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A simple method for determination of heats of ammonia adsorption on catalysts from thermodesorption data

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Abstract

The stepwise thermodesorption (TD) of NH_3 from Na and H-forms of different types of zeolites (A, Y, mordenite, erionite) was studied by the gravimetric method. The TD-experiments were carried out in the temperature range from 30 to 420°C. A correlation between the temperature of desorption and the heat of adsorption, measured calorimetrically, was discovered. It was shown that thermodesorption data can be used for a rapid estimation of heats of adsorption of NH_3 on zeolites and other acid catalysts as well as for determination of number of acid sites. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Stepwise thermodesorption; Calorimetry; NH_3; Zeolites; Acid sites

1. Introduction

The adsorption of ammonia is widely used in order to evaluate surface acidity of catalysts. The concentration of acid sites and an averaged energy of centers can be quickly determined using thermodesorption technique [1–4]. The calorimetric method is one of the most informative for characterizing the distribution of acid-site strengths in catalysts [5–7]. This relatively expensive and laborious technique has found only a limited application for studying acidity of adsorbents and catalysts.

Over the last years, we were engaged in the investigations of acidity of catalysts with the help of Calvet-type microcalorimeters [8–10]. In this work, a simple method is described that makes use of the curves of a stepwise thermodesorption in the estimation of heats of adsorption of ammonia on solid carriers.

2. Experimental

The thermodesorption of NH_3 was studied on a series of zeolites for which the heats of adsorption of NH_3 have been previously measured [10]. The samples ranging in the quantity and the strength of the acid centers were chosen for this work. The composition and the methods of preparation of the samples are given in Table 1.

The thermodesorption of NH_3 was studied in a vacuum unit with quartz spiral balances. Before the measurements, the zeolites were evacuated at 450°C to attain a constant weight, subsequently the adsorption of NH_3 was measured at 30°C at about 20 Torr (2.7×10^3 Pa) pressure followed by the evacuation at the same temperature until a further weight loss could not be recorded. Thermodesorption of NH_3 was carried out by continuous evacuation of the samples in different heating regimes. In the first series of measurements, a stepwise heating was carried out to 420°C. In each subsequent step, the temperature

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Table 1
Composition and methods of preparation of the samples taken as reference

Sample	Zeolite	SiO_2/Al_20_3	Method of preparation
1	NaY	4.7	Commercial sample
2	HY	5.6	Decationation to a 94% level by treatment with NH_4C1
3	$DY_{9.2}$	9.2	Dealumination by treatment with EDTA
4	DY_{34}	34	Dealumination by treatment with $SiCl_4$ vapor at 365°C
5	NaMor	10	Commercial sample (large-pore mordenite)
6	HMor	10	Decationation of large-pore mordenite to a 98% level by treatment with NH_4Cl
7	HMor(TEA)	20	Hydrothermal crystallization of mordenite with TEA cations, calcination for 16 h at 540°C followed by decationization
8	NaA	2	Hydrothermal crystallization

was increased by 50°C, the heating was then stopped for 5–7 h, and the amount of NH_3 remaining on the zeolites was measured. In a second series of experiments, the heating was carried out gradually, also at 40–50°C intervals, but the sample was held for only 1 h at each temperature. In the thermodesorption measurements, a correction was applied for the elongation of the spiral due to the furnace temperature. For this purpose, the balances were calibrated using a weighed sample of finely divided quartz, under the same heating regimes. The continuous evacuation of the samples was carried out at a rate of 100 l/min. At the end of each temperature step the residual pressure did not exceed 1.3×10^{-2} Pa.

3. Results and discussion

Fig. 1 presents the results of TD-experiments obtained in the tests where the samples were held for 1 h at given temperature. Acidity of the zeolites can be evaluated qualitatively from the thermodesorption curves. The main results coincide with the results of calorimetric experiments. It can be clearly seen that the Na-forms of zeolites contain much weaker acid sites than H-forms ones. In the case of samples 1, 5 and 8, the desorption is practically completed up to 250°C, while in the case of other samples the desorption is finished at higher temperature. With decrease in the Al content, the number of acid centers of zeolites decreases (curves 2–4, 6 and 7). In comparison with Y zeolites, mordenites are characterized by stronger acid sites. It is necessary to point out that for total number of acid sites we accept the amount of ammonia retained on the samples at 150°C.

The two different regimes of stepwise heating lead to practically coinciding results as it can be seen from Table 2. For NaA zeolite, the amounts of NH_3 held by the sample at two modes of heating were different, but for other samples nearly an equilibrium value of adsorption is achieved after evacuation for 1 h at a given temperature. We can therefore ascribe any desorption temperature to a specific value of amount of ammonia adsorbed at equilibrium and find the corresponding heat on the curve ‘‘heat of adsorption — the amount of adsorbed ammonia’’ (Fig. 2.). Therefore, the determination of a relation between the desorption temperature and the heat of adsorption of NH_3 becomes possible. For example, Fig. 1 indicates that about 1.79 mmol of NH_3/g is left on the sample 2 after this sample was heated to 200°C. The calorimetric curve (Fig. 2) suggests that heat of adsorption of 105 kJ/mol corresponds to the adsorbed amount. From the adsorption value of 0.41 mmol of NH_3/g retained by the sample after evacuation at 300°C a heat of 116 kJ/mol can be derived. Applying this procedure to further temperatures, the dependence of the energy of adsorption on the temperature of desorption has been plotted. In this way, mean values of heat of adsorption were calculated for different desorption temperatures for eight samples.

For all the zeolites studied, the curves describing the heat of adsorption of NH_3 as a function of filling have been previously measured. These measurements were carried out at 300°C, with the exception of samples 1, 3, 5, and 8, for which the heats were measured at 30°C. Since no variation of heats of adsorption with temperature could be recorded for these samples, the data obtained at 30°C were taken

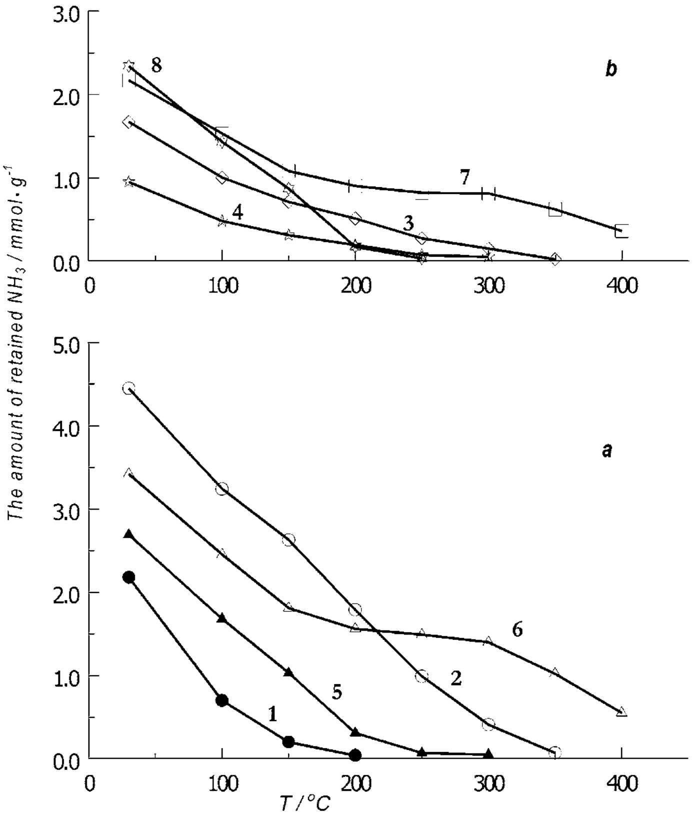

Fig. 1. Stepwise thermodesorption of NH_3 from zeolites. The numbers on the curves correspond to the numbers of samples in Table 1.

with the aim to increase the adsorption interval for these samples.

The relation between the heat of adsorption and the temperature of desorption in the temperature range from 50 to 420°C can be expressed by the following empirical equation

$$q = 0.21T + 58 \quad (1)$$

where T is temperature, °C and, q is heat of NH_3 adsorption (kJ/mol) (Calculations gave a R-squared correlation coefficient of 0.998).

Relation (1) can be used to derive the heats of adsorption from the thermodesorption curve, and to compare the calculated values with the heats of adsorption measured calorimetrically. As it can be seen from Fig. 2., results obtained by two methods are in good agreement. It is evident that the heat curves obtained from the TD-experiments during the examination of Na and H-forms of zeolites and H-forms of zeolites with different structure give practically the same results as calorimetric curves. The amount of NH_3 retained on H-forms of samples at 150°C coincides with the number of acid sites calculated from calorimetric experiments.

Table 2
Comparison of the amounts of NH_3 retained on the samples at two regimes of stepwise heating

Temperature (°C)	The amount NH_3, retained (mmol/g)					
	HY		HMor		NaA	
	1 h	5 h	1 h	5 h	1 h	5 h
100	3.24	3.28	2.45	2.40	1.43	1.36
150	2.63	2.54	1.81	1.96	0.87	0.41
200	1.79	1.84	1.56	1.65	0.17	0.08
250	0.99	0.95	1.49	1.54	0.03	0.03
300	0.41	0.38	1.40	1.48	–	–
350	0.07	0.09	1.02	1.08	–	–
400	–	–	0.55	0.35	–	–

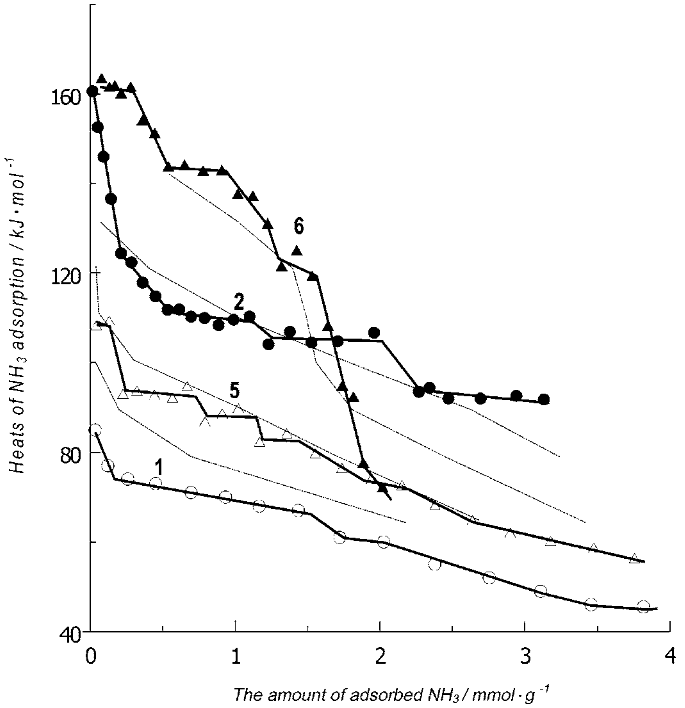

Fig. 2. Heats of adsorption of NH_3 on zeolites, determined calorimetrically and from TD-experiments (dotted lines). For designation see Table 1.

In the case of NaA and NaY zeolites, some differences were recorded between the heats calculated from TD-results and calorimetric measurements. We believe that the presence of cations on six-member rings at the entrance of sodalite unit creates an energetic barrier for desorption of NH_3 molecules from these units. It results in the overestimated heats obtained from TD-experiment for these zeolites.

Some comments ought to be said about the boundary between physical adsorption and chemisorption. In the TD-experiments aimed at studying the acidity of zeolites and aluminosilicates, elevated temperatures

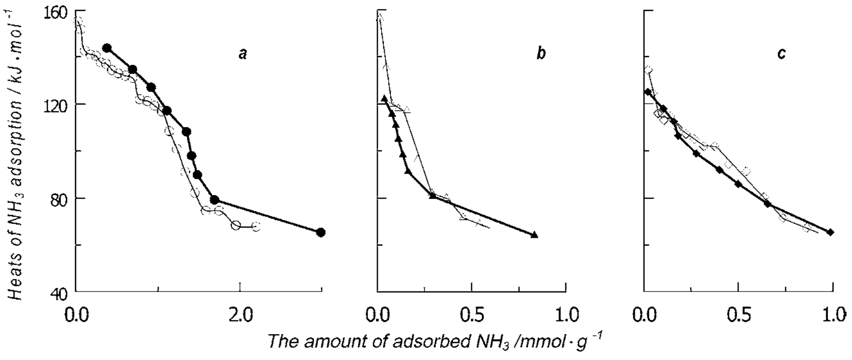

Fig. 3. Heats of adsorption of NH_3 on erionite (a), 20% $H_3W_{12}O_{40}/SiO_2$ (b) and 15% ZrO_2–SiO_2 (c) determined calorimetrically at 150°C and from TD-experiments. Solid symbols — TD-experiment.

are used to remove physically adsorbed ammonia. The choice of such temperatures is fairly arbitrary in the range from 100 to 250°C.

Comparison of our TD data obtained in the stepwise heating regime with the calorimetric data shows that the initial pretreatment temperature for zeolites should not exceed 150°C. At this temperature NH_3 is removed from the sites where it has been adsorbed with a heat of adsorption lower than 90 kJ/mol. The higher heats are characteristic for adsorption on the acid centers of zeolites.

It can be expected that the correlation between the calorimetric values and the data calculated from the thermodesorption measurements might be valid for zeolites with the different framework topologies. The support for this assumption can be found in the experiments with erionite-type zeolite. Fig. 3a shows the calorimetrically measured heats of NH_3 adsorption for H-erionite and data obtained from TD-experiments. Obviously, TD-curve gives very good representation of the number and the strength of acid sites in this sample. Moreover, relation (1) appears to be valid for other catalysts containing acid centers such as $H_3W_{12}O_{40}/SiO_2$ and $ZrO_2–SiO_2$ (Fig. 3b and c, respectively). The sample $H_3W_{12}O_{40}/SiO_2$ was obtained by the impregnation of SiO_2 with 20% of the heteropolyacid. A calculated number of acid sites is equal to 0.21 mmol/g of catalysts. This value coincides with an adsorption capacity derived from the middle of z-part of calorimetric curve. The sample $ZrO_2–SiO_2$ was obtained by combined participation of hydrates with 15% weight of ZrO_2.

It seems that the heat curves obtained from TD-experiment can serve to estimate the number and the strength of acid sites. The advantage of the novel method becomes especially obvious if one takes into account that a calorimetric experiment takes several weeks, whereas TD-curves can be obtained within 12 h. Stepwise TD-experiment is very useful to conduct a screening to select a limited number of the samples for the detailed calorimetric examination.

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