INFRARED SPECTROSCOPIC STUDY OF THE EFFECTS OF HYDRATION AND REDUCTION OF V_2O_5/Al_2O_3 CATALYST ON AMMONIA ADSORPTION

Zdeněk SOBALÍK and Vladimír POUR

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6

Received November 16th, 1982

The effects of hydration and reduction of V_2O_5/Al_2O_3 catalyst (14·7% V_2O_5) on ammonia adsorption have been studied by infrared spectroscopy. Both the oxidation-reduction state of the catalyst and the degree of surface dehydration have an influence on the proportions of Brønsted and Lewis acidic adsorption sites in the surface. For adsorption at room temperature, the proportion of ammonia bound to Brønsted acidic sites in the form of NH_4^+ is highest with oxidized and weakly dehydrated catalyst surfaces, decreasing as the degree of reduction and the dehydration temperature are increased. Negligible proportion of this form is present on strongly reduced catalyst dehydrated at 763 K.

The catalytic reduction of nitrogen oxides by ammonia to elemental nitrogen is among the most effective methods for abating nitrogen oxide emissions. An advantage of this reaction is that over suitable catalysts ammonia, unlike other reducing gases such as hydrogen, carbon monoxide, methane and other hydrocarbons, reacts with nitrogen oxide in preference to oxygen commonly present in waste gases in concentrations orders of magnitude higher than those of nitrogen oxides. Another important feature is that oxygen significantly accelerates the reaction of nitrogen oxide with ammonia[1]. Al_2O_3-supported noble metal and V_2O_5 catalysts have proved best for this reaction. Apart from high activity and good selectivity, V_2O_5 catalysts have an added attraction of being resistant to catalytic poisons, particularly to sulphur compounds, usually present in waste gases.

The catalytic reduction of nitrogen oxides by ammonia over V_2O_5/Al_2O_3 catalysts has been the subject of a number of investigations[1-3], which have provided widely differing results. There still remains uncertainty as to the essential features of the reaction mechanism and the way in which oxygen accelerates the reaction. Despite divergent concepts of the reaction mechanism, ammonia adsorption is generally considered the first step of the reaction. Because of the basic nature of ammonia, its adsorption may be expected to be significantly affected by the acidcbasic properties of catalysts. This aspect has received little attention with V_2O_5/Al_2O_3. It is only quite recently that changes in the acidity of this catalyst have been studied over wide ranges of V_2O_5 loading[4,5]. The results obtained may be summarized as follows: *a*) the concentration of acidic sites is higher on V_2O_5/Al_2O_3 catalyst surface than on Al_2O_3 alone; *b*) acidic sites on the catalyst are the result of an interaction of the two catalyst components; *c*) the presence of the vanadium ions leads to the protonization of the surface hydroxyl groups, resulting in the appearance of both the Brønsted and Lewis acidic sites on the catalyst.

As yet, little attention has been paid to how the conditions of catalyst preparation, especially the degrees of dehydration and reduction, affect the catalyst properties. We have therefore focused on this question, with the aim to elucidate how changes in the catalyst state are reflected in the formation of surface complexes in ammonia adsorption. The adsorption was studied by the infrared spectroscopic technique. Pyridine, in addition to ammonia, was used to identify the various types of acidic sites on catalysts prepared under various conditions. Being a weaker base than ammonia, pyridine provides information primarily on strongly acidic adsorption sites. Its infrared spectra in the region 1 440 – 1 640 cm^{-1} are characteristic of various types of adsorption (for a review see ref.[6]).

EXPERIMENTAL

The catalyst was prepared by kneading a mixture of γ-alumina (Condea SC) and a solution of vanadyl oxalate with an addition of oxalic acid as peptizing agent. The mass obtained was extruded, dried at 393 K, and calcined in air at 848 K for 4 h. The V_2O_5 content was 14·7 wt %. The overall BET surface area determined by nitrogen adsorption was 185 m^2 g^{-1}.

IR spectra were taken on a UR 10 spectrometer (Zeiss Jena, GDR). Plates (30 × 10 mm) of c. 12 mg cm^{-2}, prepared by pressing spread catalyst sample at 300 MPa, were placed in an all-glass cell with NaCl windows. The cell was designed so as to allow the sample to be moved out of the measuring chamber into the upper part where sample treatment and the reaction could be carried out in a desired atmosphere at temperatures up to 773 K. The spectra were recorded at the infrared beam temperature. Owing to low transmissivity of the sample, the measurement was limited to the spectral range 1 000—2 000 cm^{-1}. EPR measurements were performed on a JEOL JES 3P spectrometer.

Sample treatment before measurement. Three types of catalyst with different degrees of reduction were prepared, labelled "oxidized", "evacuated", and "reduced". In each case, the sample was first evacuated at 763 K for 2 h in the preparatory section of the cell, and then treated at the same temperature in oxygen at 15 kPa for 1 h. This treatment was followed either by evacuation at room temperature ("oxidized sample") or by evacuation at 763 K for 1 h ("evacuated sample") or by additional reduction at 553 K and an ammonia pressure of 6·7 kPa for 2 h and subsequent 2-hour evacuation at 763 K ("reduced sample"). Each sample was then hydrated by exposure to water vapour at room temperature and a pressure of c. 1·5 kPa for 10 min. Sample dehydration was performed by evacuation at 363—763 K for 0·5 h. In pyridine adsorption experiments the possibility of transformation of the Lewis to Brønsted acidic sites was examined for samples hydrated after the pyridine adsorption. Although this treatment may not lead to the same results as obtained with adsorption on primarily different dehydrated surfaces, it does serve as a suitable test of whether or not Lewis sites can be converted to Brønsted ones.[6].

Ammonia adsorption was carried out at normal temperature and a pressure of 2·5 kPa, and infrared spectra were recorded on desorption at temperatures up to 473 K. Pyridine was adsorbed at room temperature onto oxidized or reduced surfaces dehydrated at 763 K. After 30 min the gas phase was removed by evacuation at 363 K, and spectra were recorded. The surfaces were then hydrated at a water vapour pressure of c. 1·5 kPa, and spectra were recorded on 30 min standing and equally long evacuation at 365 K.

Gas purification. Cylinder oxygen was purified by repeated condensation in liquid nitrogen. Cylinder ammonia was dried by passage through solid KOH, and fractionally distilled in liquid nitrogen before being fed into the apparatus. Analytical grade pyridine was dried by standing over a molecular sieve for several days.

RESULTS AND DISCUSSION

Three types of catalyst – oxidized, weakly reduced and strongly reduced – were prepared by treating samples in oxygen, evacuating at 763 K, and reducing with ammonia. While the oxidized sample is yellow-green as pure V_2O_5, the colour changes to black on evacuation at 763 K and reduction with ammonia.

As indicated by EPR measurements, V^{4+} is present in small amount even in the "oxidized" catalyst. Evacuation at 763 K increases its content 2·6 times. With pure V_2O_5, partial dissociation to $V_2O^{4,7}$ has been reported[7] to occur under similar conditions. Further release of oxygen with the formation of V_6O_{13} was only observed[8,9] upon increasing the temperature. In our experiments, the V^{4+} content was further enhanced by reduction with ammonia. Apparently, complete reduction of V^{5+} did not occur even under these conditions, consistent with the observation of Nowińska[5] and Yoshida[10] that vanadium in this oxidation state is much more stable in $V_2O_5/$ $/Al_2O_3$ catalyst than in pure V_2O_5. The fact that the colour change from yellow-green to practically black occurs on evacuation at 763 K alone suggests that the reduction takes place preferentially in the catalyst surface layer.

Pyridine Adsorption

On adsorption of pyridine onto oxidized sample, as well as on supplementary hydration of weakly reduced catalyst, the spectrum shows an intense band at 1 540 cm^{-1} and a shoulder at 1 640 cm^{-1} due to the pyridine cation produced by adsorption onto the Brønsted site (Fig. 1). Thus, in agreement with the work of Nowińska[4,5], and in variance with the observation of Spiridonova and coworkers[11], our experiments have confirmed that both types of acidic adsorption sites exist simultaneously on $V_2O_5/$ $/Al_2O_3$ catalyst. A shift of the band at 1 454 cm^{-1} due to adsorption on Lewis acidic sites was observed during evacuation at elevated temperature, suggesting that differently strong sites of this type may exist, just as observed with Al_2O_3 support alone[6] or with a V_2O_5/Al_2O_3 catalyst[5].

The variation in the relative proportions of the two types of acidic sites for oxidized and strongly reduced samples is shown in Table I which lists the ratio of the intensities of the band at 1 454 cm^{-1} characteristic of adsorption on Lewis acidic sites and the band at 1 540 cm^{-1} due to adsorption on Brønsted sites. It is seen that the reduction and hydration of the catalyst under study produce marked changes in the proportion of the two site types. In the oxidized sample the proportion of the Brønsted acidic sites is large, and increases by about fourfold on hydration. In the strongly reduced, dehydrated sample, on the other hand, the Lewis acidic sites entirely predominate, their proportion after hydration remaining still higher than that in the oxidized catalyst.

TABLE I

Ratio of intensities of bands 1 454 cm^{-1} and 1 540 cm^{-1} for pyridine adsorption

Catalyst	Method of treatment	A_{1454}/A_{1540}
Oxidized	dehydrated at 763 K	3·2
	hydrated	0·7
Reduced	dehydrated at 763 K	>50
	hydrated	3·9

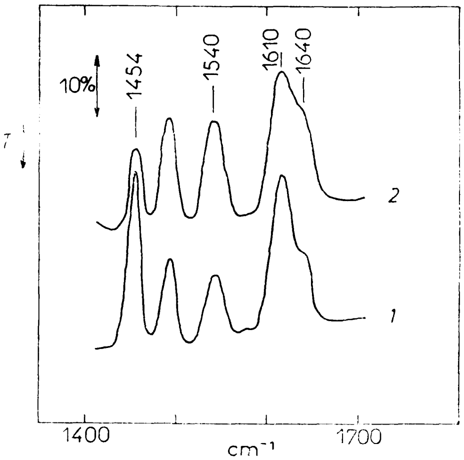

FIG. 1

IR spectra of pyridine adsorbed on "oxidized" catalyst. Measured after 30-min evacuation at 363 K. *1* dehydration at 763 K; *2* after subsequent hydration

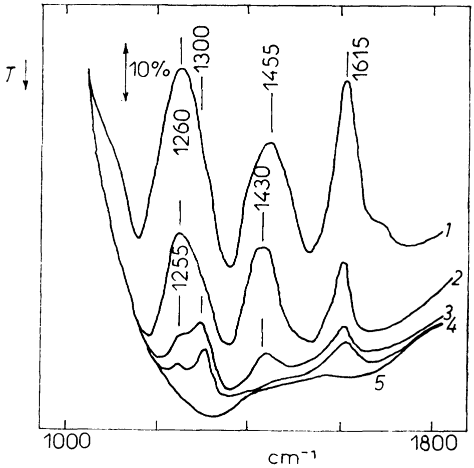

FIG. 2

IR spectra of ammonia adsorbed on a catalyst weakly reduced by evacuation at 763 K and dehydrated at the same temperature. *1* 2·46 kPa NH_3 (in the presence of the gas phase); *2* after 30-min desorption at 363 K; *3* after 15-min desorption at 473 K; *4* after 30-min desorption at 535 K; *5* background

Ammonia Adsorption

In the spectral range of the sample transmittance, infrared spectra of ammonia adsorbed on the three types of samples investigated exhibited three prominent absorption bands at 1 260 – 1 300 cm^{-1}, 1 430 – 1 450 cm^{-1} and 1 615 – 1 620 cm^{-1}. In desorption, all the absorption bands decreased in intensity as the temperature and the desorption time were increased. The second absorption band, whose maximum after ammonia adsorption lay at 1 450 cm^{-1}, simultaneously shifted to 1 430 cm^{-1}. On desorption at a temperature above 423 K this band virtually disappeared. The maximum of the band at 1 615 – 1 620 cm^{-1} did not change in position during desorption. Fig. 2 depicts the spectra for desorption of ammonia from sample weakly reduced by evacuation at 763 K,

The effect of the oxidation-reduction state of catalyst on the relative intensities of the bands after ammonia adsorption is shown in Figs 3 and 4 for samples dehydrated at 363 K and 763 K, respectively. The band at 1 430 cm^{-1} is seen to reach its maximum intensity with the oxidized catalyst in both cases, and to decrease in intensity with the degree of reduction, being virtually removed from the spectra of the weakly hydrated and strongly reduced catalysts. The band at 1 620 cm^{-1}, on the other

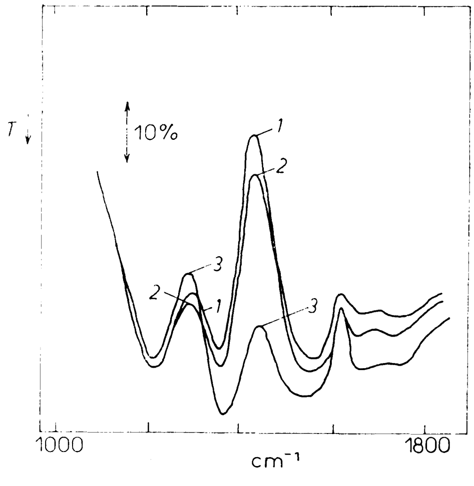

FIG. 3

IR spectra of ammonia adsorbed on catalysts dehydrated at 363 K. Measured after evacuation at 363 K. *1* "oxidized" catalyst; *2* weakly reduced by evacuation; *3* reduced by ammonia

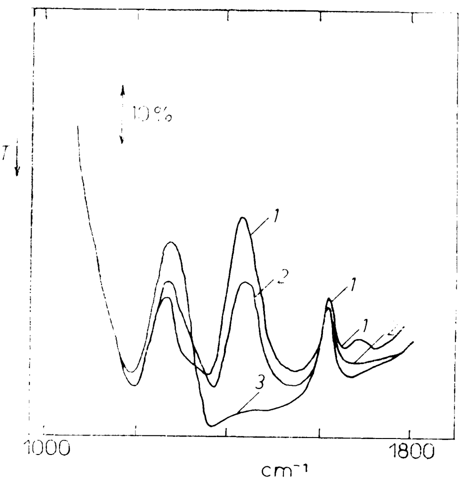

FIG. 4

IR spectra of ammonia adsorbed on catalysts dehydrated at 763 K. Measured after evacuation at 363 K. *1* "oxidized" catalyst; *2* weakly reduced by evacuation; *3* reduced by ammonia hand, attains its maximum intensity with the reduced catalyst. Comparison of Figs 3 and 4 enables us to assess the effect of different degrees of dehydration prior to ammonia adsorption onto the oxidized and ammonia-reduced samples. It is seen that as the degree of dehydration is increased, the band at 1 430 cm^{-1} decreases markedly in intensity while there is little change in the intensities of the bands at 1 260 cm^{-1} and 1 615 cm^{-1}.

In accord with previous observations, ammonia is adsorbed at room temperature predominantly on acidic sites of V_2O_5/Al_2O_3 catalysts of various degrees of reduction, dehydrated at temperatures up to 763 K. Thus, as with alumina[6], no other forms of ammonia adsorption are involved under these conditions. The absorption band at 1 430 cm^{-1} may be attributed to the NH_4^+ species generated in adsorption onto Brønsted sites. This band has also been reported for V_2O_5 alone[12], as well as for V_2O_5/Al_2O_3, *e.g.* by Takagi[2] who worked with a sample prepared by impregnation of γ-Al_2O_3 with a saturated solution of V_2O_5 in oxalic acid, followed by calcination at 773 K. There is even a report describing this form of adsorption for Al_2O_3 alone[13]. The bands at 1 260–1 300 cm^{-1} and 1 615–1 620 cm^{-1} may, respectively, be assigned to the symmetrical bending and degenerate bending vibrations of NH_3 bound to Lewis acidic sites. The two bands with well resolved maxima at 1 255 and 1 300 cm^{-1} in the frequency range characteristic of the symmetrical bending vibration[14] provide evidence for the existence of a minimum of two types of Lewis acidic sites. Of these, the form of adsorption corresponding to the spectral band at 1 300 cm^{-1} has proved to be the more stable, independently of the method of sample preparation. As this band shifts to higher frequencies and is more stable in desorption at higher temperatures, it may be attributed to adsorption on the more strongly acidic Lewis sites.

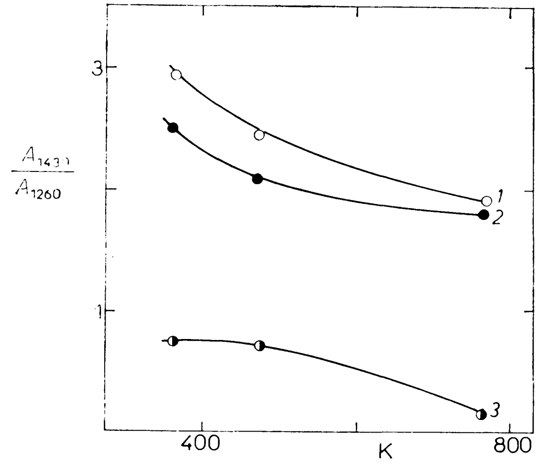

FIG. 5

A plot of the ratio of absorbancies of ammonia bands, $A_{1430cm^{-1}}/A_{1260cm^{-1}}$, against the dehydration temperature. *1* "oxidized" catalyst; *2* weakly reduced; *3* reduced by ammonia

Based on the above interpretation of the spectra, the ratio of the absorbancies of the bands at 1 430 and 1 260 cm^{-1} after removing the weakly adsorbed component by evacuation at room temperature may be regarded as approximately proportional to the ratio of ammonia adsorbed as NH_4^+ to ammonia bound to Lewis sites. A plot of this ratio against the dehydration temperature, shown in Fig. 5, gives a clear view of the effects of the state and the method of treating the V_2O_5/Al_2O_3 catalyst on the ammonia adsorption.

Thus, at the dehydration temperatures applied the ratio of ammonia bound as NH_4^+ to ammonia adsorbed on Lewis acidic sites for the oxidized sample is 4–5 times that for the strongly reduced sample. Increasing the dehydration temperature reduces this ratio, that at 363 K being about 1·5 times greater than that at 763 K.

It is apparent that at low temperatures ammonia adsorption does not occur dissociatively, as assumed – for higher temperatures, though – in some mechanisms proposed for the NO—NH_3 reaction[1]. The only form of ammonia adsorption on the catalyst under study is onto the various types of acidic sites. Apart from the oxidation state of vanadium[4,5], the decisive factor is therefore the degree of surface dehydration. In fact, whatever the oxidation state, moisture causes a portion of Lewis acidic sites to be changed into Brønsted sites, thereby increasing the proportion of ammonia adsorbed in the form of NH_4^+. The distinct differences in the strength of Lewis acidic sites observed in the adsorption of ammonia are not so marked with the less basic pyridine. It may therefore be concluded that the centres which are responsible for the band at 1 255 cm^{-1} observed in ammonia adsorption are very weakly acidic, and therefore do not give rise to a strong adsorption of pyridine.

REFERENCES

1. Markvart M., Pour V.: J. Catal. *7*, 279 (1967).
2. Takagi M., Kawai T., Soma M., Onishi T., Tamaru K.: J. Catal. *50*, 441 (1977).
3. Inomata M., Miyamoto A., Murakami Y.: J. Catal. *62*, 140 (1980).
4. Nowińska K.: Bull. Acad. Pol. Sci., Ser. Sci. Chim. *28*, 315 (1981).
5. Nowińska K.: Bull. Acad. Pol. Sci., Ser. Sci. Chim. *28*, 329 (1981).
6. Knözinger H.: Advan. Catal. Relat. Subj. *25*, 184 (1976).
7. Dziembaj R.: Bull. Acad. Pol. Sci., Ser. Sci. Chim. *24*, 965 (1976).
8. Dziembaj R., Ciembroniewicz G.: React. Kinet. Catal. Lett. *9*, 337 (1978).
9. Dziembaj R., Ciembroniewicz G., Kalicki R.: React. Kinet. Catal. Lett. *12*, 89 (1979).
10. Yoshida S., Iguchi T., Ishida S., Tarama K.: Bull. Chem. Soc. Jap. *45*, 376 (1972).
11. Spiridonova D. V., Fokina E. A., Spiridonov K. N., Krylov C. V.: React. Kinet. Catal. Lett. *7*, 53 (1977).
12. Belokopytov Yu. V., Kholyavenko K. M., Gerei S. V.: J. Catal. *60*, 1 (1979).
13. Dunken H., Fink P.: Acta Chim. (Budapest) *53*, 179 (1967).
14. Horák M., Papoušek D.: *Infračervená spektra molekul*, p. 208. Academia, Prague 1976.

Translated by M. Škubalová.