

Gas adsorption studied by pulse thermal analysis

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Abstract

The potential of pulse thermal analysis (PulseTA[®]) for measuring gas adsorption is studied. PulseTA[®] is based on the injection of a given amount of the adsorptive gas into a carrier gas stream and monitoring of changes in mass, enthalpy and gas composition, occurring as a result of adsorption–desorption phenomena. The method allows to study adsorption at atmospheric pressure and temperatures above 30°C. Continuous monitoring of the concentrations of the pulsed probe molecules in the carrier gas provides the opportunity to investigate the dynamics of physisorption processes. The desorption rate of physisorbed species is shown to depend on carrier gas flow and thickness of the sample bed. An important advantage of PulseTA[®], compared to classical volumetric methods, is that pretreatment of the adsorbent, determination of the kind and amount of preadsorbed gases, as well as temperature programmed desorption can all be carried out in the same experimental set-up. The efficiency and reliability of PulseTA[®] for gas adsorption studies is demonstrated by comparing ammonia adsorption measurements on various solids with corresponding volumetric measurements. Solids used as adsorbents include zeolites ZSM-5 and mordenite, a titania–silica aerogel and a commercial nickel catalyst. Integral heats of adsorption and the amount of chemisorbed ammonia were found to agree well with values reported in the literature. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Pulse thermal analysis; Heat of adsorption; Physisorption; Ammonia chemisorption; ZSM-5 zeolite

1. Introduction

A very frequently used method for characterising heterogeneous catalysts is gas adsorption, which includes the processes involved whenever a gas (adsorptive) is brought into contact with a solid (adsorbent). The determination of the amount of adsorbed species and the various thermal effects combined with the above process provide information on the amount and nature of active surface sites. The selective chemisorption, i.e. formation of a strongly

bound adsorbed monolayer, allows the determination of the metal surface area and metal dispersion of supported catalysts. Dispersion is expressed as the ratio of the total number of metal atoms accessible on the surface to the total number of metal atoms in the sample.

The measurement of gas uptake is carried out by static methods such, as volumetry and gravimetry, as well as with dynamic flow techniques such as gas chromatography or gas thermal conductivity [1]. In volumetry, the catalyst, previously pretreated and evacuated, is contacted by a known quantity of the adsorbate gas. The amount of adsorbed gas is determined by measuring the pressure after the adsorption equilibrium is established. Successive doses of gas

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allow the determination of the adsorption isotherm, i.e. the amount of adsorbed gas versus the equilibrium pressure. Volumetry combined with calorimetry allows the determination of the heat of adsorption, which helps in understanding the nature of the catalytically active sites [2–4]. In the gravimetric method, the amount of adsorbed gas is measured by weighing the sample. Recently, a new, so-called tapered element oscillating microbalance (TEOM) technique has been developed that offers a method for measuring mass changes in a fixed bed reactor while reaction gases are passed through the sample. The mass is determined by monitoring the frequency changes of the tapered oscillating element [5,6]. In contrast to conventional microbalances, none of the probe molecules bypass the sample holder, however, as reported by Rebo et al. [7], the maximum adsorbed amounts determined by TEOM correspond well with values obtained in conventional gravimetric systems.

Dynamic methods of measuring adsorption are faster and more convenient than static methods because they do not require vacuum systems. In the continuous flow technique, the pretreated catalyst is flushed by an inert gas at a temperature sufficient for desorbing all adsorbed species. After cooling to the required temperature, the flow is switched to the adsorbate gas until the downstream detector (generally a thermal conductivity cell) shows a constant gas phase composition. After purging with an inert gas, the adsorptive is once more switched on to investigate possible reversible adsorption.

An interesting modification of the conventional gravimetric method has been recently reported by Brown and Rhodes [8]. A combined TG–DSC instrument was equipped with a pneumatically operated three-way valve, which permitted switching between a pure carrier gas and a blend of 5% reactive gas in the carrier gas. The sample was dosed with the adsorptive in a controlled stepwise fashion by repeatedly switching the composition of the gas phase over the adsorbent.

Proper selection of temperature, when investigating adsorption phenomena, is a prerequisite irrespective of the technique used. The choice of temperature always involves a compromise between high and low. High temperatures reduce the time needed to achieve thermodynamic equilibrium between the adsorbed probe molecules and the active surface sites, whereas low

temperatures lead to a higher coverage of the surface [4]. On the other hand, too low adsorption temperatures do not allow sufficient mobility of physisorbed molecules and thus do not ensure that energetically stronger active sites would be populated before weaker sites begin to fill [9].

Adsorbate molecules should be mobile enough at the adsorption temperature so that each dose of adsorptive can interrogate all of the available adsorption sites. The mobility of the adsorbed molecules can be checked by temperature-programmed desorption (TPD), which has become a very common technique for catalyst characterisation [10]. The information collected from TPD studies contains the type and amount of desorbed species and indicates the temperature range of the desorption process, this being related to the bond energies between adsorbate and the surface.

In common practice, the determination of the amount of adsorbed species, the heat of adsorption and the study of the desorption require different experimental equipments. Here, we demonstrate that pulse thermal analysis [11] makes it possible to study all these phenomena using the same experimental set-up. Results of ammonia adsorption measurements by means of the pulse technique are compared to corresponding data derived from volumetric measurements.

2. Experimental

Experiments were carried out on Netzsch STA 409 thermoanalyser equipped with a pulse device (Netzsch) enabling injection of a certain amount of one or two different pure gases or gaseous mixtures into the carrier gas stream flowing through the system. The amount of injected gas could be changed from 0.01 to 10 ml. Mainly 0.25, 0.50 and 1.0 ml volumes were used. The flow rate was controlled by mass flow controllers, Brooks's model 5850E, based on a thermal mass flow sensing technique. The thermoanalyser was connected by a heated (ca. 200°C) stainless steel capillary to a Balzers quadrupole mass spectrometer QMG 420. The amount of the adsorbents varied from ca. 25–30 mg for DSC measurements (Pt crucible, o.d.=6.8 mm, volume 0.085 ml) to 20–400 mg (alumina crucible, o.d.=16.4 mm, volume

1.0 ml) in the experiments where the influence of the bed thickness on the adsorption process was investigated.

In order to compare the results obtained by the pulse technique with those from a conventional method, volumetric measurements with the same reactants were carried out on Micrometrics ASAP 2010 system. After measuring the first adsorption isotherm at 200°C, the system was evacuated in order to remove the physisorbed ammonia and a second isotherm was measured. The amount of chemisorbed ammonia was calculated from the difference between these isotherms, according to the generally applied procedure [12].

The zeolites, ZSM-5 and mordenite, used as adsorbents, are crystalline aluminosilicates made up of tetrahedrally coordinated Al and Si atoms bonded through bridging oxygens. ZSM-5 has a three-dimensional pore structure with interconnected channels of dimensions 0.53 nm×0.57 nm and 0.55 nm. Mordenite possesses a two-dimensional channel system with dimensions 0.67 nm×0.70 nm and small perpendicular pores with dimensions 0.29 nm×0.57 nm [13]. The zeolites were received in the Na form from Chemie Uetikon AG. After calcination at 500°C they were ion exchanged at 90°C with 1 M NH₄NO₃ and heated in

air to 500°C for 2 h to obtain the H-form. Before the adsorption experiments samples were heated in the thermoanalyser to 500°C to remove the gases adsorbed during handling, then they were cooled down to the measuring temperature and equilibrated until no mass change was detectable. Ammonia (purity 99.98%, PanGas) and helium or argon (purity 99.999%) were used as adsorptive and carrier gases, respectively.

Additionally, silica–titania aerogel [14] and a commercial nickel catalyst (Engelhard Ni-5256 E3/64) were used as adsorbents.

3. Results

Fig. 1 shows the mass changes of the H-ZSM-5 zeolite at 200°C resulting from a series of ammonia pulses, and illustrates the typical features of the pulse technique. Strong, virtually irreversible adsorption (chemisorption) of the injected ammonia occurred during pulses 1–3, pulse 4 resulted in both strong and weak (reversible) adsorption phenomena, whereas during pulses 5 and 6 only weak adsorption (physisorption) took place. The mass gain at steady state, indicated by Θ in Fig. 1, where no further mass

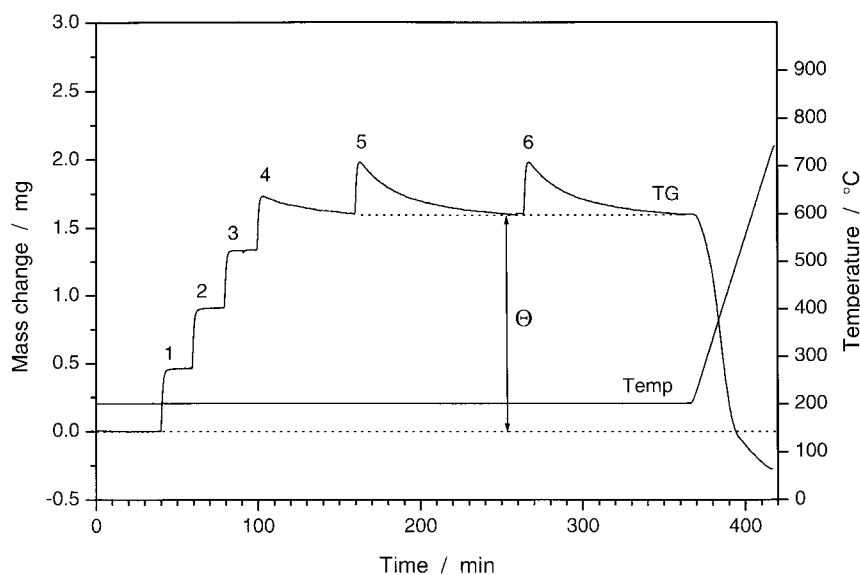


Fig. 1. Mass changes of H-ZSM-5 zeolite after exposure to a series of pulses of 1 ml ammonia at 200°C. The desorption after the sixth pulse was initiated by heating at a rate of 10 K min⁻¹. The amount of chemisorbed ammonia is marked as Θ .

changes were detectable, represents the amount of chemisorbed ammonia. The second part of the experiment depicts the temperature range of the desorption process (TPD). The weight loss at temperatures above 550°C is due to the evolution of residual water from the zeolite, the desorption of ammonia occurs in the range 205–550°C, as confirmed by monitoring the $m/z=15$ mass spectrometric signal.

In the following, experimental parameters which have the greatest influence on the adsorption process under dynamic conditions, were investigated. These parameters embrace: thickness of the adsorbent bed in the crucible, temperature and carrier gas flow.

3.1. Influence of thickness of adsorbent bed

The conditions for mass transport in the experimental set-up used are not optimal for the gas–solid interaction. As in all typical thermoanalysers the gas does not flow through the sample bed, this can influence the kinetics of the adsorption due to diffusional limitations. In order to study the influence of diffusion effects and to check the reproducibility of the method, the sample mass was varied over a range from 10 to 400 mg. Fig. 2A shows that the specific amount of chemisorbed ammonia at 200°C, related to 1 g of adsorbent, is independent of the sample mass, i.e. the bed thickness, provided the same kind of crucible was used (open symbols in Fig. 2A). The use of the DSC crucible with its different geometry (smaller diameter), resulting in a thicker bed and lower amount of zeolite, did not influence the amount of chemisorbed ammonia (solid symbols). However, the thickness of the bed significantly affected the desorption process of physisorbed ammonia. Fig. 2B presents the influence of the sample mass (indicated in mg on the curves) on the desorption of physisorbed ammonia at 200°C. The changes of the adsorption uptake indicate that the thicker the bed, the higher is the time required for total desorption at a constant carrier gas flow.

3.2. Influence of temperature

Fig. 3A shows the dependence of the amount of strongly adsorbed ammonia on temperature for H-ZSM-5, as determined by the PulseTA[®] method (solid circles). For comparison, corresponding results mea-

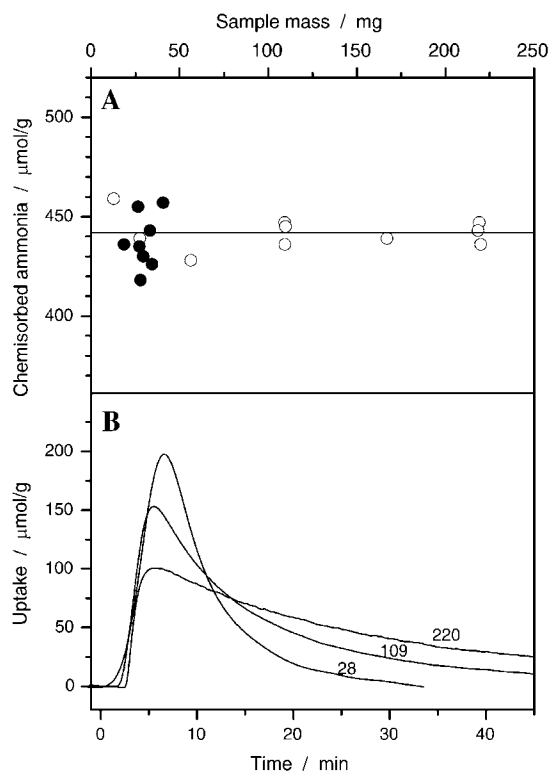


Fig. 2. Influence of the mass of adsorbent (zeolite H-ZSM-5) on: (A) amount of chemisorbed ammonia (solid circles present the results obtained in DSC crucibles) and (B) rate of desorption of physisorbed species. Masses of zeolite are indicated on curves. He flow, 50 ml min^{-1} , heating rate, 10 K min^{-1} .

sured by the volumetric method at 143°C [15,16], 150°C [4,17,18], 200°C [4,17], 250 and 300°C [4,17,18] are also shown (open circles). The influence of temperature on the desorption rate of the physisorbed species is presented in Fig. 3B.

The temperature dependence of the amount of chemisorbed species is very similar for both methods. The observed differences can, at least partly, be attributed to the different origin of the H-ZSM-5 samples and the evacuation procedure applied during the volumetric measurements. In order to compare the results of both methods for the same sample, the amount of ammonia chemisorbed on H-ZSM-5 at 200°C was measured volumetrically. The results are presented in Fig. 4 and indicated (open diamond) in Fig. 3A. This experiment demonstrates that for the same sample the difference between the results

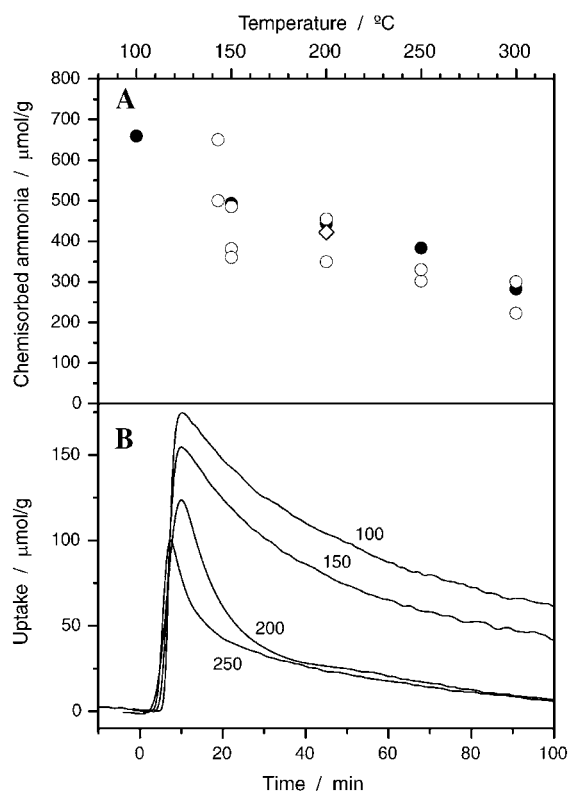


Fig. 3. Influence of temperature on: (A) amount of chemisorbed ammonia, solid circles indicate results obtained by PulseTA[®]; open circles represent volumetric results reported in the literature. Open diamond indicates our volumetric measurement and (B) rate of desorption of physisorbed species, temperatures in centigrades are marked on curves. Helium flow, 50 ml min⁻¹; heating rate, 10 K min⁻¹; sample mass, 113.5 mg.

obtained by the two methods is below 5%. In volumetry, the evacuation of the system, necessary for the determination of the physisorbed species, can lead to removal of a small amount of chemisorbed ammonia. This behaviour is illustrated by the results presented in Table 1 which compares the amount of adsorbed ammonia on different adsorbents measured with both techniques.

The difference between chemisorbed amounts of ammonia determined by PulseTA[®] and volumetry, is especially apparent in the case where the adsorption strength between adsorbate and adsorbent is weak, resulting in desorption at lower temperatures, as observed with the titania–silica aerogel. Fig. 5 com-

Table 1
Ammonia adsorption on various catalyst materials^a

Samples	T_{ads} ($^{\circ}\text{C}$)	Θ_{vol} ($\mu\text{mol g}^{-1}$)	Θ_{grav} ($\mu\text{mol g}^{-1}$)
H-ZSM-5	200	422	442
Silica–titania aerogel	50	689	1123
Ni-5256 E3/64	50	449	528
H-mordenite	200	–	1830

^a Uptakes (coverages) determined by conventional volumetric method (Θ_{vol}) and PulseTA[®] gravimetry (Θ_{grav}).

pares the TPD curves, represented by the mass spectrometric signals of $m/z=15$, for H-ZSM-5 and the aerogel. This particular m/z ratio for ammonia has been chosen, instead of the stronger $m/z=17$ signal, to exclude the contribution resulting from the fragmentation of water, especially important at higher temperatures.

3.3. Influence of carrier gas flow

During adsorption measurements carried out with the PulseTA[®] technique, the contact between adsorptive and adsorbent occurs only during a relatively short time after the injection of the adsorptive into the carrier gas stream. A change of carrier gas flow significantly influences the time in which the injected species are in contact with the solid and the rate of desorption of physisorbed species. In order to illustrate this behaviour, the carrier gas flow was changed between 20 and 100 ml min⁻¹, and 1 ml pulses of ammonia were injected at 200 and 300 $^{\circ}\text{C}$ into helium. The resulting $m/z=15$ signals, measured for an empty reactor, are shown in Fig. 6A. Fig. 6B presents the dependence of the desorption of physisorbed ammonia at 200 $^{\circ}\text{C}$ (compare to the sixth pulse in Fig. 1) on the carrier gas flow. The dashed line represents the change of ammonia concentration in an empty reactor for a flow of 100 ml min⁻¹ using the same time-scale as for the desorption curves.

The relationship between the integral intensity of the mass spectrometric signal $m/z=15$ and the characteristic time [19], defined as the ratio of injected volume of adsorptive to carrier gas flow rate, is shown in the inset in Fig. 6A for experiments at 200 $^{\circ}\text{C}$ (solid circles) and 300 $^{\circ}\text{C}$ (open circles).

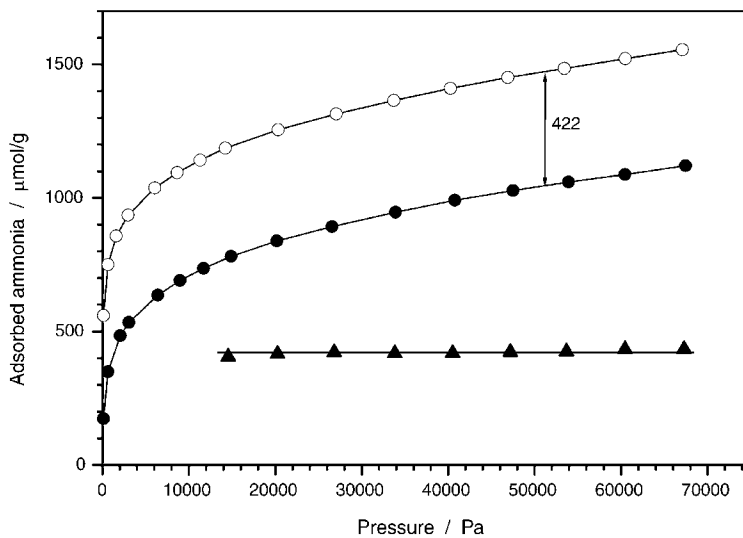


Fig. 4. Volumetric measurement of amount of ammonia chemisorbed on H-ZSM-5 zeolite at 200°C. Open circles represent the first adsorption isotherm, the second isotherm, measured after evacuation, is given by solid circles. The triangles show the difference between both isotherms.

3.4. Determination of the adsorption heat

The goal of the final set of experiments was to check if it is possible to determine the thermal effects that occur during adsorption, in relation to the amount of chemisorbed adsorptive, simultaneously measured by thermogravimetry. The difficulties in determination of the thermal effects resulting from the interaction of an adsorptive with an adsorbent lie in the accurate measurement of the heat evolved and the amount adsorbed. The results presented above indicate that the determination of the amount of chemisorbed species is possible using a standard thermobalance when it is equipped with a pulse device that enables the injection of a known amount of adsorptive into the carrier gas stream. The procedure allows the quantification of both chemi- and physisorbed species. Moreover, it is also possible to investigate the desorption process.

The experimental set-up used for determining the amount of adsorbed species allowed measurements without significant diffusional constraints. The thickness of the adsorbent bed was decreased by spreading the solid in a thin layer in a large alumina crucible. Furthermore, helium was used as a carrier gas in order to increase the rate of diffusion during adsorption and

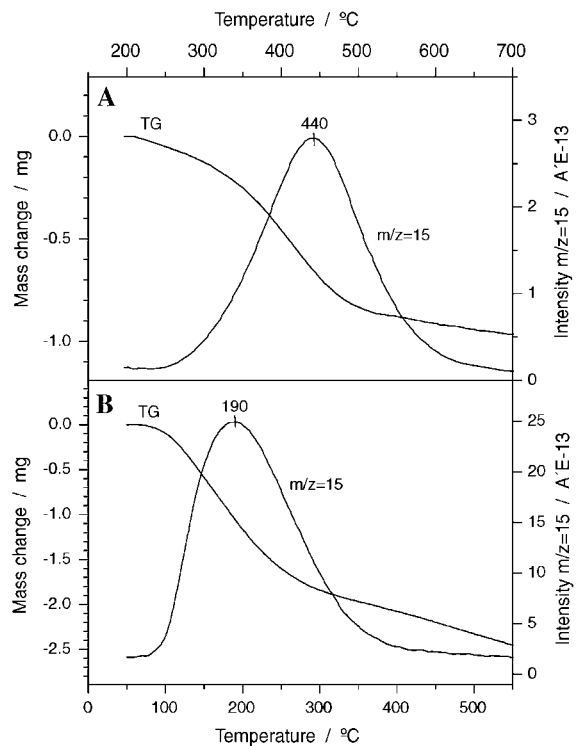


Fig. 5. Desorption of chemisorbed ammonia ($m/z=15$) from: (A) H-ZSM-5 zeolite and (B) silica-titania aerogel. Heating rate, 10 K min⁻¹; helium flow, 50 ml min⁻¹.

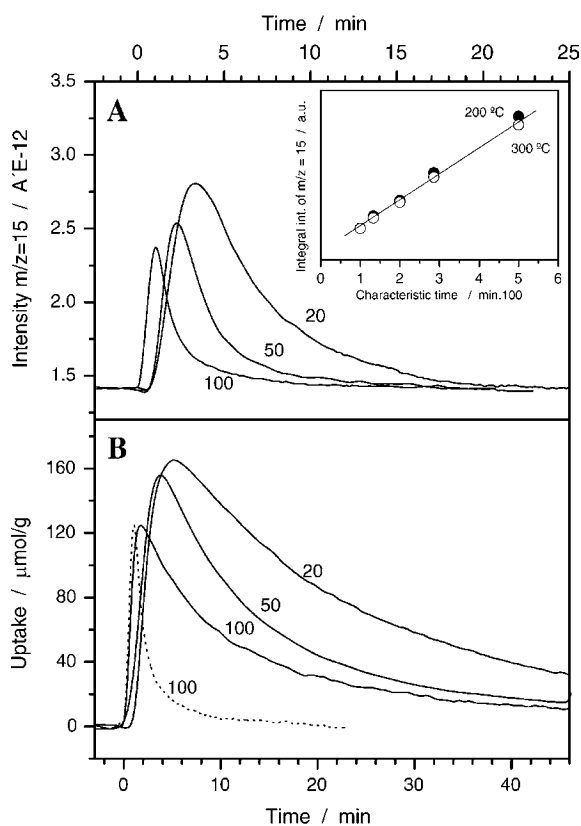


Fig. 6. Influence of carrier gas flow (in ml min^{-1} indicated on curves) on: (A) response signal ($m/z=15$) of 1 ml pulse of injected ammonia in an empty reactor and (B) rate of desorption of physisorbed ammonia at 200°C . The dashed line represents the change of the ammonia concentration for a flow of 100 ml min^{-1} using the same time-scale as for the desorption curves. The inset in Fig. 6A presents the dependence of the integral intensity of $m/z=15$ signal on the characteristic time (defined in text).

desorption of the physisorbed species. Albeit favourable for mass transfer, these conditions were not optimal for determining thermal effects. Hence, it was necessary to check if the change in experimental parameters, optimal for DSC measurements, were suitable for measuring the heat of adsorption, in relation to the amount of adsorbed species.

The DSC measurements were carried out in a platinum crucible with a sample mass of 25–30 mg. Helium, used for the TG measurements, was replaced by argon. Under normal conditions the thermal conductivity of Ar is 0.0176 , and for He it is

$0.1511 \text{ W m}^{-1} \text{ K}^{-1}$. Helium is not recommended for DSC measurements because it lowers the intensity of DSC signals, due to its high thermal conductivity. Preliminary experiments, with indium as a standard, have shown that the integral intensity of the melting peak (measured as area below the baseline) is 2.6 times smaller for helium than for argon. On the other hand, the use of argon as a carrier gas increases the buoyancy effect and reduces the rate of diffusion due to its higher density and lower diffusion coefficient. The normal densities of He and Ar and the diffusion coefficients of ammonia in He and Ar at 200°C are: 0.1785 g l^{-1} ; 1.7837 g l^{-1} ; $9.27 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ and $2.45 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, respectively.

Quantitative calibration of the DSC signals was carried out by the standard procedure of measuring the enthalpy changes of a synthetic sapphire cylinder (NBS Standard Reference Material 720). Typical thermal effects recorded during the adsorption of ammonia are presented in Fig. 7. The first pulse of NH_3 leads to strongly bound (chemisorbed) ammonia only, whereas the third one is characteristic for weakly bound (physisorbed) ammonia. The physisorbed ammonia desorbs completely (note the endothermic effect of the desorption) after ca. 25–30 min. During the second pulse, both processes chemi- and physisorption are discernible. By decreasing the amount of injected gas it was possible to follow the interdependence between the adsorption heat and the uptake (coverage). Fig. 8 depicts the adsorption of ammonia on H-ZSM-5 (A) and H-mordenite (B). The results listed in Table 2 indicate that for both zeolites the adsorption heat is only weakly dependent on the

Table 2

Ammonia adsorption on zeolites, H-ZSM-5 and H-mordenite, at 200°C^a

H-ZSM-5 ^b		H-mordenite ^c	
Coverage Θ ($\mu\text{mol g}^{-1}$)	ΔH (kJ mol^{-1})	Coverage Θ ($\mu\text{mol g}^{-1}$)	ΔH (kJ mol^{-1})
0–187	138.2	0–484	141.4
187–328	136.3	484–916	141.2
328–436	135.6	916–1277	135.9
		1277–1615	137.2

^a Heats of adsorption (kJ mol^{-1}) at different coverages.

^b Si/Al ratio 25.

^c Si/Al ratio 8.

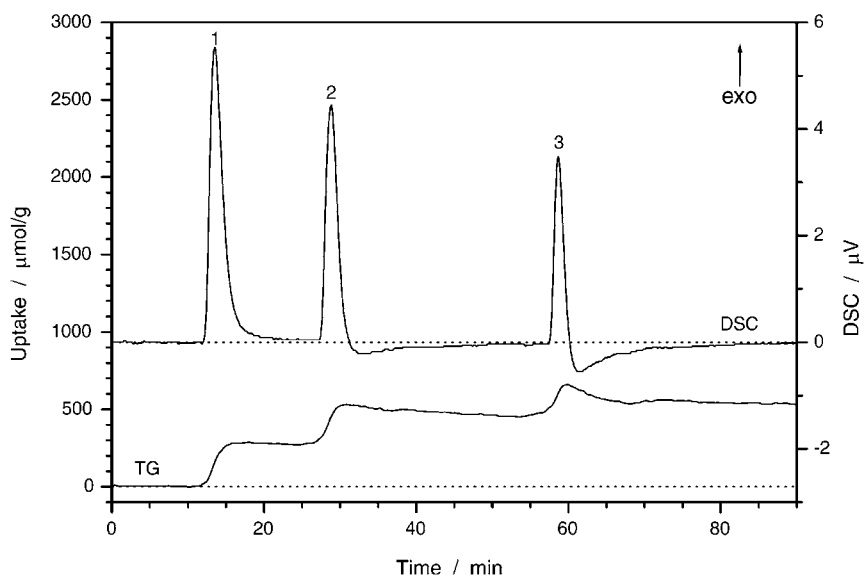


Fig. 7. DSC and TG signals occurring during adsorption of ammonia at 50°C on nickel catalyst. Argon flow, 50 ml min⁻¹, ammonia pulse, 1.0 ml, mass of adsorbent, 31.6 mg.

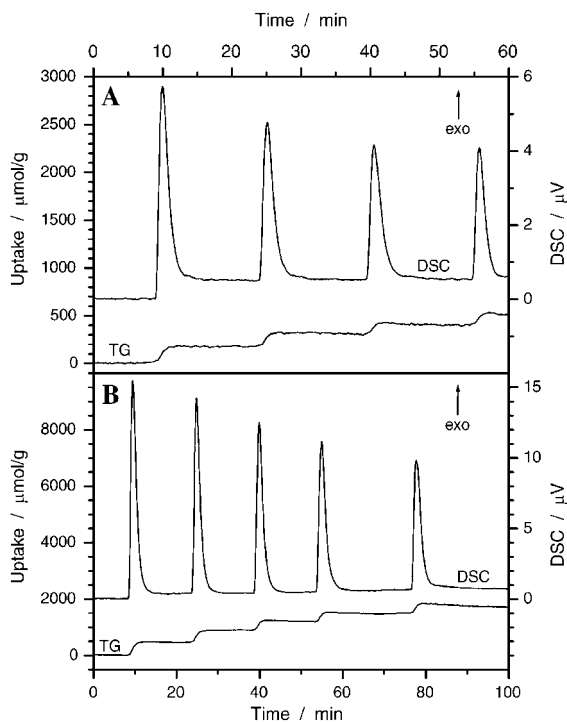


Fig. 8. DSC and TG signals occurring during adsorption of ammonia at 200°C on zeolites: (A) H-ZSM-5, (B) H-mordenite. Adsorption heats determined for different coverage ranges are listed in Table 2.

coverage, as has been reported in the literature (see [20]).

4. Discussion

The method for determining the amount of adsorbed probe molecules used in this study differs from the commonly used volumetric and gravimetric methods. The main difference are:

- Typical thermoanalytical experiments (TG, DSC) focus on the desorption processes only, the adsorbent is usually exposed to an atmosphere containing the probe molecules beforehand [21–24]. Pulse thermal analysis allows to study both, adsorption and desorption processes in the same experimental set-up.
- Contrary to the normal volumetric procedure, the adsorption process is investigated under atmospheric pressure.
- The contact between solid and adsorptive is limited to the short duration of the pulse.

Despite the above differences, the results on ammonia adsorption of this study agree well with those reported in the literature. Both the amount of chemisorbed ammonia and the heat of adsorption agree well

with the values reported for H-ZSM-5 and H-mordenite having similar Si/Al ratios, i.e. 25 and 8, respectively. The amount of chemisorbed ammonia at 200°C, as determined by PulseTA[®], is 442 $\mu\text{mol g}^{-1}$, whereas the values reported in the literature vary from 384 [4] through 420 [25] to 450 $\mu\text{mol g}^{-1}$ [2]. The heats of ammonia adsorption, determined for the two zeolites, also agree with those reported in the literature. For both samples, the differential heats of adsorption are constant up to a coverage of one molecule of ammonia per aluminium site [26], therefore the integral heats derived here can easily be compared with the reported differential values. The adsorption heat found in this study for H-ZSM-5 is 138 kJ mol^{-1} for coverages 0–187 $\mu\text{mol g}^{-1}$, and 135.6 kJ mol^{-1} for coverages 328–436 $\mu\text{mol g}^{-1}$. Parillo et al. [9] report 145 kJ mol^{-1} (0–400 $\mu\text{mol g}^{-1}$) and 150 kJ mol^{-1} [20] (between zero and one ammonia molecule per aluminium site), Auroux [4] found 140 kJ mol^{-1} in the same range and Cardonna-Martinez and Dumesic [2] 143 kJ mol^{-1} . For H-mordenite, our value,

141 kJ mol^{-1} , for the coverage 0–484 $\mu\text{mol g}^{-1}$ is also comparable to the heats reported: 132–146 kJ mol^{-1} [2], and 160 kJ mol^{-1} [20].

Unfavourable mass transfer conditions, induced by the fact that carrier gas does not flow through the adsorbent bed in the applied thermoanalytical system, were not a severe limitation for the adsorption measurements. This emerges from the present study and a comparison of conventional gravimetric results (carrier gas not flowing through the bed) with data reported in the studies using the TEOM method (gases pass through the bed). The similarity of the results [7] confirms that the final state of chemisorption is unaffected by the nonoptimal contact between gas and solid.

The total amount of chemisorbed gas per unit mass of adsorbent does not depend on the pulse volume or the amount of solid sample used (see Fig. 2A). These parameters mainly influence the physisorption process, as illustrated in Fig. 9. Complete coverage of the surface can be reached between one (Fig. 9B) and 13

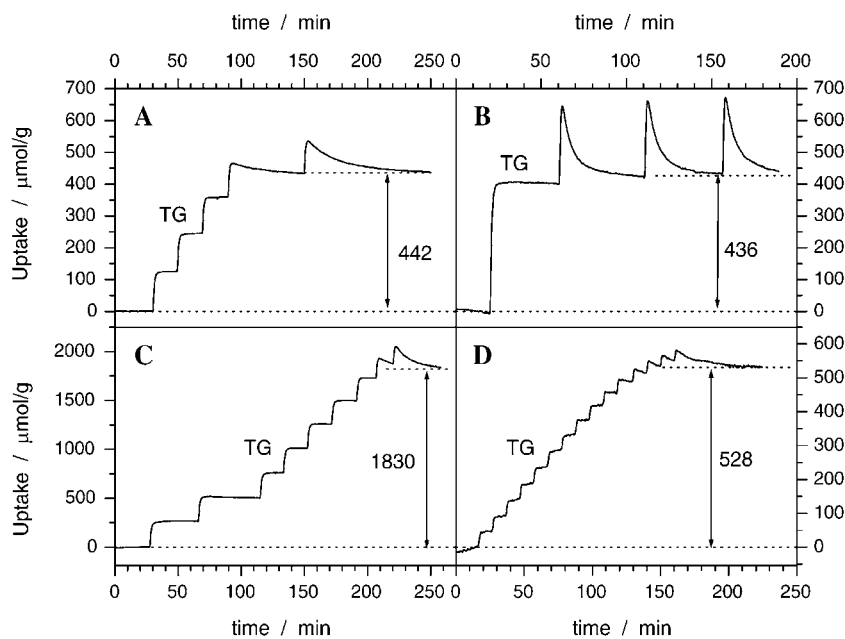


Fig. 9. Influence of experimental parameters (temperature, kind of carrier gas and its flow, amount of injected adsorptive, mass of adsorbent) on the shape of thermogravimetric curves resulting from chemisorption of ammonia on various catalyst materials. (A) H-ZSM-5, 200°C, He, 50 ml min^{-1} , 1 ml, 219.9 mg; (B) H-ZSM-5, 200°C, He, 50 ml min^{-1} , 1 ml, 56.3 mg; (C) H-mordenite, 200°C, He, 50 ml min^{-1} , 1 ml, 109.6 mg and (D) Ni-5256 E3/64, 50°C, Ar, 100 ml min^{-1} , 0.5 ml, 135.1 mg. Comparison of (A) and (B) illustrates the effect of the sample mass. (C) and (D) show that proper adjustment of the ratio of pulse volume to the total uptake (coverage) allows more detailed recording of the adsorption process.

pulses (Fig. 9D), depending on the ratio between the amount of injected probe molecules and the mass of the solid. In the second case it is possible to measure the differential heats of adsorption if the evolved heat during one pulse is greater than ca. 150–200 mJ. The thermal effects presented in Fig. 8A are between 760 and 530 mJ for the first and third pulses, respectively.

Even at the relatively high temperature of 200°C, a fraction of the probe molecules in the last few pulses before saturation are physisorbed. For a particular adsorptive the rate of physisorption depends mainly on the thickness of the adsorbent bed (diffusion limitation) and the flow and kind of carrier gas. The rate of desorption decreases with increasing thickness of the adsorbent layer, and increases with higher flow rate of the carrier gas. However, even for small masses and high flows, the time of desorption of the physisorbed species is in the order of 30–40 min. The 6 min periods of desorption, as applied by Brown and Rhodes [8], would be much too short to fully remove all physisorbed species in our experiments.

Monitoring physisorption *in situ* seems to be a necessary prerequisite for a better understanding of the observed adsorption phenomena. The amount of adsorbed species and the heat of adsorption result from different contributions of chemi- and physisorption which becomes apparent with the last few pulses before saturation. The opportunity to distinguish between physisorption and chemisorption makes it possible to individually assign mass and thermal effects to these phenomena, thus avoiding misinterpretations.

The total characterisation of the interaction between adsorptive and adsorbent requires the pretreatment of the solid at an optimal temperature, proper selection of the temperature of adsorption, and the determination of the strength of the adsorbed species by temperature programmed desorption. The PulseTA[®] technique makes it possible to carry out all these procedures in the same experimental set-up, a commercial thermoanalyser.

Finally is worthy to mention that the described method has been successfully applied in our laboratory for the study of ammonia adsorption on various catalyst materials, including mesoporous titania–silica aerogels [14], cobalt [27] and nickel [28] catalysts, and for the study of CO, CO₂ and O₂ adsorption on Au/TiO₂ and Au/ZrO₂ [29].

5. Conclusions

The PulseTA[®] technique provides the opportunity to study several phenomena occurring during adsorption in a conventional thermoanalyser. Processes which can be monitored include pre-treatment of the adsorbent, adsorption and desorption. Characteristic features of PulseTA[®] for gas adsorption measurements are:

- Monitoring of the mass change and the kind and amount of evolved species during pre-treatment allows the determination of the optimal temperature needed to remove all pre-adsorbed species.
- Monitoring of the concentration of the adsorptive in the system and the mass changes, during and after injection of the probe molecules, provides the opportunity to study both chemi- and physisorption.
- The relationship between the measured heats of adsorption and changes in mass enables the correct interpretation of thermal effects involved in the adsorption process.
- The possibility of carrying out temperature programmed desorption just after completion of the adsorption process prevents the introduction of artefacts caused by the contact of the sample with the surrounding atmosphere.

The reliability of the method has been demonstrated by studying adsorption of ammonia on zeolites, H-ZSM-5 and H-mordenite. Measured coverages and heats of adsorption agree well with corresponding data reported in the literature.

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