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CHARACTERISATION OF HETEROGENEOUS CATALYSTS BY MODIFIED FLOW MICROCALORIMETRY

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ABSTRACT

A modified batch gas sampling–carrier gas flow (BGS–CGF) microcalorimetric method is described and discussed. The values of the heats of differential adsorption of ammonia on ZSM-5 measured by this method agree well with those obtained from other calorimetric techniques. The differential and integral heats of adsorption of ammonia on SiO_2–Al_2O_3, on zeolites and on some commercial catalysts were determined. The calorimetric measurements of ammonia adsorption were used to characterise the acidity of those samples. The acidity of the samples measured by the calorimetric method were correlated with their activities evaluated on a pulse reactor.

INTRODUCTION

It is well known that various techniques have been successfully used to characterise the acidity of solid surfaces [1,2]. Among these, IR spectroscopy and microcalorimetry combined with ammonia adsorption are particularly useful. Ammonia molecules are capable of diffusing into the intra-crystalline channels of zeolites and of probing their acid sites. Calorimetric measurement is a very informative method both for the acid strength and the amount of acid on the solid surface. Most calorimetric methods currently used for the study of catalysts are usually based on a vacuum line, as described by Gravelle and Teichner in ref. 3. These authors emphasised that the importance of careful design and calibration of the volumetric measurements is much greater than that of the corresponding microcalorimetric measurements. Moreover, a small change in the temperature and, hence, in the partial pressure of gas adsorbate in the system may cause adsorption–desorption fluctuation which would influence the sensitive microcalorimetric measurements.

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It is necessary to introduce a calorimetric system to accurately determine the quantity of adsorbate gas in the adsorption measurements. The purpose of the present study is to introduce a batch gas sampling–carrier gas flow microcalorimetric method (BGS–CGF microcalorimetry) for determining the heat of adsorption and for characterising the acidity of solid surfaces. The correlation between the activity and the acidity of the catalysts is also discussed.

EXPERIMENTAL

Materials

High purity nitrogen and ammonia (both from a gas product factory in Beijing) were used as carrier gas and probe gas for the calorimetric system, respectively. The detailed analyses of the gases are listed in Table 1.

The zeolite used (ZSM-5), a commercial product, was pretreated at 923 K. The chemical composition of the zeolite is given in Table 2. The H-ZSM-5 zeolite was used to test the repeatability of the method. The chemical compositions of ZSM-5-type zeolites modified with copper are also listed in Table 2.

TABLE 1

Analysis of nitrogen and ammonia

Gas	Purity (%)	Impurities (ppm)					
		O_2	H_2O	H_2	CO_2	CH_4	C_nH_m
Nitrogen	99.999	< 3	< 2.6	< 1.0	< 0.5	< 1.0	–
Ammonia	99.999	< 5	< 10	–	–	–	< 2

TABLE 2

The chemical composition of ZSM-5-type zeolites

Sample	Chemical composition (wt.%)					SiO_2/Al_2O_3 (mole ratio)
	Na_2O	CuO	Al_2O_3	SiO_2	H_2O [a]	
H-ZSM-5	0.13	–	3.02	94.82	2.03	53.4
Cu-ZSM-5 (synth.)	0.78	0.69	2.65	90.49	5.39	58.0
Cu-ZSM-5 (exch.)	0.11	0.89	2.84	90.11	6.05	54.0

[a] Data obtained from the weight loss of the samples calcined at 1073 K.

Three kinds of SiO_2–Al_2O_3 supports, S–A-1, S–A-2 and S–A-3 with different alumina contents (3%, 6% and 12%, respectively) and four commercial catalysts were tested in this work.

Techniques

An HT-1000 Calvet microcalorimeter with a metal circulating cell (Setaram, France) was used to determine the heats of adsorption of the probe gas on the solid surface. A 6-port valve on the carrier gas line is used for sampling the probe gas. Adsorption of probe gas takes place in a sample cell. The unadsorbed portion of the probe gas sample goes through an absorption trap (containing water or HCl solution) for analysis or for the sample gas calibration. One dose of sample gas (such as ammonia) carried by nitrogen and picked up by the 6-port valve device is calibrated by chemical titration.

Figure 1 shows a block diagram of the BGS–CGF microcalorimeter.

Procedure

The sample (typically 1.0000 or 2.0000 g) was placed in the sample cell of the calorimeter. The experimental cell and a reference cell were placed in the vessels of the microcalorimeter. Pure nitrogen was passed through the cells at a constant flow rate of 15 ml min^{-1}, monitored by a rotameter. After the calorimetric baseline became stable, the sample gas (NH_3) was introduced into the carrier gas line by the 6-port valve, and passed through all the on-line devices. The heat effect of NH_3 adsorption on the solid samples in the sample cell was detected by the calorimeter.

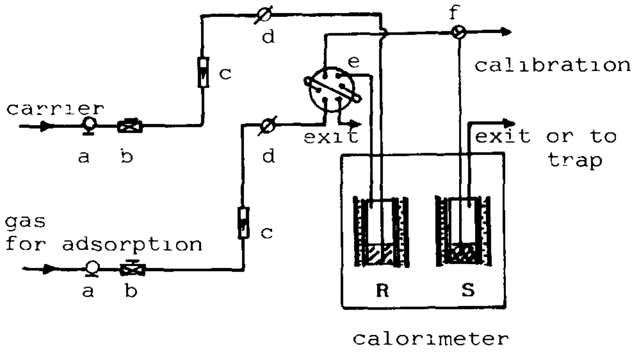

Fig. 1. A gas-line assembly for batch gas sampling–carrier gas flow (BGS–CGF) microcalorimetry associated with a heat-flow calorimeter for the measurement of the adsorption of successive doses of gas: a, pressure stabilising valve; b, flow stabilising valve; c, rotameter; d, stop valve; e, 6-port batch gas sampling valve; f, 3-port valve; R, reference cell; S, sample cell.

TABLE 3

Energy equivalent at various temperatures

T (K)	323	360	420	463
Energy equivalent E (kJ N^{-1})	5.6528×10^{-6}	5.2552×10^{-6}	5.0269×10^{-6}	4.8131×10^{-6}

RESULTS AND DISCUSSION

Electrical calibration tests using the Joule effect were carried out in a calibration heater, a standard Joule cell for calibration (Setaram, France) of calorimeters, with the EJP-30 power supply (also Setaram). The results of the calibration of the microcalorimeter at different temperatures are presented in Table 3.

Before the adsorption experiment, the quantity of sample gas (NH_3) in one dose was calibrated by chemical titration. The result of the calibration was $43.6 \pm 1.5 \times 10^{-6}$ mol dose^{-1} in the temperature range 294.0–296.5 K in the period July to December 1987.

The results of NH_3 adsorption of ZSM-5 are shown in Fig. 2 and Table 4. The initial differential heats of NH_3 adsorption on ZSM-5 pretreated at 923 K were detected at 420 K [4].

The results of the initial differential heat of NH_3 adsorption obtained from this BGS–CGF microcalorimeter are in good agreement with those obtained by normal (heat-flow) microcalorimetry combined with a volumet-

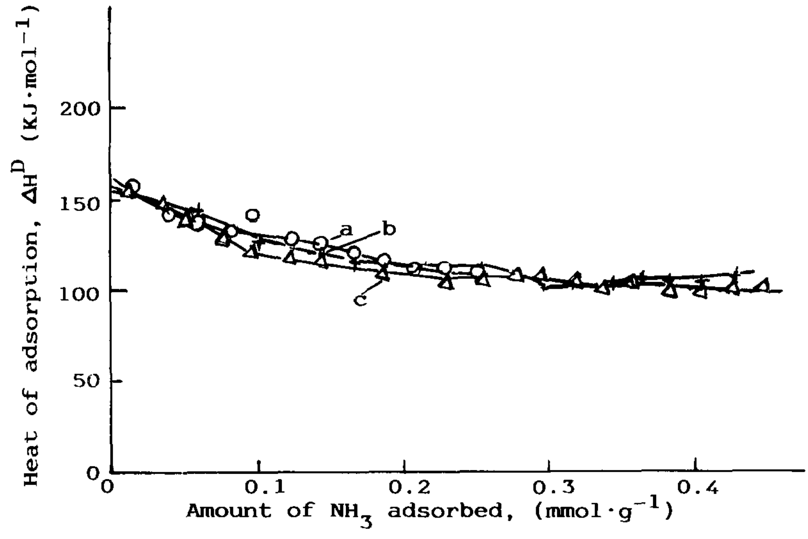

Fig. 2. Ammonia adsorption microcalorimetric results of three repeat experiments on ZSM-5 zeolites: a, sample 1; b, sample 2; c, sample 3.

TABLE 4

The results of NH_3-adsorption microcalorimetry on ZSM-5-type zeolite

No.	Sample weight (g)	Differential heats of NH_3 initial adsorption at 420 K ΔH^D (kJ mol^{-1})	Average value (kJ mol^{-1})	Relative standard deviation (%)
1	2.0126	157.6	156.2 ± 3.1	2.0
2	2.0112	152.7		
3	2.0146	158.3		

ric system in a vacuum line [5]. However, all the information concerning the heat evolved in microcalorimetry could be obtained from the BGS–CGF microcalorimeter.

A theoretical model derived from the surface physical chemistry could be used to correlate the experimental data obtained here. It gives a linear relationship between the differential heats of NH_3 adsorption on the ZSM-5 and the amount of NH_3 adsorbed, with a good correlation coefficient of about 0.99 [6]. The result clearly shows the applicability of the theoretical model for liquid–solid adsorption processes [7] to our gas–solid adsorption data.

Some applications

It is well known that the differential heats of adsorption on catalysts characterise the acid strength of their surface, and that the integral heat may be applied to determine the number (or concentration) of acid sites on the catalyst surface.

Determination of the acidities of SiO_2–Al_2O_3 supports

The results in Table 5 indicate that BGS–CGF microcalorimetry could be used in the characterisation of the acidity of a catalyst support. A comparison between the acid strength of samples deduced from the calorimetric data of NH_3 adsorption and those obtained from titration with *n*-butylamine is shown in Table 5. Minor differences between the acid strength defined by NH_3 differential adsorption heats of the above samples could be detected with the BGS–CGF microcalorimeter, and the number of acid sites of these samples (expressed as the integral heats of those sites with adsorption heats of more than 100 kJ mol^{-1}) is also clearly discriminated (Fig. 3).

The experimental data indicates that the number of acid sites increases with the Al_2O_3 content in these samples. As shown in Fig. 4, the conversion of toluene in the hydrogenation reaction of the dual metal catalysts with these samples as supports appears to depend strongly on the acidity of the catalyst supports, in particular, on the number of acid sites which have

TABLE 5

Variations in the acidity of SiO_2–Al_2O_3, expressed by differential and integral heats, and the activity of the catalyst in toluene hydrogenation with Al_2O_3 content of the supports

Sample	Catalyst active metal contents (wt.%)	Al_2O_3 content (wt.%)	Acidity						Conversion of toluene (%)	
			Differential heats of NH_3 initial adsorption ΔH^D (kJ mol^{-1})	Integral heats of more than 100 kJ mol^{-1} ΔH^I (J g^{-1})	Determined by butylamine titration H_0 (meq g^{-1})[a]				498K	523 K
					$> +3.3$ $\leqslant +4.8$	> -3.0 $\leqslant +3.5$	$\leqslant -3.0$ > -5.6	$\leqslant 5.6$		
S–A-1	–	3	145.10	16.84	–	–	–	–	–	–
S–A-2	1.2	6	146.76	22.45	0.2	0	0	0.2	78.6	100
S–A-3	1.2	12	152.84	28.40	0.3	0	0	0.19	12.2	37.7

[a] H_0, Hammett acidity function.

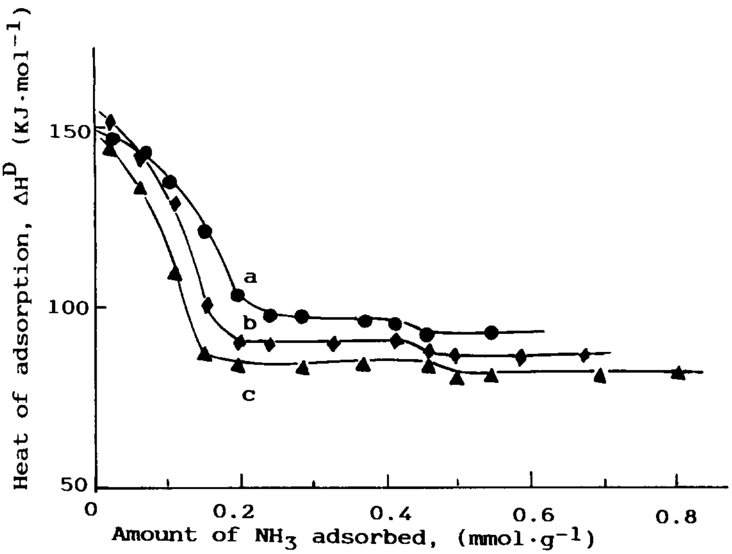

Fig. 3. Variations in the differential heats of adsorption of NH_3 on $SiO_2-Al_2O_3$ supports with amount of NH_3 adsorbed: a, 12% Al_2O_3; b, 6% Al_2O_3; c, 3% Al_2O_3.

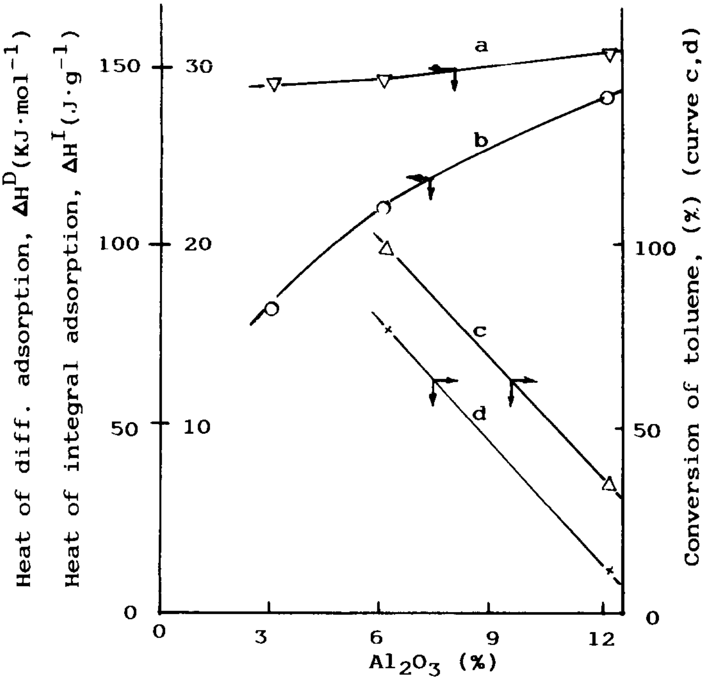

Fig. 4. Acidities and Al_2O_3 content of supports vs. conversion (or hydrogenation activity) of toluene: a, differential heat; b, integral heat; c, conversion (523 K); d, conversion (498 K).

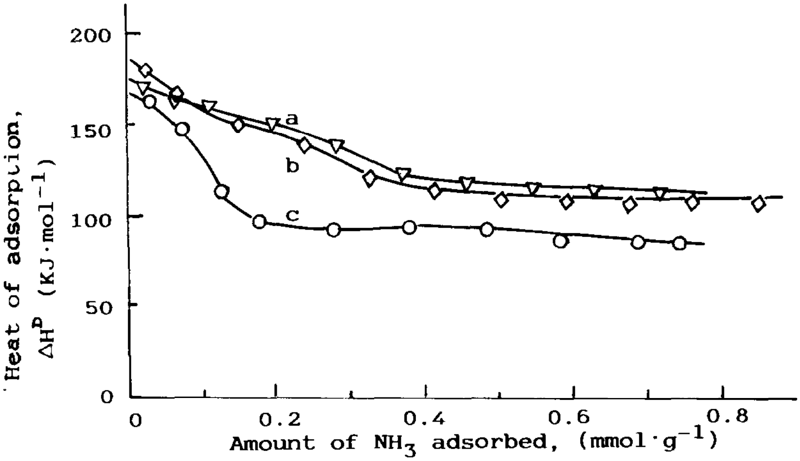

Fig. 5. Variations in the differential heats of adsorption of NH_3 on H-ZSM-5 and copper-containing ZSM-5 zeolites with amount of NH_3 adsorbed: a, Cu-ZSM-5 (synthesised); b, Cu-ZSM-5 (exchanged); c, H-ZSM-5.

differential heats of adsorption of ammonia over 100 kJ mol^{-1}, i.e. the conversion of toluene decreases with increasing number of acid sites (whose NH_3 differential adsorption heats are greater than 100 kJ mol^{-1}) on the supports.

Determination of the acidity of Cu-modified ZSM-5 zeolites

The heats of ammonia adsorption on Cu-ZSM-5 zeolite, modified by different methods and their activity are presented in Fig. 5 and Table 6.

The results in Table 6 show that the differential heats of ammonia adsorption on Cu-modified ZSM-5 zeolites are greater than on non-modified H-ZSM-5. Their integral heats of irreversible chemical adsorption are three

TABLE 6

Data of NH_3 adsorption by microcalorimetry and catalytic activity on ZSM-5-type zeolites

Sample	Pretreatment temperature (K)	Data from calorimetric heats of NH_3 adsorption		Pulse MA in hexane hydrocracking conversion (%)	
		Differential heats of NH_3 initial adsorption ΔH^D (kJ mol^{-1})	Integral heats of irreversible chemical adsorption of NH_3 ΔH^I (J g^{-1})	Total	C_3% in cracking products
ZSM-5	1073	162.83	15.99	20.76	11.70
Cu-ZSM-5 (synth.)	1073	180.38	46.58	80.71	43.39
Cu-ZSM-5 (exch.)	1073	172.28	47.25	83.71	43.67

times greater than those on the unmodified one. It is interesting to note that the activity of these samples in *n*-hexane hydrocracking has the same trend as the variations in the integral heats of adsorption. This clearly indicates that the introduction of copper is responsible for the change in the acidity or activity of the catalyst. According to Ward [8], the Cu on the zeolites may generate acid sites which are catalytically active in *o*-xylene isomerisation. Suzuki et al. [9] determined the effect of the concentration of alkali and alkaline earth metals introduced by ion-exchange on the dealumination of ZSM-5 zeolites. The introduced Cu may inhibit the dealumination process of ZSM-5 during their treatment at high temperature, and therefore prevent the acid sites on ZSM-5 from changing; but this is not the case for H-ZSM-5. These observations confirmed our results shown in Table 6. It is also interesting to note that there is quite a difference between Cu in solution and Cu on ZSM-5 zeolites.

Determination of the acidity of commercial FCC catalysts

The heats of NH_3 adsorption on commercial FCC catalysts were determined. The results for four commercial catalysts aged with 100% steam at 1073 K for 4 h are shown in Fig. 6 and Table 7.

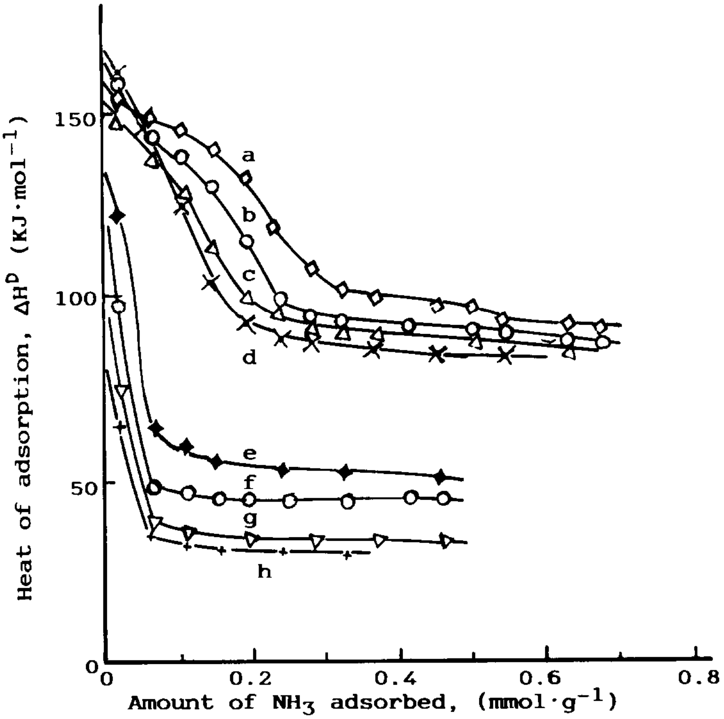

Fig. 6. Variation in the differential heats of adsorption of NH_3 on four catalysts with amount of NH_3 adsorbed: a, CC-1; b, CC-2; c, CC-3; and d, CC-4 (fresh catalyst), e, CC-1; f, CC-2; g, CC-3; and h, CC-4 (aged catalyst).

TABLE 7

Pulse MA in hexane cracking on four different aged catalysts

Sample	CC-1	CC-2	CC-3	CC-4
Acidity order	Very strong	Strong	Weak	Weaker
Total *n*-hexane conversion (%)	11.48	10.17	6.77	6.62
Products (%)				
CH_4	0.53	0.52	0.51	0.38
$C_2^0 + C_2^{2-}$	2.05	1.98	1.87	1.50
$n\text{-}C_3^0$	1.39	1.05	0.29	0.30
C_3^{2-}	4.16	3.53	2.11	1.95
$C_3^{2-}/n\text{-}C_3^0$	2.99	3.36	7.28	6.50
$i\text{-}C_4^0$	0.27	0.17	0.03	0.04
$n\text{-}C_4^0$	0.43	0.37	0.13	0.16
$i\text{-}C_4^{2-} + C_{4-1}^{2-}$	0.74	0.63	0.48	0.37
trans-C_{4-2}^{2-}	0.20	0.16	0.12	0.10
cis-C_{4-2}^{2-}	0.27	0.34	0.37	0.35
C_4^{2-}/C_4^0	1.73	2.09	6.06	4.10
$i\text{-}C_5^0$	0.18	0.12	0.04	0.04
$n\text{-}C_5^0$	0.05	0.05	0.03	0.01
C_5^{2-}	0.23	0.27	0.19	0.13
C_5^{2-}/C_5^0	1.00	1.59	2.71	2.60
Others	0.98	0.98	0.60	1.29
$n\text{-}C_6^0$	88.53	89.83	93.23	93.38
Total	100.00	100.00	100.00	100.00

It is well known that there are several important parameters for the characterisation of cracking catalysts: the acidity of the catalyst and its stability after aging with steam are two of them. From Fig. 6, it is clear that there are obvious differences in the acidity (or differential heats of ammonia adsorption) on those catalysts before and after aging. Either the differential heats (as the acid strength) or the integral heats (as the number of acid sites) of the aged catalysts are much lower than in the fresh samples. However, the trends of the changes in the calorimetric curves are all similar. It seems that the stability of CC-1 and CC-2 following steam treatment is a little better than that of CC-3 and CC-4.

The adsorption heats mentioned above are in a good agreement with the catalytic activity of these samples in *n*-hexane cracking, and there should be a good correlation between the acidity and the catalytic activity of the samples. For instance, the order of acidity of the four aged zeolites, as shown in Table 7, is CC-1 > CC-2 > CC-3 > CC-4; and their total *n*-hexane conversion in the cracking reaction has the same order. However, the order of catalytic selectivity for these catalysts is different from the acidities, namely CC-3 > CC-4 > CC-2 > CC-1 for the ratio of total alkenes to total alkanes in the cracking products.

CONCLUSIONS

Our work has shown that batch gas sampling–carrier gas flow (BGS–CGF) microcalorimetry can be used to investigate adsorption phenomena on solid surfaces, such as heterogeneous catalysts, etc. It is very simple and easy in operation. The heat evolved in fast or slow adsorption, or during surface investigation may be measured with a good precision by this method. It is suitable for investigating surface phenomena on solids even with a poor heat conductivity, such as various commercial catalysts, etc. From the calorimetric data, it is very easy to obtain a correct energy spectrum of the adsorbent surface with respect to a given adsorbate by batch gas sampling with carrier gas flow into the microcalorimeter vessel containing the adsorbent. The technique could be used to distinguish between a physical or chemical adsorption process, as mentioned in ref. 10. It can be particularly useful for chemisorption studies in a wide temperature range (from room temperature up to the required high temperature), which would include the useful temperatures of most industrial catalytic processes. It is obvious that the data from the results of calorimetric experiments could be closely related with the activity of the studied catalysts.

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