_2O$  using oxygen from the  $V_2O_5$  lattice. To test the possibility of such a mechanism several experiments were performed in which, after adsorbing 25 Torr of  $NH_3$  at room temperature, a.m.u. 44 ( $N_2O^+$ ) and 30 ( $NO^+$ ) were monitored instead of analyzing the signal corresponding to a.m.u. 15 ( $NH^+$ ). In both cases a similar TDS profile was obtained showing a peak at 643K, Fig. 3, indicating that  $V_2O_5$  is reduced by  $NH_3$  which in turn is oxidized to  $N_2O$ .

The adsorption of  $NH_3$  on  $V_2O_5$  has also been studied at 575 and 675K. AES spectra of the interaction of 25 Torr of  $NH_3$  at 575 and 675K are shown in Fig. 4; the experimental procedure was as follows: after oxidizing the  $V_2O_5$  sample, 25 Torr of  $NH_3$  were introduced in the high pressure cell and heated to the reaction temperature for 15 minutes, then cooled down to room temperature in such an atmosphere and outgassed in the UHV chamber until the chamber base pressure was reached. After this treatment a nitrogen peak appears in the AES spectrum that cannot be eliminated by heating at the reaction temperature in UHV, as shown in Fig. 4; only by heating at 775K in vacuum does the nitrogen peak disappear. However, this nitrogen peak which cannot be eliminated by heating in UHV at the reaction temperatures readily disappears by heating in  $O_2$  at 675K.

Figure 5 shows a plot of the TDS profile for the desorption of  $NH_3$  from the  $V_2O_5$  sample previously heated to 675K in 25 Torr of  $NH_3$ . One peak is obtained, giving the same desorption energy as the one obtained after ammonia adsorption at room temperature. Since after the heat treatment in ammonia the sample is cooled down in an ammonia atmosphere, this peak may correspond to the adsorption of  $NH_3$  at room temperature. However, after heating in vacuum at 675K for 10 minutes the nitrogen peak remains in the AES spectrum, as shown in Fig. 4, but after heating to 775 K a new TDS peak appears at 740K, as shown in Fig. 5. On

the basis of TDS and AES experiments, the identification of this peak remains uncertain. However, XPS and ESR spectra of  $V_2O_5/TiO_2$  samples after treatment with  $NH_3$  at reaction temperatures showed additional evidence for the homolytic dissociation of  $NH_3$  [38]. After reaction with ammonia, the  $V_2O_5$  sample showed a sharp signal in the ESR spectrum that may be ascribed to electrons trapped in oxygen vacancies; at the same time a N(1s) signal at 399.6eV can be observed in the XPS spectrum; this binding energy is 1.3eV lower than the one reported for  $NH_4VO_3$  or  $NH_4^+$  adsorbed on  $V_2O_5$  [15] suggesting the homolytic dissociation proposed. The observed value (399.6 eV) is close to the one reported for Au and Roberts [39] for  $NH_2$  species adsorbed on clean and oxidized Mg(0001) crystals (399.0 eV) in the presence of  $O_2$ . However, although reporting the amide species, they do not characterize the bonding of the  $NH_2$  species to the Mg(0001) surface.

While adsorption of NO was not achieved on a clean oxidized surface, Fig. 6, over the whole range of temperatures studied, or over  $NH_3$ -preadsorbed vanadia, NO adsorption at room temperature was observed on a  $V_2O_5$  sample previously reduced with ammonia and outgassed in UHV at 775K, Fig. 6. Heating the sample after NO adsorption to 775K, the adsorbed species disappears. This result indicates that NO can interact with the reduced vanadium sites. In Fig. 7 the TDS (following a.m.u. 28 ( $N_2^+$ )) of that adsorbed species as shown. A peak centered at 405K is observed which indicates that at reaction temperatures the NO can reoxidize the reduced vanadium sites while being reduced to  $N_2$ .

In a semi-quantitative approach the N/V peak-to-peak ratio has been obtained from the AES spectra plotted in Figs. 2,3, and 6, (Table 1). From this ratio it is possible to state that at least two different nitrogenated species are held by the  $V_2O_5$  surface in adsorbing  $NH_3$ : one has its maximum desorption rate at temperatures between room temperature and 575K while the second one has its maximum desorption rate between 575 and 775K; this is in agreement with the TDS results, Fig. 5. Surprisingly, after reaction in  $NH_3$  at 575 or 675K the vanadia surface

undergoes modifications that prevent any further  $\text{NH}_3$  adsorption at room temperature. If we compare the N/V ratio for  $\text{NH}_3$  adsorption at room temperature (0.21) with the value obtained after reaction at 675K and further cooling down to room temperature (0.12) we must assume modification of the surface relative to the original one. This surface modification of the clean oxidized  $\text{V}_2\text{O}_5$  surface cannot be ascribed to its reduction since the reduced surface adsorbs even more  $\text{NH}_3$  than the oxidized one, Table 1. Since the reaction proceeds in a closed system, the reaction products are present in the high pressure cell; these products, as demonstrated by TDS (Fig. 3) are  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$ ; assuming, according to Miyamoto et al. [18], that  $\text{N}_2\text{O}$  may react with the reduced sites reoxidizing them, then only  $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$  should be present in the reactor and the presence of water should be responsible for the difference observed in Table 1. From this result it is possible to deduce either that  $\text{H}_2\text{O}$  adsorption on the  $\text{V}_2\text{O}_5$  surface prevents any further ammonia adsorption or the interaction of the  $\text{NH}_3$  molecules with the hydroxylated surface is so weak that  $\text{NH}_3$  desorption takes place at room temperature in an UHV environment.

Furthermore, the N/V peak-to-peak ratio for NO adsorption at room temperature is similar to the one obtained for ammonia adsorption, Table 1. This indicates that the number of adsorbed NO species is equal to the number of  $\text{NH}_3$  adsorbed species pointing to a NO to  $\text{NH}_3$  ratio equal to one in the  $\text{NO}+\text{NH}_3$  reaction.

b) Studies on  $\text{TiO}_2$

The adsorption of NO on  $\text{TiO}_2$  has been studied by TDS as a function of temperature. The shape of the TDS spectra is independent of temperature, characterized by a peak centered at 385K. Neither  $\text{N}_2$  nor  $\text{N}_2\text{O}$  was observed indicating that NO adsorbs weakly on the  $\text{TiO}_2$  surface, Fig. 8. However, the amount adsorbed decreases when the reaction temperature increases. If successive 18L (1 Langmuir= $10^{-6}$  Torr x sec) doses of NO are provided to the  $\text{TiO}_2$  surface, the amount

adsorbed decreases up to a level in which no more NO can be adsorbed indicating a poisoning of the  $TiO_2$  surface by NO species. When the adsorption is carried out in the high pressure cell at 25 Torr of NO, a single broad peak is observed in the TDS. This peak has higher desorption energy, the maximum appearing at 468K.

$NH_3$  adsorption also takes place on  $TiO_2$  (Fig. 9). The TDS spectrum of ammonia is characterized by a single broad peak which is centered at 445K after 5L adsorption at R.T. The temperature corresponding to the maximum in the TDS peak shifts to higher values when increasing the  $NH_3$  dose indicating either a dependence of the binding energy on coverage or a population of different  $TiO_2$  sites. On adsorbing  $NH_3$  at either 373K or 473K, a decrease in the amount adsorbed is observed as well as a shift to higher desorption temperatures (Fig. 9). When the  $NH_3$  adsorption is at 373K, there results a  $NH_3$  desorption peak in the TDS profile at 495K; this peak position is independent of the  $NH_3$  dose pointing to the existence of different adsorption sites on the  $TiO_2$  surface. The TDS after  $NH_3$  adsorption at 473K results in a hardly noticeable peak at about 600K, indicating that at this temperature almost all the active surface sites on the  $TiO_2$  surface have been removed.

This points to an interaction between the ammonia molecule with the  $TiO_2$  surface through weakly bound hydroxyl groups that are easily removed by heating at mild temperatures. However, the proposal of the existence of strongly adsorbed  $NH_3$  species as reported by Busca et al. [13] which cannot be removed at temperatures below 750K should not be dismissed since the presence of nitrogenated species on the surface of the catalyst cannot be observed due to the coincidence of the N and Ti AES signals at 377 eV.

The reaction of NO and  $NH_3$  on the  $TiO_2$  surface has also been studied by leaking a NO+ $NH_3$  (2:3 ratio) mixture into the UHV chamber at doses up to 20L. This experiment showed that neither  $N_2$  nor  $N_2O$  are

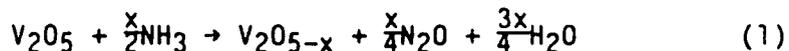
desorbed from the  $\text{TiO}_2$  surface in the temperature range 300-700K and that, therefore, there is no reduction of NO by  $\text{NH}_3$  occurring on  $\text{TiO}_2$  in this temperature range.

### DISCUSSION

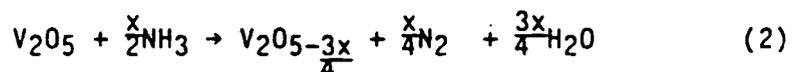
Although the  $\text{NH}_3 + \text{NO}$  reaction has been the subject of numerous investigations [1] the nature of the active sites and the reaction mechanism are still undetermined. The results described above provide some information on the role of the support and on the active phase of  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts for the removal of nitrogen oxides in stack and power gas exhaust systems.

The reduction of  $\text{V}_2\text{O}_5$  in the presence of  $\text{NH}_3$ , either as a bulk oxide or when supported, is generally proposed in the literature [18,27].

Our results clearly indicate that the surface of the  $\text{V}_2\text{O}_5$  catalyst is reduced in the presence of  $\text{NH}_3$  and in the absence of NO, leaving behind a surface vacancy according to the following scheme:



The reduction of the  $\text{V}_2\text{O}_5$  surface and the subsequent oxidation of the  $\text{NH}_3$  molecule to  $\text{N}_2\text{O}$  has been demonstrated by TDS, Fig. 4. Although the experimental conditions in this work are far from those of Miyamoto [18,28], it may be considered that the present result is in contradiction to the  $\text{NH}_3$ -NO adduct proposed in Miyamoto's work since vanadium reduction is attained by  $\text{NH}_3$  alone. On the other hand, this result agrees with the scheme proposed by Bosch et al. [23].

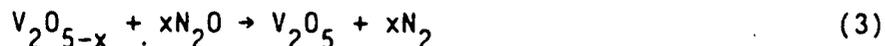


in which case, according to Bosch et al. [23], the oxygen defect may be present as a surface vacancy or a surface hydroxyl group.

Our results do not exclude the possible presence of hydroxyl groups or surface vacancies. However, the presence of a surface vacancy or a hydroxyl group should depend on the temperature at which the reaction is carried out. Dehydroxylation of  $V_2O_5$  and  $V_2O_5/TiO_2$  at temperatures below 550 K has been mentioned in the literature [13,40]. The reduction of the vanadium site by dehydroxylation also has been pointed out by Busca et al. [13].

Although it has been shown that the presence of water in the reactant mixture does not affect the temperature at which the maximum NO conversion occurs [41], it will be shown later in this article that surface hydroxylation is an important factor in the role of  $O_2$  species during the reaction.

A difference between the stoichiometric scheme proposed by Bosch et al. [23] and the one proposed here is the presence of  $N_2O$  instead of  $N_2$ . Thermodynamically the  $N_2O$  species is stable with respect to its decomposition into  $N_2$  and  $O_2$  at the reaction temperatures (575-675K) and the stability increases with increasing temperature. Thus, the presence of  $N_2$  instead of  $N_2O$  in the reaction products, as postulated in [23], must be due to a further interaction of  $N_2O$  with surface vacancies:

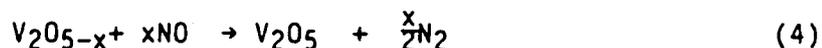


Thus the surface is reoxidized to  $V^{5+}$  while the  $N_2O$  in turn is reduced to  $N_2$ . In fact combining eq. (1) and (3) the scheme proposed by Bosch et al. [23], eq. (2) is obtained. Further support for the reduction of  $N_2O$  to  $N_2$  on partially reduced vanadia surfaces is obtained from literature data; in effect, using nitrogen-15 tracer techniques this reduction has been observed [18]. The competition for reduced  $V_2O_5$  surface sites between NO and  $N_2O$  can lead to a decrease in the rate of NO reduction.

A reduction of  $N_2O$  with  $NH_3$  to produce  $N_2$  and  $H_2O$  which occurs on metals is not likely to occur on oxides.

As pointed out previously, NO species cannot adsorb on  $V_2O_5$  or ammonia preadsorbed  $V_2O_5$ , Fig. 6. Therefore, the activated complex proposed by Miyamoto et al. [18,28] seems unlikely. Even when considering the mass spectrometric evidence for the formation of  $NH_2NO$  in the  $NH_3+NO$  reaction on vanadium oxide catalysts [42] this pathway should be discarded as the main reaction path on  $V_2O_5$  on the basis of our results.

The desorption of  $N_2O$  at reaction temperatures leaving behind a reduced site raises the question of which species is able to reoxidize such vanadium sites. Since the adsorption of NO on the reduced sites is possible [Fig. 6) and results in NO being reduced to  $N_2$  at reaction temperatures (Fig. 7), the following elementary step can also be proposed:



By combining eq. (1), (3), and (4) the overall reaction can be described:

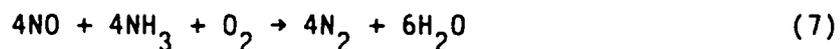


This stoichiometry proposed by Nam et al. [26] for the  $NH_3+NO$  reaction on  $V_2O_5/TiO_2$  catalysts, cannot account for the drop in NO conversion in the absence of  $O_2$  reported in the literature [11,23,25,41].

Taking into account the presence of  $O_2$  in the reaction mixture, the following step can also be hypothesized:



The overall reaction may then be written:



which is in good agreement with the stoichiometries proposed in the literature [43,44]. This stoichiometry also fits the NO and  $NH_3$  coverages obtained by AES on  $V_2O_5$ , Table 1.

The kinetics of the  $\text{NH}_3 + \text{NO}$  reaction has been extensively studied [14,27]. Some disagreement, however appears in the literature data. While Inomata et al. [11,45] found first order dependency for the NO partial pressure and zero order for ammonia either in the presence or absence of  $\text{O}_2$  over oxidized or reduced vanadium oxide catalysts, other workers found fractional orders for NO. In [24] over a commercial  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  an activation energy of 53.3 kJ/mol for the reduction of NO to  $\text{N}_2$  was found as well as 0.62 for the order in NO and -0.05 in  $\text{NH}_3$ . These results are in agreement with the ones reported in [23] although the activation energy is slightly lower, 35-44 kJ/mol, and the reaction order in  $\text{NH}_3$  was found equal to zero [23].

Activation energies around 19 kJ/mol were found in the presence [17] or absence [16] of  $\text{O}_2$  over vanadia supported on silica. Fractional orders for both  $\text{NH}_3$  and NO were found in these cases; 0.3 and 0.22 [17] and 0.2 and 0.12 [16] for NO and  $\text{NH}_3$ , respectively. Wong and Nobe [21] reported an activation energy of 54 kJ/mol for a vanadia impregnated on anatase while on rutile it was reduced to 27.4 kJ/mol. A mixture of both anatase and rutile used as support shows an intermediate activation energy [21].

Using titania-silica as support positive orders: a 0.6, 0.25 and 0.25 were found for NO,  $\text{NH}_3$  and  $\text{O}_2$ , respectively. The order in  $\text{O}_2$  increased with decreasing temperatures while in  $\text{NH}_3$  it decreased with lower temperatures reaching a negative value at 475K [22].

Despite these differences in reaction orders and activation energies as a function of the support, Wong and Nobe [25] found over a wide range of supports and promoters of vanadium oxide catalysts the same reaction orders, 1.0 in NO and zero in  $\text{NH}_3$  with an activation energy of 50 kJ/mol.

Finally Nam et al. [26] have reported first order kinetics in both NO and  $\text{NH}_3$  introducing a different approach; two competitive and simultaneous reactions: the reduction of NO and the oxidation of  $\text{NH}_3$ .

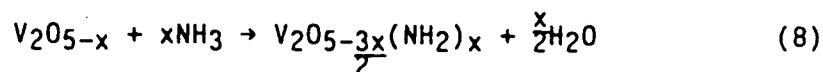
Other than for the last model, the kinetic results reported in the literature may be summarized in an oversimplified manner: a positive order in NO and a zero or even slightly negative order in NH<sub>3</sub>. One has to consider, however, that these results are obtained at temperatures lower than 590K, while the rate order Nam et al. [26] proposed fits the experimental results in the range 475-775K. Further it has been reported that in the presence of O<sub>2</sub> there is a change in the selectivity for the NO+NH<sub>3</sub>+O<sub>2</sub> reaction above 525K [23].

Our results on V<sub>2</sub>O<sub>5</sub> indicate that NO can interact at low temperatures with a reduced vanadia surface but that it cannot be adsorbed on an oxidized one (Fig. 6). To comply with the kinetic results described in the literature, one needs to assume NO adsorption on the support. On anatase at least two different NO species can adsorb. The first one is weakly bound to the titania surface, Fig. 8, the second one remains adsorbed even at 775K and poisons the titania surface preventing further adsorption of NO molecules. When the NO pressure increases the adsorption energy of the weakly bound NO species increases and the maximum in the TDS spectra shifts from 385 to 468K; there is then a possible source of NO molecules for the reduced vanadium sites at the TiO<sub>2</sub> surface. Also a positive dependence on the amount adsorbed with pressure is observed fitting the positive order in NO observed in kinetic experiments.

Miyamoto et al. [18,28] proposed a reoxidation of V-OH groups by O<sub>2</sub> for closing the reaction cycle; considering that Wehrli and Stumm [46] have reported a first order rate in O<sub>2</sub> for the oxidation of hydroxyvanadyl groups on the surface of titania or alumina the positive order in O<sub>2</sub> for the NH<sub>3</sub>+NO+O<sub>2</sub> reaction [22] is explained. In the low temperature range, 350-525K, O<sub>2</sub> should only be required for oxidizing V-OH groups, since no effect of the O<sub>2</sub> partial pressure on the production of N<sub>2</sub>O in this temperature range has been reported [11]. Above 525K a change in selectivity has been reported in the presence of O<sub>2</sub> [23]. This change in the selectivity is explained by

the dehydroxylation of the vanadia surface, which in turn modifies the oxidation kinetics of the reduced vanadium sites leading to a change in  $O_2$  reaction order as reported in [22]. In the high temperature range, 525-675K,  $O_2$  molecules oxidize the nitrogenated species held by the surface after heating in  $NH_3$  at 575 or 675K, Fig. 4.

However the elementary steps, eq. (1) to (7), described above cannot explain the presence of ammonia adsorbed on the vanadium catalyst in the high temperature range; in addition these ammonia species are unreactive towards NO. This strongly adsorbed species might be understood as  $NH_3$  molecules that dissociate on the surface of the reduced  $V_2O_5$  sample according to the following:



Existence of this  $VNH_2$  species finds support in XPS and ESR data [38]. Moreover Otto et al. [14,47] claim that the primary step in the  $NH_3+NO$  reaction is the formation of  $NH_2$  species. In addition to this spectroscopic evidence for the formation of  $NH_x$  species has been also extensively reported [48,49,50].

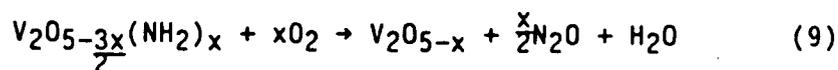
Janssen et al. [27] proposed the heterolytic dissociation of  $NH_3$  over two adjacent VO groups, which after reaction with adsorbed NO is the source of  $N_2$  in the products mainstream. This proposal is in agreement with the observation of Faber and Harris [42] of the formation of  $NH_2NO$ . However, the fact that  $NH_3$  can adsorb on a reduced vanadia surface, leading to an apparent oxidation of vanadium species as observed by XPS [38] and the presence of ESR signals corresponding to electrons trapped in oxygen vacancies after  $NH_3$  treatments [38] support the idea of a dissociative homolytic adsorption on the reduced surface activated at the reaction temperatures.

Table 1 shows that ammonia does not adsorb or does so very weakly on fully hydroxylated vanadia surfaces. In the absence of  $O_2$  the

removal of the adsorbed water is needed to reach a steady state reaction [18,28]. If molecular oxygen is present, the oxidation of the hydroxylated reduced sites is easier than in the absence of  $O_2$  according to Wehrli and Stumm [46].

At temperatures below 525K, provided  $NH_3$  has reduced the vanadia surface and water has been formed, ammonia and nitric oxide can compete for the reduced surface sites, which in the absence of  $O_2$  leads to a decrease in the rate of NO reduction. This explains the generally agreed on effect of  $O_2$  on the rate of NO reduction [1,23,25,45] namely a sharp increase in the NO conversion in the presence of  $O_2$ .

$O_2$  treatment at 675K restores the original  $V_2O_5$  surface suggesting the oxidation of such  $VNH_2$  species in the presence of  $O_2$ . The stoichiometric step should be described by:



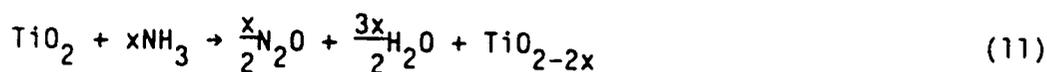
By combining the elementary steps described by eq. (5) and (7) to (9) the side reaction that leads to the increase in  $N_2O$  concentration as the reaction temperature increases is obtained:



Over  $V_2O_5$  the evolution of  $N_2O$  at temperatures above 675K in the oxidation of  $NH_3$  has been reported [51]. This side reaction may explain the change in selectivity for the NO reduction at temperatures above 525K [23]. If a competitive adsorption takes place, the number of sites available for the reduction of NO may decrease leading to a drop in NO conversion; additionally, in the presence of  $O_2$  the  $VNH_2$  species are oxidized to  $V^{5+}$  and  $N_2O$  increasing the  $N_2O$  concentration in the reaction products.

On the basis of the large number of observations reported, the two simultaneous reaction mechanisms proposed by Nam et al. [26] seem to agree with our results.

However, for the case of supported  $V_2O_5$  other pathways for the production of  $N_2O$  may be considered, particularly the report that  $TiO_2$  is able to produce  $N_2O$  [25]. But, as shown earlier,  $N_2$  or  $N_2O$  is not produced by the reaction of  $NO$  and  $NH_3$  on the  $TiO_2$  surface. Thus, the reported production of  $N_2O$  in the  $NO+NH_3$  reaction over  $TiO_2$  samples [25] could be associated with the reduction of the  $TiO_2$  surface by  $NH_3$  at high temperatures leading to the formation of  $N_2O$  which is thermodynamically stable at temperatures of ca. 675K. In fact Busca et al. have reported the presence of  $NH_3$  species held by  $TiO_2$  at temperatures higher than 750K, and the presence of  $Ti^{3+}$  ions on vanadia/titania catalysts after reduction [52] gives support to the following step:



Interaction of two  $NO$  molecules at the titania surface should be dismissed as a source of  $N_2$  or  $N_2O$  since it has not been possible to detect either species by TDS or TPRS.

#### SUMMARY AND CONCLUSIONS

The adsorption of  $NH_3$  and  $NO$  on pure vanadia and on  $TiO_2$  at pressures (up to 25 Torr) and temperatures (room temperature to 675K) near industrial ones, has been studied by AES and TDS using an UHV chamber equipped with a built-in high pressure cell (up to 1 atm.).

$NH_3$  adsorption takes place over the whole range of temperatures studied on both  $V_2O_5$  as well as reduced  $V_2O_5$  surfaces while  $NO$  adsorption occurs only on reduced  $V_2O_5$  surfaces.  $TiO_2$  adsorbs  $NH_3$  as well as  $NO$ .

The  $V_2O_5/TiO_2$  catalyst currently employed for reducing  $NO_x$  emission from power plants can be understood as a bifunctional catalyst.

Extrapolating from the data with pure  $V_2O_5$  and pure  $TiO_2$  to  $V_2O_5/TiO_2$  catalysts, one can propose that the adsorption of ammonia takes place mainly on the vanadium component causing the reduction of the original  $V^{5+}$  species. In turn the NO adsorption takes place on the  $TiO_2$  support since oxidized vanadia samples are completely unable to adsorb NO. The reduction of NO to  $N_2$  would occur through a Langmuir-Hinshelwood mechanism or a spill-over onto the surface of the vanadia component that implies the migration of the adsorbed NO species from the support to the reduced vanadium sites. In the absence of  $O_2$ , however, the catalyst loses activity since the reduced vanadium species can interact with ammonia molecules in the gas phase leading to the formation of  $VNH_x$  species which are completely unreactive towards NO.

Furthermore, oxidation of the  $NH_3$  to  $N_2O$  has been demonstrated by TDS on oxidized vanadium species. It has also been shown that reduced vanadia can be oxidized by reduction of  $N_2O$  to  $N_2$ . Since  $TiO_2$  was not able after heating in NO at reaction temperatures to generate  $N_2O$ , a similar redox cycle on the surface of the support involving ammonia is proposed. This also leads to the formation of  $NH_x$  species on the surface of the catalyst that, in the presence of  $O_2$ , leads to the formation of  $N_2O$  as has been reported in the literature. This process also explains the decrease in the catalytic activity as a function of the temperature because of the poisoning of active surface sites.

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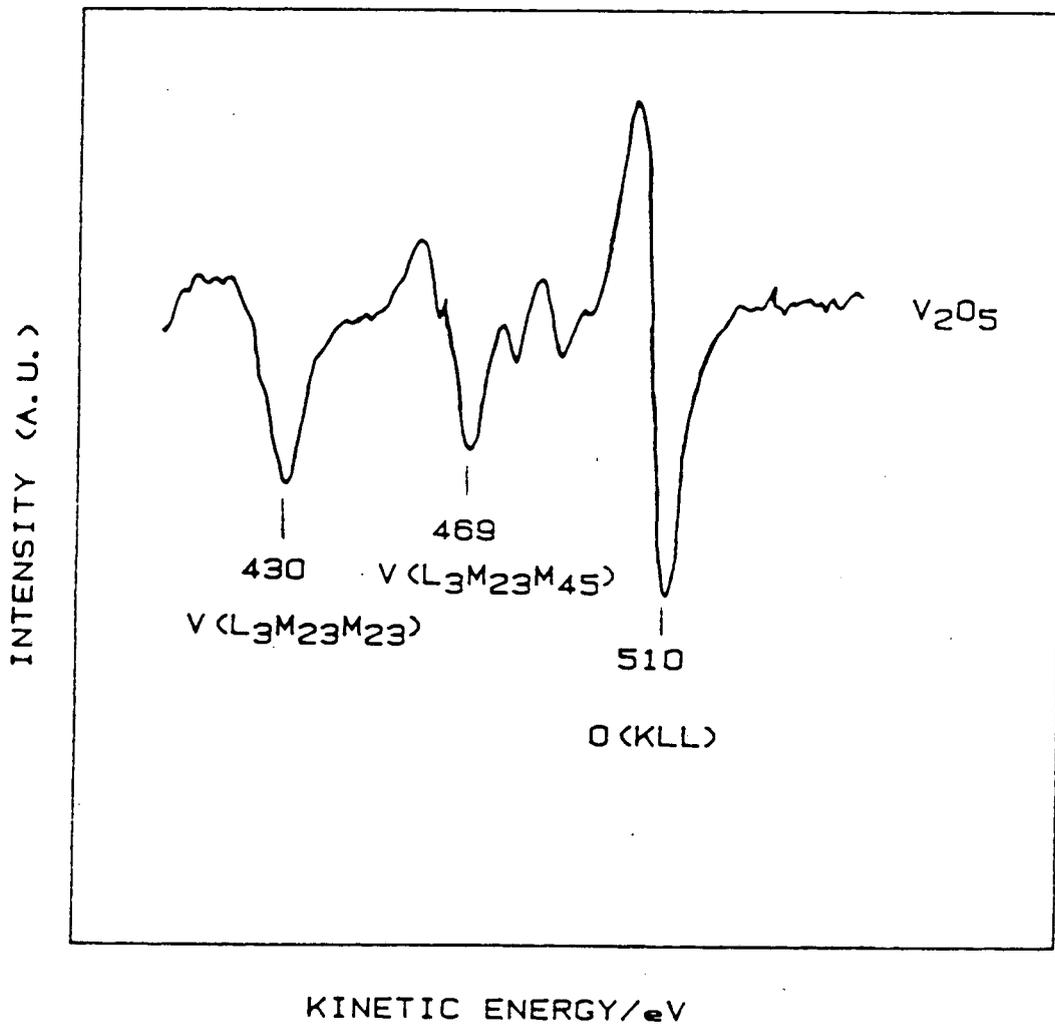
TABLE 1

N/V peak-to-peak ratio

Adsorbate	Treatment	Temperature (K)	N/V
NH <sub>3</sub>	Oxidized	300	0.21
NH <sub>3</sub>	NH <sub>3</sub> -reduced	300	0.29
NH <sub>3</sub>	Cooled down to R.T. in NH <sub>3</sub>	575	0.18
NH <sub>3</sub>	Heated to 575 K in UHV	575	0.15
NH <sub>3</sub>	Cooled down to R.T. in NH <sub>3</sub>	675	0.12
NH <sub>3</sub>	Heated to 675 K in UHV	675	0.13
NO	Oxidized	300	0.00
NO	Reduced	300	0.22

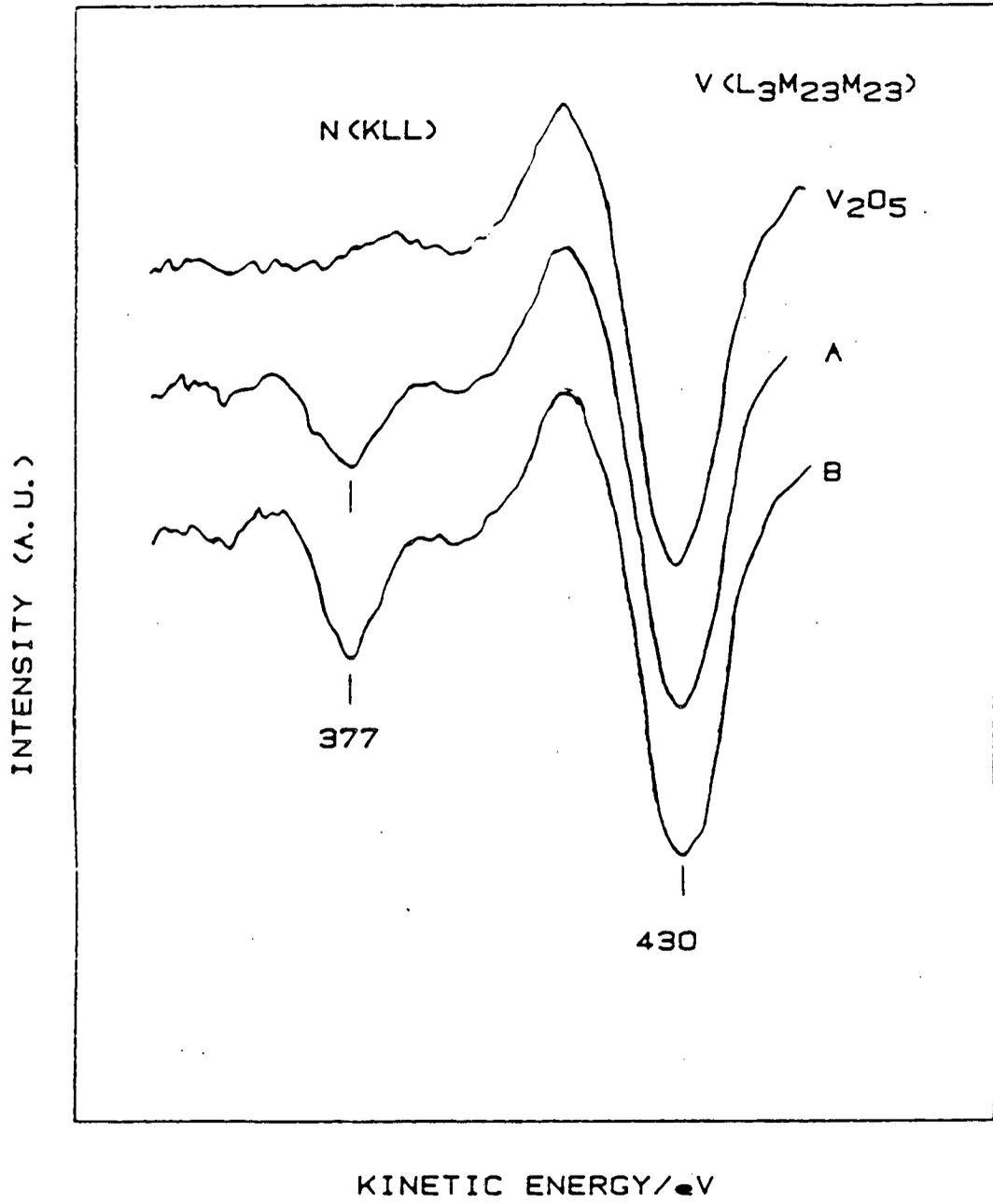
FIGURE CAPTIONS

- Figure 1. AES spectrum of a clean oxidized  $V_2O_5$  sample. Peak-to-peak modulation 2eV.
- Figure 2. AES spectra for the adsorption of  $NH_3$  at R.T. A) on a clean oxidized  $V_2O_5$  sample, B) on a  $NH_3$ -reduced  $V_2O_5$  sample.
- Figure 3. TDS spectrum for the desorption of  $N_2O$  after adsorbing 25 Torr of  $NH_3$  at R.T. on a clean oxidized  $V_2O_5$  sample.
- Figure 4. AES spectra for the adsorption of  $NH_3$  on a clean oxidized  $V_2O_5$  sample at 575 and 675K.
- Figure 5. TDS spectra for the desorption of  $NH_3$  after adsorbing 25 Torr of  $NH_3$  at 675K. First run: the sample was heated to 675K and cooled down in UHV. Second run: heated to 775K in UHV after the first run.
- Figure 6. AES spectra for the adsorption of NO at R.T. A) on a clean oxidized  $V_2O_5$  sample, B) on a  $NH_3$ -reduced  $V_2O_5$  sample heated in UHV to 775K and C) after heating B) to 775K in UHV.
- Figure 7. TDS spectrum for the desorption of  $N_2$  after adsorbing 25 Torr of NO at R.T. on a  $NH_3$ -reduced  $V_2O_5$  sample.
- Figure 8. TDS spectra for the desorption of NO after adsorbing successive 18L doses of NO to an oxidized  $TiO_2$  surface. The bottom profile corresponds to the first dose.
- Figure 9. TDS spectra for the desorption of  $NH_3$ . A) 5L at RT; B) 5L at 375K; C) 5L at 475K.



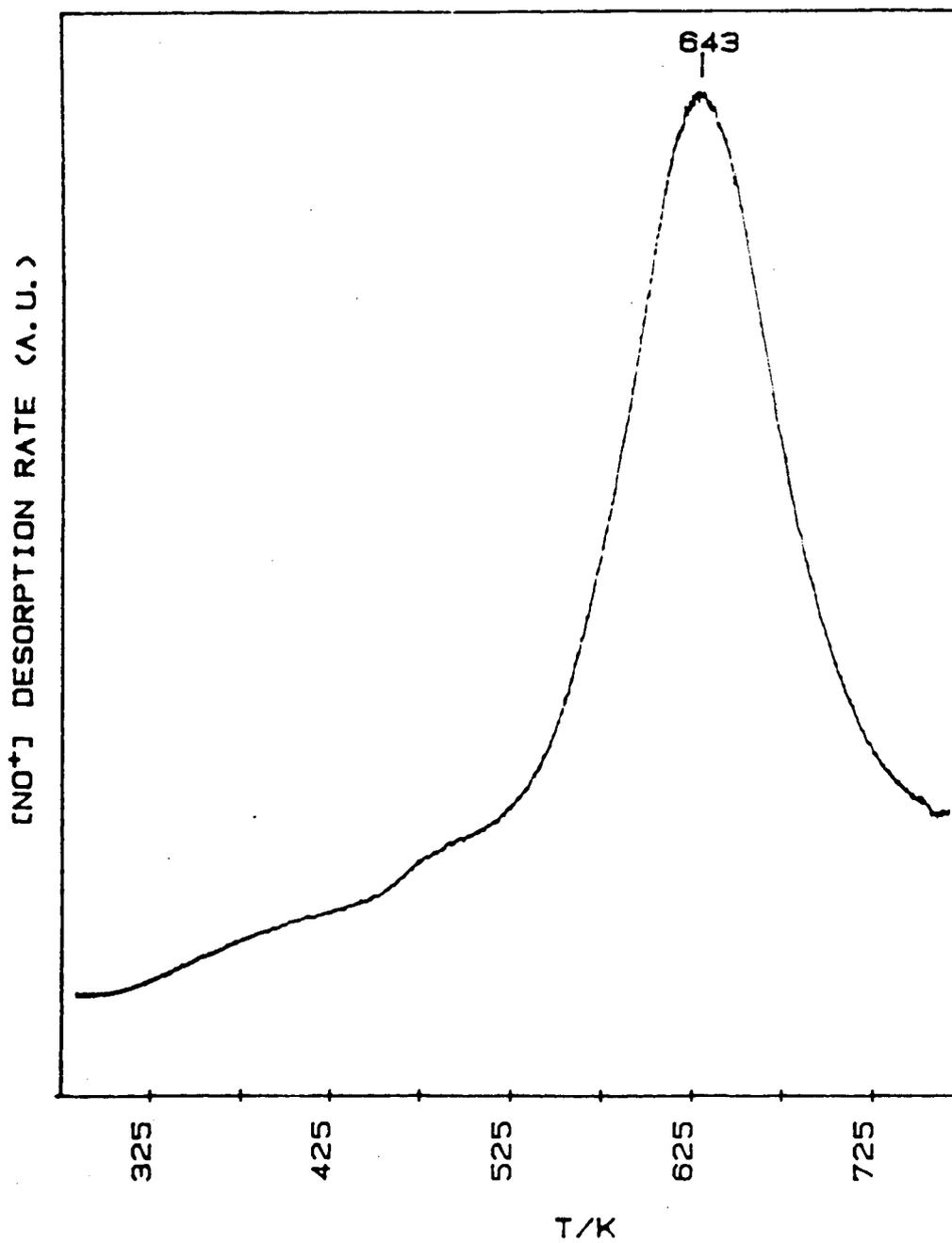
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Fig. 1



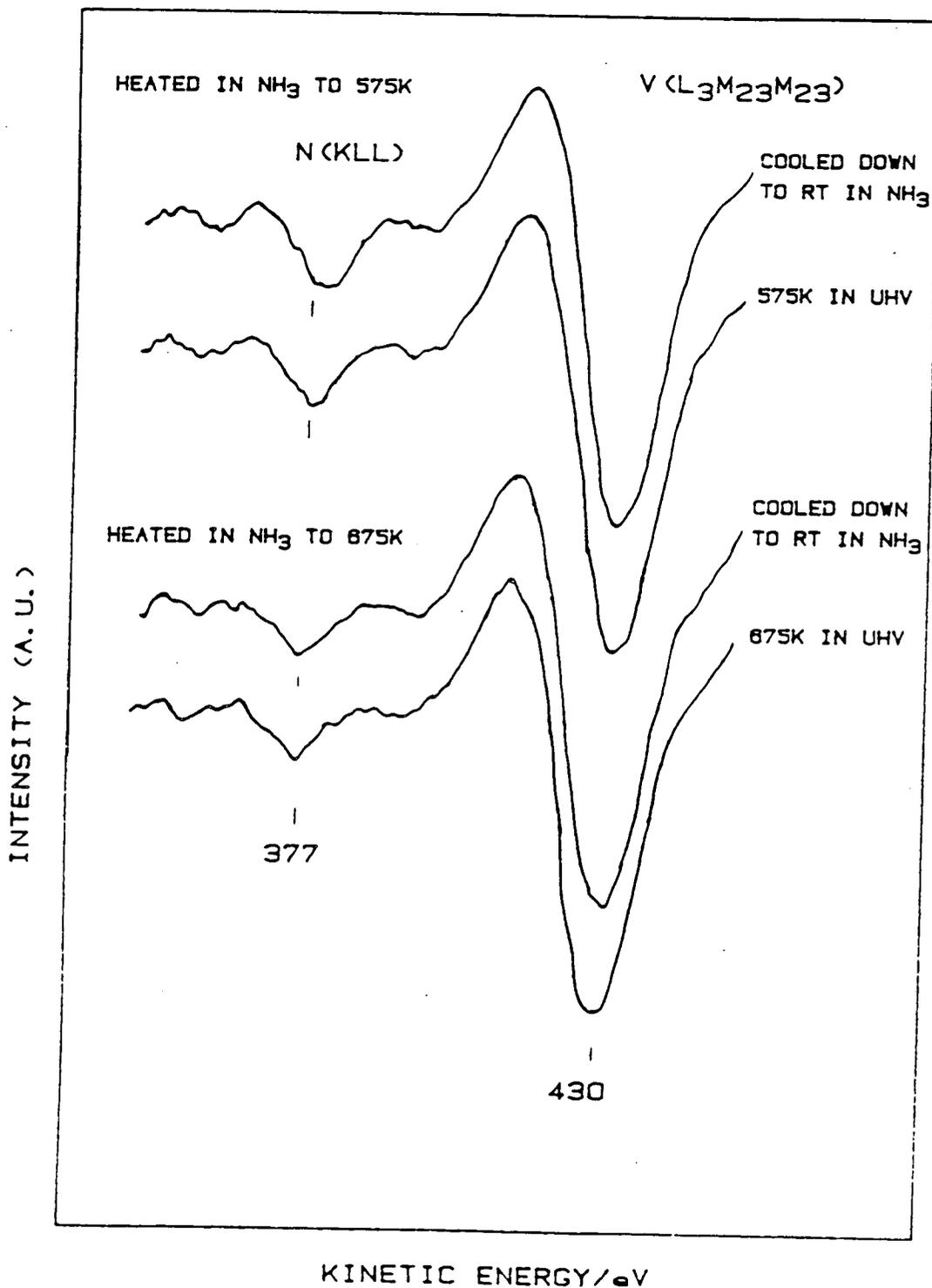
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Fig. 2



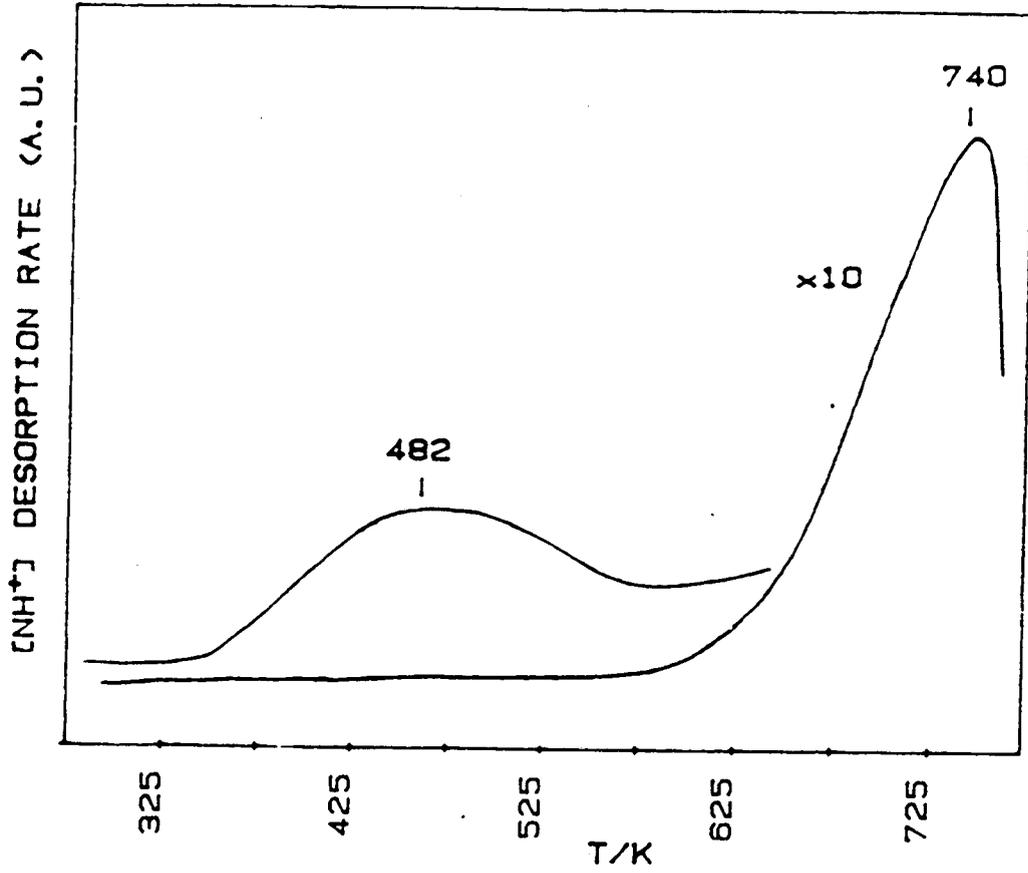
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Fig. 3



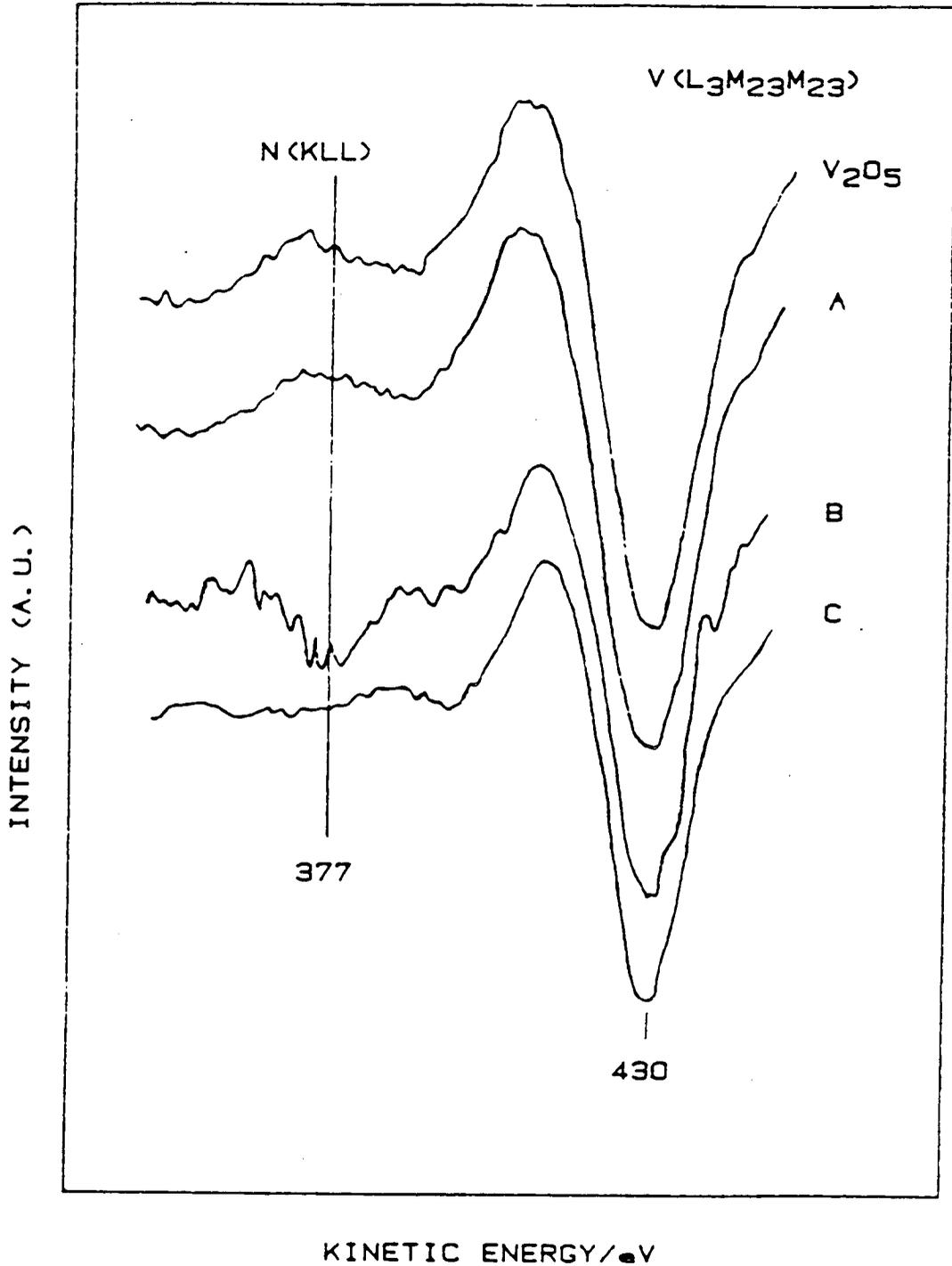
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Fig. 4



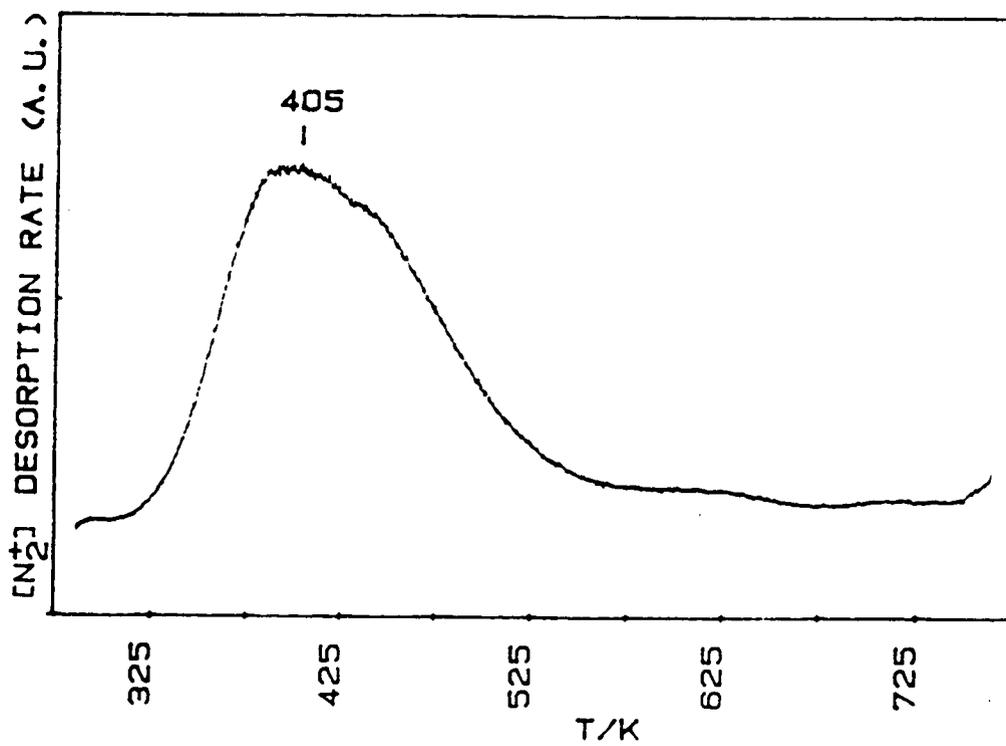
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Fig. 5



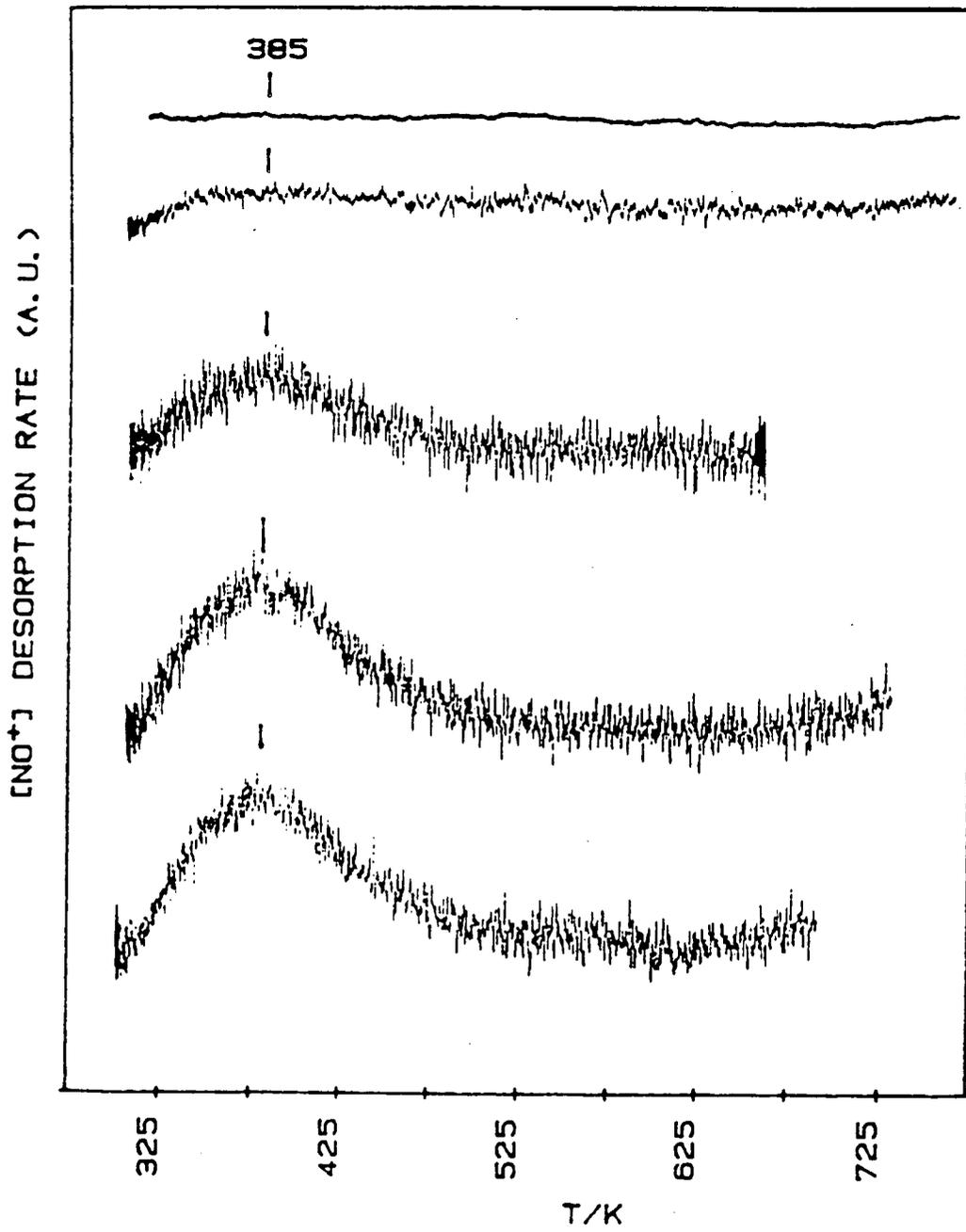
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Fig. 6



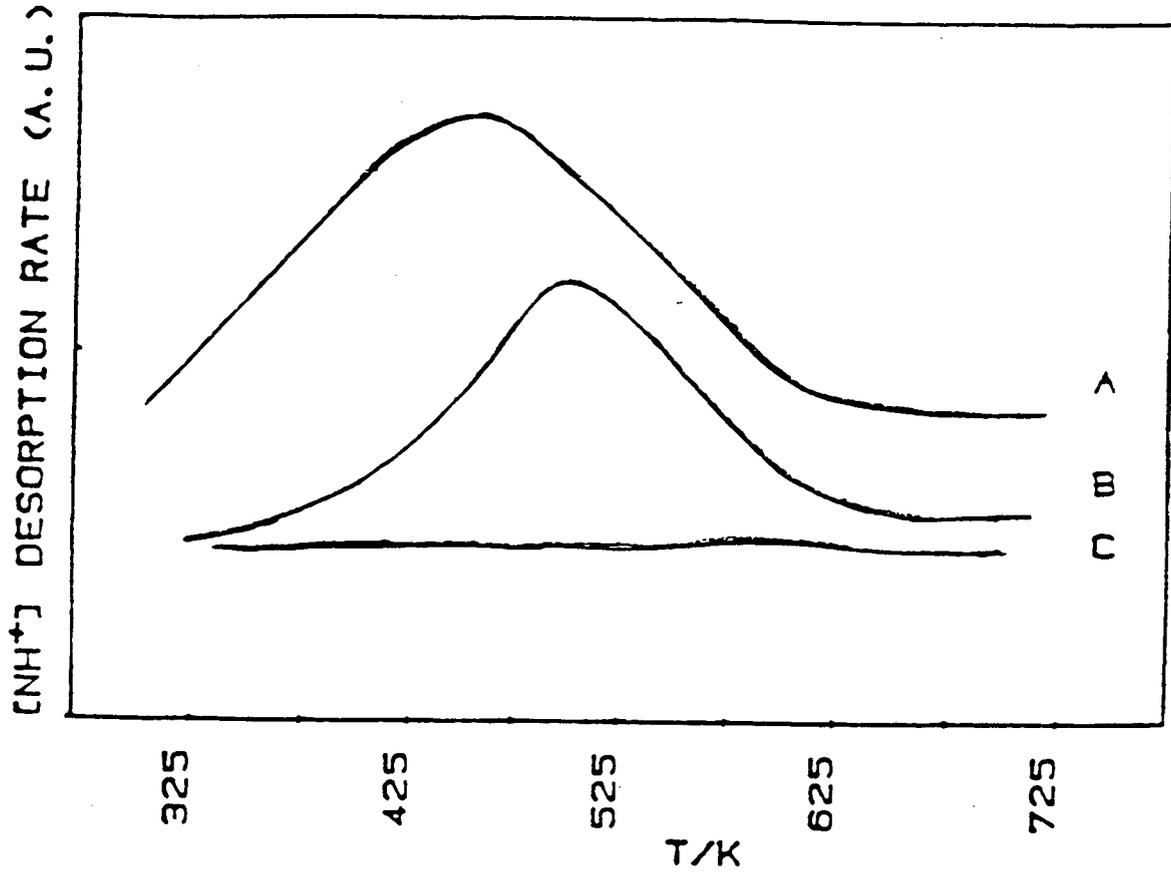
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Fig. 7



XBL 889-3166

Fig. 8



XBL 892-540

Fig. 9

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