ELSEVIER

Thermochimica Acta 379 (2001) 123–130

thermochimica acta

www.elsevier.com/locate/tca

Determination of surface acidity of powdered porous materials based on ammonia chemisorption: comparison of flow-microcalorimetry with batch volumetric method and temperature-programmed desorption

J. Zajac*, R. Dutartre, D.J. Jones, J. Rozière

Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, Université Montpellier II, UMR 5072, C.C. 015, Place E. Bataillon, 34095 Montpellier Cedex 5, France

Abstract

Flow-calorimetric measurements of the transfer of matter and thermal effects accompanying one adsorption–desorption cycle of pure ammonia in helium carrier gas at 373 K have been carried out on powdered porous materials belonging to three series: acid-treated clays (K5, K30, KSF), HY zeolites with varying Si:Al ratio (HY30, HY20, HY9, HY6) and surfactant-templated aluminosilicates (MSA20, MSA10, MSA5). These data were subsequently used to determine the number and mean strength of surface acid sites. The same experiments were performed on three selected samples pre-saturated with water vapour the end of the clause. The non-negligible influence of vicinal water on the results of surface acidity tests was demonstrated. The comparison of the flow-microcalorimetry (FMC) method with two-cycle ammonia adsorption and thermoprogrammed ammonia desorption revealed some differences in the number of surface acid sites which could be ascribed to various experimental conditions used during desorption or pre-treatment stages in each of these methods.

Keywords: Surface acidity; Ammonia chemisorption; Flow-microcalorimetry; Experimental conditions

1. Introduction

It is a common premise that the evaluation of surface acidity is of great importance if the catalytic action of solid acid catalysts is to be understood. Spectroscopic, microcalorimetric and volumetric methods based on chemisorption of basic probe molecules, like gaseous ammonia, at high temperatures have already been shown to be very useful for the assessment of the number and strength of active sites on a large class of solid supports [1–13]. Nevertheless, classical acidity tests are usually carried out under ideal experimental conditions (e.g. vacuum pre-treatment of solids, adsorption from a single gas phase) which do not correspond to those encountered in real applications of adsorbents and catalysts. In particular, the catalytic performance of many materials may be to a great extent modified in the presence of an additional component or impurities having high affinity for surface acid sites (e.g. water vapour). There is, thus, a question whether 'standardised' surface acidity could be used to predict catalytic performance under operational conditions.

* Corresponding author. Tel.: +33-4-67-14-33-40; fax: +33-4-67-14-33-04.
E-mail address: zajac@univ-montp2.fr (J. Zajac).

0040-6031/01/$ – see front matter
PII: S0040-6031(01)00611-6

Recently, a flow-microcalorimetric method has been proposed for the determination of surface acidity under conditions which reproduce, as far as possible, a working environment [14–17]. A flow-through system permits a single gas or a gas mixture to enter the cell, interact with the solid sample placed inside the cell, and exit the chamber for further analysis downstream. Microscal's flow-microcalorimeter is equipped with a computer-operated, two-channel data acquisition and processing system, allowing precise levels of heat and mass-transfer to be measured in one experiment. This methodology provides data which can be used to quantify and characterize types of surface sites, study reversibility of interactions, and deduce the enthalpic/entropic components of interactions. The rates of heat evolution or absorption occurring during interactions at the solid–gas interface, combined with the rates of changes of mass-transfer of mixture components can be also evaluated, thereby providing important information on the kinetics of these processes.

The objective of the current work was to check the adequacy of the flow-microcalorimetry (FMC) technique for the assessment of the surface acidity of solid materials. A variety of powdered porous samples were tested for surface acidity with the use of FMC and two other techniques, viz. a volumetric adsorption method and temperature-programmed desorption. The numbers of surface acid sites inferred from the different methods under conditions of non-competitve adsorption of NH_3 at 373 K were compared and the reasons for the observed differences were considered.

2. Experimental

2.1. Materials

Three acid-treated clays based on calcium montmorillonite, K5, K30 and KSF, were graciously supplied by Süd-Chemie AG (Germany). Zeolites Y were kindly supplied in the H^+ form by the Laboratoire des Matériaux Catalytiques (UMR CNRS 5618, Montpellier). These samples are referred to as HY*x*, where *x* is the mole Si:Al ratio. The clays and zeolites were used in the as-received form. Mesoporous aluminosilicates with different Si and Al contents were prepared in the H^+ form in the laboratory with the use of a surfactant-assisted sol–gel method [18]. These materials are designated MSA*x*, where *x* represents the mole Si:Al ratio.

Table 1
Various porous materials used in the present study and some of their characteristics

Solid material	BET specific surface area ($m^2\ g^{-1}$)	Si:Al ratio (mole)
Acid-treated clays		
K5	200	7
K30	330	16
KSF	20	
Zeolites		
HY30	772	30
HY20	738	20
HY9	716	9
HY6	680	6
Mesoporous aluminosilicates		
MSA20	786	20
MSA10	650	10
MSA5	756	5

For each solid sample, the specific surface area was determined from N_2 gas adsorption measurements at 77 K using BET analysis taking the surface area per nitrogen molecule as 0.162 nm^2. The Si and Al contents were either supplied (clays, zeolites) or confirmed by elemental analysis (MSA*x*). These characteristics of the samples used are collected in Table 1.

Gaseous ammonia, nitrogen and helium of ultra high purity were purchased from Air Liquide (France).

2.2. Methods

The number of surface acid sites was evaluated by two-cycle adsorption (TCA) of ammonia from the gas phase [8,16]. The amounts of NH_3 adsorbed at different partial pressures in the equilibrium bulk phase were measured using a Micromeritics ASAP 2010 Chemi System apparatus. Prior to adsorption measurements, the sample (about 200 mg) was outgassed at 773 K in vacuum for 3 h. Then it was cooled down to 373 K in a flow of helium. Successive ammonia doses were sent onto the sample until a final equilibrium pressure of about 40 Torr was reached. The equilibrium pressure was measured after each adsorption step and the amount of NH_3 adsorbed was calculated. At the end of the first adsorption cycle, the sample was outgassed under vacuum at 373 K for 30 min and a

second adsorption cycle was then performed at the same temperature.

Determination of surface acidity was carried out by thermoprogrammed desorption (TPD) of ammonia. Samples were pre-treated in a nitrogen flow of 30 ml min^{-1} at 723 K for 4 h and then saturated in an ammonia flow of 30 ml min^{-1} at 373 K. To completely remove the NH_3 molecules physisorbed on the surface, nitrogen carrier gas was subsequently flowed through the sample at the rate of 30 ml min^{-1} and 373 K for 4 h. Ammonia desorption between 373 and 923 K (heating rate 10°C min^{-1}) was analysed using an on-line conductivity cell with a HCl solution for trapping the effluent gases.

A flow-calorimetric study of the adsorption of gaseous ammonia at 373 K was carried out with the use of a 4Vms Microscal flow-microcalorimeter [15] to evaluate the strength and the number of surface acid sites. The continuous flow method was used as operation procedure. Prior to measurement, the solid sample was placed in the calorimetric cell, outgassed at 373 K overnight, and subsequently flushed with a helium flow of 2 ml min^{-1} for 4 h. The flow of carrier gas was then stopped and replaced by a stream of pure ammonia flowing at the same rate. The progress of adsorption was continuously monitored by the evolution of heat measured by thermistors sensing temperature changes in the adsorbent bed and simultaneously adsorbate transfer from the gas phase to the solid–gas interface was monitored by measuring composition changes in the effluent leaving the adsorbent and passing through a TC detector. Adsorption proceeded until the surface had taken up sufficient adsorbate to come to equilibrium with the pure ammonia. The corresponding changes in the thermal conductivity of the effluent were recorded as a gradually increasing set of values until a steady state was reached. Heat evolution then ceased and the recorder returned to its base-line. Desorption of the physically adsorbed NH_3 molecules was performed by interchanging the supply of ammonia with the original flow of helium carrier gas at the same temperature of 373 K. Calibration of the areas under the thermal peaks was carried out by dissipating a known amount of energy in the cell under the same flowing conditions (Joule heating using a calibration probe incorporated into the outlet tube) and integrating the related exothermic peak. The TC detector calibration factor was determined from the injection of 500 μl of pure ammonia into the stream of helium carrier gas percolating through the detector.

3. Results and discussion

3.1. Two-cycle adsorption and thermoprogrammed desorption of ammonia

Fig. 1 shows the example of NH_3 adsorption isotherms obtained in two successive cycles for a selected sample, K30. The total amount adsorbed increases quickly with increasing bulk pressure in the region of very low-pressure values. This indicates the presence of very active surface sites, which give strong acid–base interactions with ammonia molecules. For higher-pressure values, the rate of increasing adsorption diminishes and the isotherm becomes quasi-linear. This linearity may be ascribed to physical adsorption on some other surface sites. A linear adsorption part can be also distinguished in the second-cycle isotherm. The slopes of both linear segments are almost identical, which means that further adsorption of ammonia molecules progresses in much the same way. The two straight lines are suitably extrapolated to zero pressure. The Γ-difference for points at which the curves reach zero pressure determines the maximum irreversible adsorption of NH_3

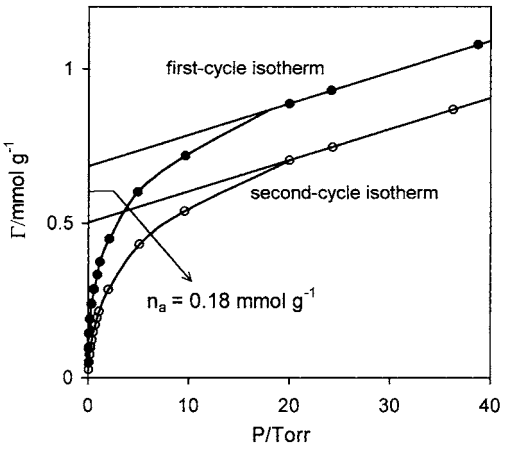

Fig. 1. Two-cycle adsorption of gaseous ammonia onto acid-treated clay K30 at 373 K. The linear parts of the two adsorption isotherms extrapolated to zero equilibrium pressure are used to determine the number of surface acid sites, n_a.

Table 2
Surface acidity parameters, as determined from two-cycle adsorption of ammonia and thermoprogrammed desorption of ammonia[a]

Sample	Two-cycle NH_3 adsorption n_a (mmole g^{-1})	Thermoprogrammed NH_3 desorption	
		n_a (mmole g^{-1})	T_{max} (K)
K5	0.23	0.25	576
K30	0.18	0.25	531
KSF	1.10	–	–
HY30	0.16	0.16	644
HY20	0.24	0.30	661
HY9	0.64	0.75	724
HY6	0.48	0.82	527, 686
MSA20	0.22	0.47	520
MSA10	0.39	0.75	509
MSA5	0.44	0.79	522

[a] Number of surface acid sites — n_a; temperature at which the TPD distribution function attains its maximum value — T_{max}.

on the K30 surface and provides the total number of acid sites in this sample.

The numbers of surface acid sites, determined with the use of the above procedure for all the solid materials studied, are given in Table 2.

Fig. 2 presents the results of thermoprogrammed ammonia desorption from the surface of MSA5. Changes in the composition of the effluent from the TPD reactor may be seen in the figure above, in which the conductivity, κ, of the HCl solution in the conductivity cell, neutralised successively by the desorbed ammonia, is plotted as a function of the temperature. The amount of chemisorbed NH_3 molecules that have been removed from the solid surface between 373 and 923 K is proportional to the total decrease, $\Delta\kappa$, in the conductivity of the reference HCl solution. Therefore, the value of $\Delta\kappa$ multiplied by an appropriate scaling factor, f_κ, gives the number of surface acid sites on the solid sample. The proportionality constant f_κ depends on the initial acid conductivity, κ_1, the initial acid concentration, $[HCl]_1$, and its volume, V, in the conductivity cell. The generalised plot of the first derivative of κ with respect to temperature is shown in the figure below. Notice that, in the TPD method, thermal stability of the adsorbed ammonia species may be related to the strength of ammonia bonding. For example, the temperature T_{max}, at which the plot of $d\kappa/dT$ against T reaches its

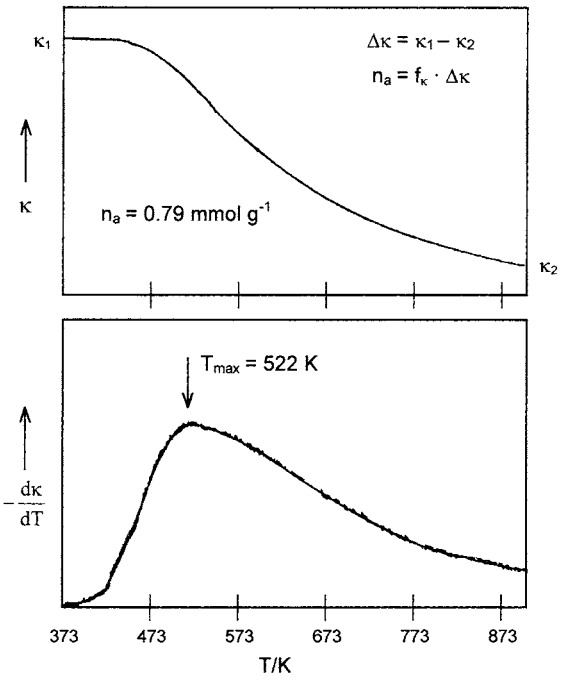

Fig. 2. Thermoprogrammed desorption of ammonia from the surface of aluminosilicate sample MSA5: generalised plot of values of the conductivity, κ, for the HCl solution in the conductivity cell, neutralised successively by the effluent ammonia from the TPD reactor, as a function of the temperature, T, (the curve above) and the first derivative of κ with respect to T as a function of the temperature (the curve below).

maximum value, provides information about the most probable energy of bonding between the basic ammonia molecules and the surface acid sites. Temperature is, thus, regarded as the direct measure of the strength of the acid sites exposed on the solid surface. Nevertheless, this correlation should be treated with caution. Among other parameters, the different diffusion rates of ammonia in porous solids can affect the results. Therefore, the correlation between the temperature and the site strength is probably adequate only for solid samples of the same kind.

The numbers of surface acid sites and the values of T_{max}, as determined by TPD of ammonia, are included in Table 2. For zeolite HY6, a bimodal distribution function has been obtained and, consequently, two values of T_{max} are reported in the table. In the case of KSF, the TPD results are missing. A sudden increase in the solution conductivity, κ, has been observed on heating the clay between 723 and 923 K. This effect

can be likely attributed to removal of mineral acid from the sample. According to the manufacturer, this catalyst contains indeed a significant amount of free acid introduced during treatment of the original montmorillonite. This leads to irreproducibility in TPD measurements.

3.2. Flow adsorption microcalorimetry

Fig. 3 shows a typical trace for a two-channel run obtained in one adsorption–desorption cycle of pure ammonia in helium carrier gas onto acid-treated clay KSF at 373 K. The thermal profiles for adsorption and desorption can be directly integrated and compared to the thermal calibration peak, resulting in the integral enthalpy change on adsorption, $\Delta_{ads}H$, and on desorption, $\Delta_{des}H$. The downstream detector provides a plot of effluent composition, the profile of this curve being influenced by the amount of ammonia molecules adsorbed by the adsorbent. These data should be related to composition changes obtained in a 'blank' experiment with the use of a 'non-adsorbing' solid (80 μm glass balls) through which pure ammonia and helium carrier gas have been passed at the same flow rate and temperature as those for the adsorbing sample. The two sets of data can be matched and presented in the form of net mass-transfer for adsorption and desorption, as shown in Fig. 3. The areas of the segments, resulting from the subtraction of the peaks obtained on adsorbing and non-adsorbing solids, provide a direct measure of the quantity of ammonia which fails to emerge, due to its adsorption by the adsorbent held in the calorimetric cell.

Ammonia adsorption at 373 K is partly reversible, because the amount of NH_3 removed by helium from the solid surface during desorption is less than the amount adsorbed in the adsorption cycle. The difference between these two values is equal to the quantity of ammonia irreversibly adsorbed, Γ_{IR}. The integral enthalpy of irreversible adsorption, $\Delta_{ads}H_{IR}$, can be calculated in the same way, since the enthalpy of desorption taken with the opposite sign is considered as the integral enthalpy of reversible adsorption. Ultimately, quantities Γ_{IR} and $\Delta_{ads}H_{IR}$ provide direct access to the molar enthalpy of irreversible adsorption, $\Delta_{ads}h_{IR}$. The value of Γ_{IR} is identified with the number of surface acid sites, whereas that of $\Delta_{ads}h_{IR}$ is the measure of the mean strength of acid sites. It should be emphasised that, if surface sites on a given solid are heterogeneous, their mean strength will be lower than the maximum value usually reported in [6–8].

Table 3 summarizes the foregoing discussion regarding the mass-transfer data and the related thermal effects for one adsorption–desorption cycle on various porous materials, as well as resultant parameters of irreversible NH_3 adsorption.

The molar enthalpy of irreversible ammonia adsorption, $\Delta_{ads}h_{IR}$, as calculated based on the results

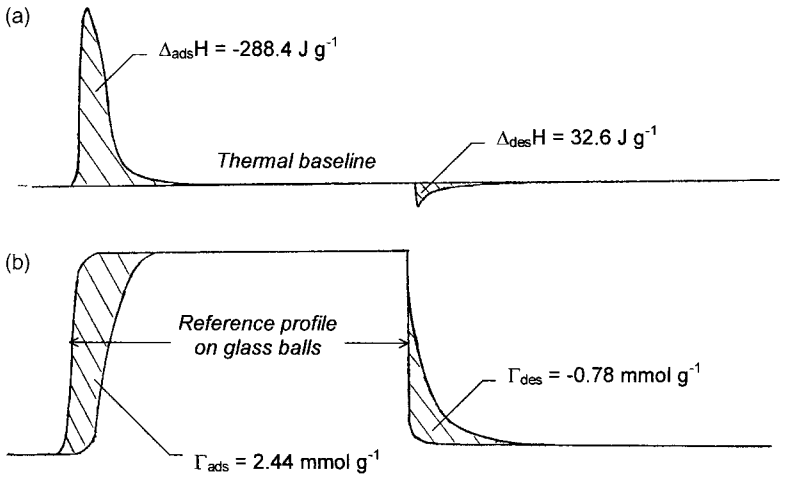

Fig. 3. Two-channel output data showing one adsorption–desorption cycle of pure ammonia in helium carrier gas onto acid-treated clay KSF at 373 K recorded in the continuous flow-calorimetric experiment: (a) thermal profile, (b) mass-transfer profile corresponding to gas percolation through the adsorbent superimposed on the reference profile for the percolation through a non-adsorbing solid.

Table 3
Amounts of NH_3 exchanged between the solid–gas interface and the gas phase percolating through the adsorbent, together with the related integral enthalpy changes, corresponding to a flow-microcalorimetry adsorption–desorption cycle of pure ammonia in helium carrier gas at 373 K (flow rate of 2 ml min^{-1})[a]

Sample	Adsorption cycle		Desorption cycle		Irreversible adsorption	
	Γ (mmole g^{-1})	ΔH (J g^{-1})	Γ (mmole g^{-1})	ΔH (J g^{-1})	Γ (mmole g^{-1})	Δh (kJ $mole^{-1}$)
K5	1.72	−106.4	−1.47	55.9	0.25	−202
K30	1.63	−101.1	−1.29	49.2	0.34	−153
KSF	2.44	−288.4	−0.78	32.6	1.66	−154
HY30	2.33	−113.3	−2.14	80.9	0.19	−171
HY20	1.34	−75.4	−1.05	44.1	0.29	−108
HY9	2.02	−112.4	−1.45	56.0	0.57	−99
HY6	1.84	−89.0	−1.25	39.9	0.59	−83
MSA20	2.01	−125.5	−1.60	52.1	0.41	−179
MSA10	2.19	−146.0	−1.55	51.6	0.64	−148
MSA5	2.29	−163.6	−1.59	52.9	0.70	−158

[a] These data have been used to calculate the extent and the enthalpy effect of the irreversible NH_3 adsorption.

of FMC experiments, allows the samples to be put in order of decreasing mean site strength. The acid-treated clay catalysts clearly possess more strong acid sites than the two other classes of materials. The mean strength of acid sites on an HY zeolite is lower than that for a MSA*x* aluminosilicate with a similar Si:Al ratio. Within the same category of samples, the mean site strength decreases with decreasing Si:Al ratio. However, to complete the image of surface acidity given by the FMC results, it is necessary to determine strength distribution functions [16,17], which will be reported in future publications.

3.3. Comparison of the results inferred from the various methods

In Fig. 4, the numbers of acid sites determined by TCA, TPD and FMC are compared for the powdered porous samples belonging to three families of materials. As can be seen, the three methods are not completely equivalent, TPD giving the greatest acidity values in most cases. The FMC results lie somewhere between those obtained in TCA and TPD measurements. Nevertheless, general trends in surface acidity revealed by these methods are the same. For example, the surface acidity of zeolites HY*x* and that of mesoporous aluminosilicates MSA*x* increases with decreasing Si:Al ratio. The detailed analysis of the Lewis/Brønsted acidity on the various samples with respect to their composition, structure and the pre-treatment used is beyond the scope of this paper.

The differences observed in Fig. 4 may originate from the various experimental conditions used during pre-treatment, adsorption and desorption stages. In the case of TCA measurements, the time of the vacuum treatment between the two adsorption cycles is probably too short for all the physically adsorbed NH_3 molecules to be removed from the solid surface. The desorption conditions in TPD measurements are the

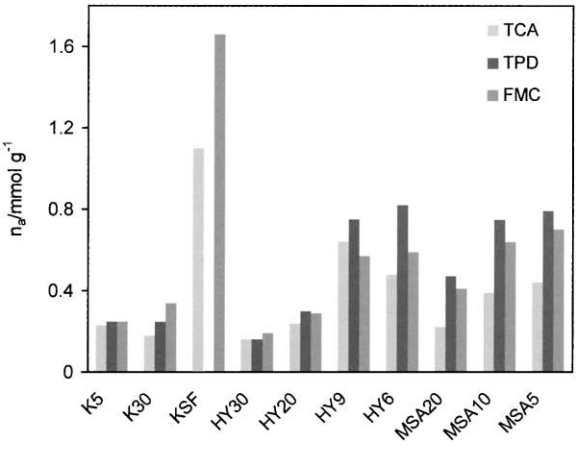

Fig. 4. Schematic diagram of the difference in number of surface acid sites, determined by two-cycle adsorption, thermoprogrammed desorption and flow adsorption microcalorimetry, on various porous materials.

Table 4
Results of acidity measurements by flow-microcalorimetry performed on solid samples pre-saturated with water vapour at 373 K

Sample	Adsorption cycle		Desorption cycle		Irreversible adsorption	
	Γ (mmole g^{-1})	ΔH (J g^{-1})	Γ (mmole g^{-1})	ΔH (J g^{-1})	Γ (mmole g^{-1})	Δh (kJ mole^{-1})
KSF	2.47	−251.5	−1.15	23.5	1.33	−171
HY6	1.72	−86.5	−1.51	44.8	0.21	−199
MSA5	2.18	−147.8	−1.71	49.9	0.47	−208

most drastic, resulting in the greatest values of n_a. However, the use of this method is restricted to materials with structural and textural properties that do not undergo any changes during heating [16]. From this point of view, the FMC method is more appropriate since it allows the solid sample to be maintained under the same temperature during experimentation.

The temperature of sample outgassing may be another source of differences between TPD and FMC acidity results. It is known that some water vapour cannot be removed from very fine pores during pre-treatment at low temperatures. In the case of FMC, the outgassing procedure at 373 K is probably not capable of releasing all adsorbed water from surface sites located inside micropores or small mesopores. To verify this hypothesis, FMC acidity experiments were carried out on selected samples prepared as follows. The solid sample was first outgassed at 373 K overnight inside the calorimetric cell and then saturated in a flow of water vapour and helium at 373 K for 3 h. The excess of water in the system was subsequently removed by a flow of helium. The corresponding mass-transfer data and thermal effects for one adsorption–desorption cycle of ammonia in helium at 373 K are reported in Table 4.

The comparison of the data reported in Tables 3 and 4 illustrates the influence of water vapour on the results of surface acidity tests. The amount of NH_3 adsorption on 'wet' samples and the related enthalpy effects per unit mass of the adsorbent are quite similar to those obtained on 'dry' solids. Some significant differences appear in the desorption stage, especially for the amounts desorbed which are markedly increased. Consequently, the amounts of irreversible NH_3 adsorption on 'wet' samples diminish and the molar enthalpy effects are more negative. It is really difficult to provide a plausible explanation for the observed trends and further studies are required. Generally, water vapour may modify both the nature of surface sites and the accessibility of the pore space to the adsorbate. In the latter case, the total number of acid sites would decrease and the proportion between weak and strong sites would undergo much alteration, thereby leading to a change in the mean site strength. It may be that some ammonia molecules can interact with strongly adsorbed water in the vicinity of acid sites giving rise to hydrogen-bounded adduct formation, which contributes to the total thermal effect. Another explanation is that ammonia displaces vicinal water from the solid surface and this process modifies the composition of the effluent gas analysed by the TC detector. This hypothesis will be checked thoroughly in a future study, using mass spectrometric downstream detection in the FMC system. Note, however, that the displacement process should be much less exothermic than single adsorption.

4. Conclusion

The simultaneous determination of the amount of gaseous ammonia irreversibly adsorbed on powdered porous materials and the related molar heat effect in a single flow-microcalorimetric experiment provides important information about the number and mean strength of surface acid sites. When compared with more classical methods, FMC yields results lying between those obtained with the use of two-cycle NH_3 adsorption and thermoprogrammed NH_3 desorption. The differences in the number of acid sites may be ascribed to various experimental conditions used during desorption or pre-treatment stages in each of these methods. Therefore, much attention should be paid to this aspect when comparing the results of surface acidity tests reported in the literature. An important advantage of flow-calorimetry is that it

can operate at constant temperature and in the presence of additional gas components, such as water vapour. The resulting surface acidity parameters are believed to be closely related to the practical performance of catalysts in industrial applications.

Acknowledgements

The authors thank Dr. Robert Durand of Ecole Normale Supérieure de Chimie, Montpellier, France, for the results of TPD measurements.

References

[1] M.V. Juskelis, J.P. Slanga, T.G. Roberie, A.W. Peters, J. Catal. 138 (1992) 391.
[2] P.J. Anderson, H.H. Kung, Catalysis 11 (1994) 441.
[3] D.J. Parillo, G.T. Kokotailo, R. Gorte, Appl. Catal. 67 (1990) 107.
[4] W.E. Rarneth, R.J. Gorte, Chem. Rev. 95 (1995) 615.
[5] S.M. Babitz, B.A. Williams, M.A. Kuehne, H.H. Kung, J.T. Miller, Termochim. Acta 312 (1998) 17.
[6] A. Gervasini, A. Auroux, J. Phys. Chem. 97 (1993) 2628.
[7] A. Gervasini, G. Bellussi, J. Fenyvesi, A. Auroux, J. Phys. Chem. 99 (1995) 5117.
[8] M.J. Meziani, J. Zajac, D.J. Jones, S. Partyka, J. Rozière, A. Auroux, Langmuir 16 (2000) 2262.
[9] J. Jänchen, H. Stach, M. Busio, J.H.M.C. van Wolput, Termochim. Acta 312 (1998) 33.
[10] E. Löffler, U. Lohse, Ch. Peuker, G. Öhlmann, L.M. Kustov, V.L. Zholobenko, V.B. Kazansky, Zeolites 10 (1990) 266.
[11] M.A. Makarova, A.F. Ojo, K. Karim, M. Hunger, J. Dwyer, J. Phys. Chem. 98 (1994) 3619.
[12] V. Bolis, G. Cerrato, G. Magnacca, C. Morterra, Thermochim. Acta 312 (1998) 63.
[13] D.R. Brown, C.N. Rhodes, Thermochim. Acta 294 (1997) 33.
[14] A.J. Groszek, Thermochim. Acta 312 (1998) 133.
[15] A.J. Groszek, M.J. Templer, Chemtech 29 (1999) 19.
[16] D.J. Jones, G. Aptel, M. Brandhorst, M. Jacquin, J. Jiménez-Jiménez, A. Jiménez-Lopez, P. Maireles-Torres, I. Piwonski, E. Rodriguez-Castellon, J. Zajac, J. Rozière, J. Mater. Chem. 10 (2000) 1957.
[17] D.R. Brown, A.J. Groszek, Langmuir 16 (2000) 4207.
[18] J. Rozière, M. Brandhorst, R. Dutartre, M. Jacquin, D.J. Jones, J. Zajac, Submitted for publication in J. Mater. Chem.