Journal of Thermal Analysis, Vol. 44 (1995) 1079-1085

ON THE LOW- AND HIGH-TEMPERATURE INTERACTIONS OF AMMONIA WITH AlPO-5

*E. Segal**, *Irina Ivanova and E. G. Derouane*

Facultés Universitaires Notre Dame de la Paix, Laboratoire de Catalyse, 61, rue de Bruxelles, B-5000, Namur, Belgium

(Received May 3, 1994)

Abstract

Results are presented on the low-temperature interaction of ammonia with AlPO-5, the TPD of the adsorbed ammonia and the high-temperature interaction of ammonia with the AlPO-5 framework.

Keywords: AlPO-5, ammonia

Introduction

Following research concerning the interaction of ammonia with microporous aluminophosphates [1], this note reports result on the low-temperature sorption of ammonia on AlPO-5, the TPD of the adsorbed ammonia and the high-temperature interaction of ammonia with the AlPO-5 framework.

As an unsubstituted aluminophosphate, AlPO-5 exhibits few Brönsted centers [2] and consequently low acidity [3], although acidity arising from structural defects has been reported [4]. This is the reason for only the weak adsorption of ammonia on AlPO-5 [3].

Experimental

AlPO-5 was synthesized according to a procedure given elsewhere [5]. The mean size of the crystallites, determined by means of a Philips XL 20 SEM, was 1 μm. The TG and DSC curves were recorded with SETARAM TG-DSC 111 equipment.

* On leave from the Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bd. Republicii I, nr. 13, Bucharest, Romania; corresponding author.

0368–4466/95/ $ 4.00
© 1995 Akadémiai Kiadó, Budapest
John Wiley & Sons, Limited
Chichester

For the low-temperature absorption of ammonia (20–100°C), the standard operating procedure was as follows:

– The sample of AlPO-5 was heated in the temperature range 20–550°C at 4 deg·min^{-1} in flowing nitrogen (20 cm^3/min) in order to remove water and the adsorbed template.

– The sample was kept in flowing nitrogen (20 cm^3/min) for 2 h at 550°C and in flowing oxygen (17 cm^3/min) for 12 h in order to remove the carbonaceous residue.

– The sample was cooled rapidly in a nitrogen flow (20 cm^3/min) to the working temperature.

– Isothermal adsorption of ammonia, using helium as gas carrier (14 cm^3/min).

– Nonisothermal desorption of ammonia (TPD) at a heating rate of 5 deg·min^{-1} in flowing nitrogen (20 cm^3/min).

As far as the high-temperature isothermal interaction of ammonia with AlPO-5 is concerned, the standard treatment of the samples consisted in:

– Heating in the temperature range 20–550°C at a rate of 4 deg·min^{-1} in flowing nitrogen (20 cm^3/min).

– The sample was kept at 550°C in flowing nitrogen (20 cm^3/min) for 2 h and in flowing oxygen (17 cm^3/min) for 12 h.

– The sample was heated in flowing nitrogen (20 cm^3/min) at a rate of 10 deg·min^{-1} up to the working temperature.

– Isothermal interaction of ammonia with the sample, using helium as carrier gas (14 cm^3/min).

As ammonia source, we used the coordination compound $[Ni(NH_3)_6]Br_2$, synthesized according to Flora [6], kept at 132°C by means of a constant-temperature paraffin oil bath. An amount of 5–6 g of this compound proved sufficient for dry ammonia generation for 5–6 h under the above-mentioned conditions.

TPD data handling

In order to obtain the nonisothermal kinetic parameters of ammonia desorption, in the framework of the 'reaction order' model three integral methods were applied: the Coats and Redfern method [7], the Flynn and Wall method for a constant heating rate [8] and the modified Coats and Redfern method [9]. The experimental data were processed by a program written in BASIC language [10].

Results and discussion

Low-temperature adsorption of ammonia

A typical isothermal curve in the coordinates ammonia uptake (%) *vs.* time is given in Fig. 1.

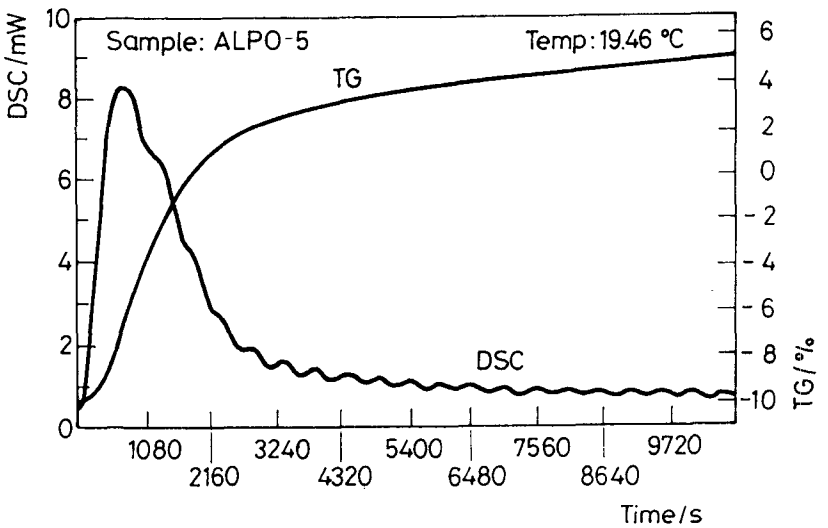

Fig. 1 Isothermal ammonia uptake *vs.* time curve (t=19.46°C)

It is necessary to note the oscillations in the DSC curve and also the oscillations which modulate the TG curve, but do not alter it. Thus, it is possible to fit a kinetic equation to describe the ammonia uptake *vs.* time curves.

Table 1 Maximum ammonia uptake at various temperatures

Temparture of adsortpion / °C	Maximum ammonia uptake (mass percentage)
19.46	15.3
49.32	12.3
64.26	3.0
79.19	1.2

As shown in Table 1, the maximum ammonia uptake decreases as the temperature of adsorption is increased.

As concerns the maximum ammonia uptake for each isothermal curve, corresponding to the total conversion of ammonia in the adsorbed state (the degree of conversion, α, is unity), the following integral kinetic equation (a variant of the Bangham-Burt equation [11] was found to fit the experimental data:

$$\alpha = kt^p \tag{1}$$

where t is time. The rate constant, k, and the exponent, p, are specific for the given adsorbate – adsorbed system. With the data in the coordinates ln α *vs.* ln t the results listed in Table 2 were obtained.

Table 2 Values of k and p for isothermal sorption of ammonia on AlPO-5

Temperature / °C	k / s^{-n}	p	$\|r\|$*
19.46	$2.76 \cdot 10^{-3}$	1.70	0.9851
49.32	$1.00 \cdot 10^{-2}$	1.58	0.9926
64.26	$3.59 \cdot 10^{-3}$	1.72	0.9923

* r is the correlation coefficient of the linear regression.

An inspection of the data in Table 2 shows that the kinetic Eq. (1) is satisfied. Constant k decreases with increasing temperature in the temperature range 49.32–64.26°C. Such an abnormal change in the apparent rate constant with temperature is probably due to an interplay between a true rate constant which increases with increasing temperature and an adsorption equilibrium

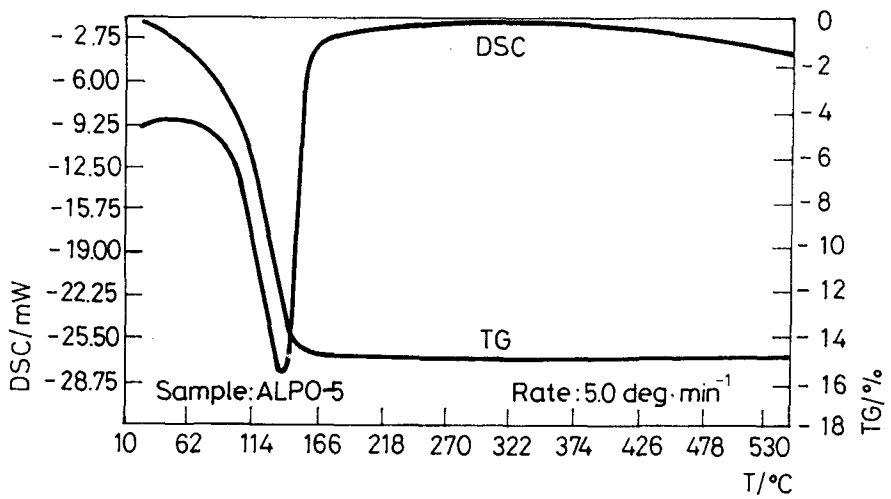

Fig. 2 TG and DSC (TPD) curves for ammonia adsorbed at 19.46°C

constant which decreases with increasing temperature. This decrease in constant k with increasing temperature, which was not observed for the system ammonia – SAPO-5 [1], is probably evidence of the contribution of the physical character of the adsorption of ammonia on AlPO-5 in the reported temperature range.

Table 3 Shift in TPD peak temperature with variation of temperature of adsorption

Temperature of adsorption / °C	TPD peak temperature / °C
19.46	136.5
49.32	129.0
64.26	98

Figure 2 shows a TG, TPD curve (in fact, the DSC curve correctly approxi-mates the TPD curve) for the desorption of ammonia adsorbed at 19.46°C.

Table 4 Kinetic parameters of ammonia TPD

t_{ads} = 19.46°C			
Kinetic parameter	Method		
	Coats-Redfern	Flynn-Wall	Modified Coats-Redfern
E / kcal·mole^{-1}	6.70	7.70	7.00
A/s^{-1}	4.90	6.84·10	9.69
n	0	0	0
$\|r\|$	0.9980	0.9990	0.9970
t_{ads} = 49.32°C			
Kinetic parameter	Method		
	Coats-Redfern	Flynn-Wall	Modified Coats-Redfern
E / kcal·mole^{-1}	19.40	19.50	20.50
A/s^{-1}	$6.0 \cdot 10^8$	$8.04 \cdot 10^8$	$8.04 \cdot 10^8$
n	2	1.9	1.9
$\|r\|$	0.9952	0.9959	0.9959
t_{ads} = 64.26°C			
Kinetic parameter	Method		
	Coats-Redfern	Flynn-Wall	Modified Coats-Redfern
E / kcal·mole^{-1}	25.80	26.00	27.00
A/s^{-1}	$2.25 \cdot 10^{13}$	$2.75 \cdot 10^{13}$	$2.75 \cdot 10^{13}$
n	2.6	2.6	2.6
$\|r\|$	0.9985	0.9987	0.9987

As shown in Table 3, the temperature corresponding to the peak in the TPD curve sifts to lower values as the temperature of adsorption is increased. Such a shift was observed for the system ammonia – SAPO-5 too.

Table 4 lists the values of the nonisothermal kinetic parameters (activation energy, E, preexponential factor, A, and reaction order, n) for the desorption of ammonia from AlPO-5.

The results in Table 4 reveal an increase in the desorption order from 0 for $t_{ads}=19.46$°C to 2.6 for $t_{ads}=64.26$°C. As shown earlier [12], the value $n=0$ is accounted for by a diffusional loss of ammonia, probably from the pores of AlPO-5. As in the case of the system ammonia – SAPO-5, the higher values of the desorption order obtained for higher temperatures of adsorption can be ascribed to the desorption of structural units which consist of more than one molecule of ammonia.

This change in the value of the desorption order is probably due to the weaker interactions of ammonia with the surface at higher temperatures, which permits the association of ammonia molecules before desorption.

All the reported results show the mainly physical character of the low-temperature adsorption of ammonia on AlPO-5.

High-temperature interaction of ammonia with AlPO-5

Figure 3 shows TG and DSC curves corresponding to the isothermal interaction of ammonia with AlPO-5 at 795.96°C.

After an initial mass increase of 1.5%, a mass decrease (~0.4%) followed by smaller mass increases can be observed. This quite irregular change in mass

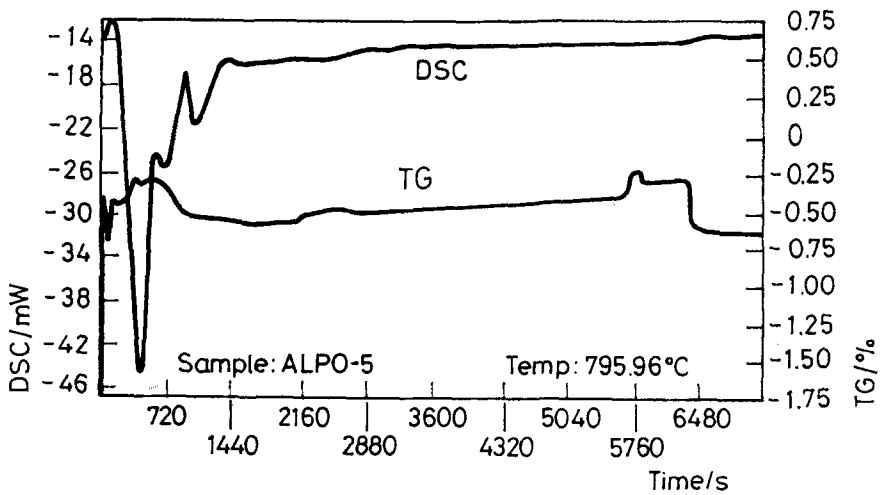

Fig. 3 TG and DSC curves demonstrating changes in time for the system ammonia – AlPO-5 at 795.96°C

was recorded even on isothermal treatment of AlPO-5 with ammonia for 12 h at the same temperature. These mass changes probably indicate the occurrence of ammonolysis, and thus the incorporation of nitrogen by AlPO-5.

Conclusions

1) The low-temperature interaction of ammonia with AlPO-5 consists mainly in physical adsorption

2) The high-temperature interaction of ammonia with AlPO-5 curves indicate an incorporation of nitrogen into the AlPO-5 framework through ammonolysis.

* * *

E. S. and I. I. thank the Interuniversity Attraction Pole in Interface Sciences sponsored by the Scientific Policy Services of the Prime Minister for financial support.The authors thank Dr. Lutgard Maistriau for the synthesis of AlPO-5.

References

1 E. Segal, Irina Ivanova and E. G. Dorouane, Thermochim. Acta, 231 (1994) 277.
2 K. J. Chao and L. J. Leu, Stud. Surf. Sci. Catal., 46 (1989) 19.
3 S. G. Hedge, P. Ratnasamy, L. M. Kustov and V. B. Kazansky, Zeolites, 8 (1988) 137.
4 N. J. Tapp, N. B. Milestone and D. M. Bibby, Stud. Surf. Sci. Cat. 37 (1988) 393.
5 S. T. Wilson, B. M. Lok and E. M. Flanigen, U. S. Patent, 4310440 (1982).
6 S. Flóra, Acta. Chim. Acad. Sci. Hung., 37 (1963) 395.
7 A. W. Coats and J. P. Redfern, Nature (London), 201 (1968) 68.
8 J. H. Flynn and L. A. Wall, Polym. Lett., 4 (1966) 323.
9 E. Urbanovici and E. Segal, Thermochim. Acta, 81 (1984) 379.
10 N. Dragoe and E. Segal, Thermochim. Acta, 185 (1991) 129.
11 D. H. Bangham and F. F. Burt, Proc. Roy. Soc., (L) 105 (1924) 481; J. Phys. Chem., 29 (1925) 540.
12 E. Segal, 'Kinetik und Mechanismen der thermischen Zersetzungsreaktionen von Komplexverbindungen', in 'Festkörperchemie', eds. V. V. Boldyrev and K. Meyer, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1973, p.404.

Zusammenfassung — Vorliegend werden die Ergebnisse über die Tieftemperaturwechselwirkung von Ammoniak mit AlPO-5, dem TPD adsorbierten Ammoniaks und über die Hochtemperaturwechselwirkung von Ammoniak mit AlPO-5 Gerüst beschrieben.