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New method for the study of surface acidity of zeolites by NH_3-TPD, using a pH-meter equipped with an ion selective electrode

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Desorbed ammonia is captured by an acetic acid solution whose concentration of ammonium ions formed by neutralization, is continuously recorded by a pH-meter equipped with an ion-selective electrode (ISE). This technique allows the study of both the acidity density and the distribution of acid site strengths. Such "strength profile" was obtained by plotting the relative rate of desorbed NH_3 versus the temperature. Results obtained can be fairly well correlated with those already published. It is shown that by investigating several H-ZSM-5 zeolites with different SiO_2/Al_2O_3 ratios, the data of acid density obtained by the ISE method are very close to those calculated from the Al content. The slight shift of the desorption peaks towards higher temperature suggests a slightly higher strength for more isolated acid sites. Zeolite structures, which are richer in Al, contain weaker acid sites, as evidenced by the H-Y when compared to the H-mordenite, while the acid sites density of the former is much higher. The ultra-stabilized Y zeolite (H-USY) shows a lower acidity density than the parent H-Y owing to the removal of some of the tetrahedral Al atoms from the framework during the preparation. The strength profile of the H-USY is also quite different from that of the H-Y. The new technique appears to be much simpler, more rapid, more informative and quite accurate when compared to the technique using a gas chromatograph equipped with a thermal conductivity detector (GC-TCD).

KEY WORDS: surface acidity; zeolites; ion-selective electrode; acid density and strength.

1. Introduction

Acidic solids have been extensively used as catalysts in petroleum chemistry [1,2] and in organic synthesis [3,4]. Many solids such as natural clay minerals, mounted acids, cation exchange resins, charcoal heat-treated, metal oxides and sulfides, metals salts and mixed oxides, can exhibit surface acidity [5,6]. Zeolites and other molecular sieves are the most known acidic catalysts because of their surface acidity and their shape-selectivity, two important factors that may result in very appreciated catalytic performances [1].

Main characteristics of surface acidity comprise the density and strength of acid sites, and the acidity type (Brönsted or Lewis). Techniques for the characterization of these acid sites include methods of gaseous base (ammonia, or another base) adsorption/temperature programmed desorption (TPD), and FT-IR using pyridine and dimethylpyridine as probes [5,7,8].

In particular, with zeolites and related materials, ammonia adsorption and desorption (NH_3-TPD) method can be used to measure the density of acid sites and to determine their distribution in terms of acid strength [9,10]. Most of the time, a gas chromatograph equipped with a thermoconductivity detector (GC-TCD) is used to record the amount of the ammonia desorbed as a function of the heating temperature, thus allowing the assessment of the distribution of the acidity strength in a ZSM-5 zeolite [9]. However, it is extremely difficult to obtain an accurate analysis because the quite slow response of the TCD combined with the gas back-mixing effect in the outlet tubing as well as in the detector volume infers a serious peak overlapping. This problem cannot be solved even by using deconvolution techniques or stepwise heating programs [9]. A "water" purging technique used to eliminate the weakly adsorbed ammonia has been recently developed [11].

In this work, the use of a pH-meter equipped with an ion selective electrode (pH-ISE) is found to be more rapid and less disadvantageous than the technique making use of a GC-TCD. The newly developed method has been successfully applied to several zeolites including H-ZSM-5, H-Y, H-mordenite and H-USY.

2. Experimental

2.1. Preparation of catalysts

2.1.1. H-ZSM5 zeolite

All zeolite materials with ZSM-5 structure were obtained from Chemie Uetikon AG (Switzerland) in the powder H-form. They were Zeocat PZ-2/25 Na, Zeocat PZ-2/50 H, Zeocat PZ-2/100 H, Zeocat PZ-2/400 H and Zeocat PZ-2/1000 H. Prior to use, they were all calcined at 500 °C for 3 h, without further treatment except for

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the Zeocat PZ-2/25 Na. Zeocat PZ-2/25 Na was treated with aqueous solution of NH_4Cl (20 wt.% solution), in order to convert it into H-form. The procedures were as follow; 20.0 g of Zeocat PZ-2/25 Na was mixed with 400.0 mL of NH_4Cl (20.0 wt.% solution, Aldrich). The resulting suspension was mildly stirred for 7 days at ambient temperature with everyday replacing the solution with fresh NH_4Cl solution. The mixture was then filtrated by vacuum and washed with distilled water. The resulting solid was dried overnight at 120 °C and then calcined stepwise from 300 to 500 °C, with heating rate of 50 °C/h, and then left at 500 °C for 24 h.

2.1.2. Other zeolite structures

H-Y and H-USY

HY zeolite was obtained by calcining the NH_4Y (Linde LZ-Y62, Aldrich) at 400 °C for 3 h. USY material in the H-form was obtained from Chemie Uetikon AG (Switzerland) and prior to use it was calcined at 500 °C for 3 h.

H-Mordenite

H-Mordenite was obtained by calcining the NH_4 form of Mordenite (CBV20Azeolite Mordenite, Zeolyst International) at 500 °C for 3 h.

2.1.3. Extrusion with bentonite clay

All samples prior to the acidity determination were extrudated with bentonite clay (Aldrich). These extrudates were dried in air overnight at 120 °C and then calcined in air at 500 °C for 3 h, except for HY extrudates which was calcined at 400 °C for 3 h. The final composition contained 80.0 wt.% of the active zeolite and 20.0 wt.% bentonite. Particularly, samples containing HY and HUSY which were expected to have higher acid sites density, the final composition was 20.0 wt.% active zeolite and 80.0 wt.% bentonite.

2.2. Catalyst characterization

2.2.1. Determination of [Al] and SiO_2/Al_2O_3 ratio

Al concentration and the corresponding SiO_2/Al_2O_3 molar ratio were determined by Atomic Absorbance Spectroscopy (AA). Perkin-Elmer 2380 spectrometer equipped with Al hollow cathode lamp and nitrous oxide burner was used for the analyses. The obtained AA results were within accuracy of $\pm$ 7.0%. These data were used to calculate the [Al] concentration of the material, so that the equivalent concentration of acid sites could be determined, assuming that one (tetrahedral) Al atom corresponded to one H^+ site.

2.2.2. Acidity investigations

NH_3-TPD of various samples was carried out in a fixed-bed reactor equipped with a programmable temperature controller, at ambient pressure. About 1.0 g of sample extrudates was loaded into a quartz tube having the following dimensions: 42 cm in length and 0.13 cm in diameter. The sample was preheated at 300 °C for 3 h in flowing (dry) nitrogen at a flow rate of 60.0 cm^3 min^{-1}. After cooling to 100 °C, these extrudates were exposed to a stream of (dry) ammonia for 1 h at a flow rate of 20.0 cm^3 min^{-1}. Then, the sample was left in flowing nitrogen at the same temperature for 10 h in order to purge any excess of ammonia and physically adsorbed ammonia. Finally, the TPD operation was performed by heating from 100 to 650 °C at a heating rate of 15.0 °C min^{-1}.

NH_3-TPD/back-titration method

The desorbed ammonia was reacted with 0.05 N HCl solution that was then back-titrated with 0.05 N NaOH solution [10, 12]. The equivalence point was determined by using the indicator method (1.0 wt.% phenolphthalein) and pH electrode attached to Lab Works interface.

NH_3-TPD/ISE method (using an ammonium ion-selective electrode)

Typically, the evolved ammonia was flown into a container filled with 90.0 cm^3 of trapping solution (CH_3COOH, 0.001745 N). The concentration of the resulting ammonium ions was measured (and recorded) using a pH-meter equipped with an ion-selective electrode (NH_4^+-ISE). The digital display of the pH-meter displayed both the total concentration of the NH_4^+ ions in the solution and the evolvement profile as a function of temperature. This allowed the determination of both the density and the profile strength of acid sites. Table 1 reports the specifications of the OAKTON bench pH 2100 meter and Cole-Parmer NH_4^+ ion-selective electrode [13], which were important because they had influenced the choice of the acidic trapping medium, as well as, its initial concentration. The calibration of the ISE was performed weekly using an ammonium acetate standard solution.

It is also worth mentioning that the bentonite clay used in this work did not show any acidity, which could be detected by NH_3-TPD/back-titration or ISE methods.

Procedure used to record the acidity profile

Computer software was used in order to record the variation of the concentration (of ammonium ions formed in the trapping solution) versus the time. This time derivative of the concentration was then transformed into temperature derivative since the heating was done at constant increase of temperature. Finally, the plot of the relative desorption rate of ammonia versus the temperature gave the curve of sites distribution in terms of acid strength. Such relative desorption rate was defined as follows: $v = (1/W) \times d[\Delta C/C]/\mathrm{d}T$, W, C, T, being the % weight of the zeolite component (in the sample), the concentration in ammonium ions of the

Table 1
OAKTON pH 2100 meter and Cole-Parmer NH_4^+ ISE specifications

OAKTON pH 2100 meter		Cole-Parmer NH_4^+ ISE	
Specifications			
Range	0.001–19,999	Concentration range	1.0 M to 5.0×10^{-6} M (18,000 ppm to 0.1 ppm)
Resolution	High resolution mode (± 500.0 mV) and low resolution mode (± 1850.0 mV)	pH range	3–10
Calibration	2–5 points	Temperature range	0–40 °C (continuous), 40–50 °C (intermittent
Average slope	Minimum average slope = 10 mV/decade Maximum average slope = 75 mV/decade	Size	110 mm (l) × 12 mm (d)
Accuracy	± 0.5% and ± 1.0 % of full scale for monovalent and divalent ions, respectively	Accuracy	± 2.0%

trapping medium and the desorption temperature, respectively.

3. Results And discussion

To show the reproducibility of the new method, all the acidity measurements were carried out in triplicate, and the obtained results were compared with those calculated from the AA analyses and also from the "classical" back-titration method. In table 2 are reported the data recorded for the H-ZSM-5 zeolite (SiO_2/Al_2O_3 ratio = 29). Thus, the two methods, NH_3-TPD/ISE (in short, ISE) and NH_3-TPD/back-titration (in short, back-titration) gave very similar results for the acid sites density, with acceptable (experimental) standard deviations. A similar reproducibility was also obtained with other H-ZSM-5 zeolites (having a SiO_2/Al_2O_3 ratio ranging from 59 to 1000, tables 3 and 4). However, the difference between the value of acid sites density measured by the back-titration method and that of the acid equivalence calculated from the AA (i.e. from the Al concentration) increased with increasing SiO_2/Al_2O_3 ratio (table 3), to reach more than 100% for a SiO_2/Al_2O_3 ratio of 1000 (i.e. with very low acidity). The same difference but observed for the ISE method was acceptable even at very low acidity (table 4), thus suggesting that the ISE was still sensitive to quite small amounts of ammonium ions formed in the acetic acid solution.

Essentially, the acidity profile of the H-ZSM-5 zeolites showed two well separated peaks (which normally were overlapped [9,11,14]), the one recorded at higher desorption temperature corresponding to the stronger acid sites (figure 1). As the SiO_2/Al_2O_3 ratio increased, these two peaks slightly shifted to higher temperatures, meaning that the fewer the acid sites, the slightly stronger they were (table 5 and figure 1). This was not in disagreement with conclusions of previous works since it was said that the acid strength of H-ZSM-5 zeolites increased to a plateau at high Si/Al ratios [1,14,15]. However, in the case of the zeolites having SiO_2/Al_2O_3 ratio equal or higher than 400, it was quite impossible for the ISE to provide useful information of acidity profile because of the too small (thus not accurately measurable) variations of the concentration of ammonium ions.

The values of the acid sites density of the H-Y and the H-mordenite are reported in table 6 (back-titration) and table 7 (ISE). With respect to the acidity values calculated

Table 2
Comparison of reproducibility of the two NH_3-TPD methods used (zeolite: H-ZSM-5, SiO_2/Al_2O_3 = 29)

Trial #	Calculated [Al] concentration (mmol g^{-1}) by AA measurements	Acid site density (mmol g_{cat}^{-1})	
		Ion selective electrode (ISE)	Back-titration
1	1.086	0.95	1.15
2		1.15	1.31
3		1.05	1.25
Average (X)		1.05	1.24
Standard deviation (s)		0.074	0.08
Relative standard deviation (s_t)		0.071	0.065
Difference (%) between the ISE and back-titration methods		19.0%	
Difference (%) between the calculated [Al] concentration and acidity method		4.0%	14.0%

Table 3
Acid sites density of H-ZSM-5 with different SiO_2/Al_2O_3, obtained by NH_3-TPD/back-titration

SiO_2/Al_2O_3 ratio of H-ZSM-5	Calculated [Al] concentration (mmol g^{-1})	Acid sites density (mmol g_{cat}^{-1}) determined by back-titration method	Difference (%)
29	1.086	1.24 ± 0.08	14.0
59	0.546	0.510 ± 0.05	7.0
102	0.322	0.390 ± 0.02	18.0
400	0.083	0.100 ± 0.08	21.0
1000	0.033	0.117 ± 0.01	> 100

Table 4
Acid sites density of H-ZSM-5 with different SiO_2/Al_2O_3, obtained by NH_3-TPD/ISE

SiO_2/Al_2O_3 ratio of H-ZSM-5	Calculated [Al] concentration (mmol g^{-1})	Acid sites density (mmol g_{cat}^{-1}) determined by ISE method	Difference (%)
29	1.086	1.05 ± 0.07	4.0
59	0.546	0.488 ± 0.07	11.0
102	0.322	0.345 ± 0.02	7.0
400	0.083	0.075 ± 0.01	10.0
1000	0.033	0.027 ± 0.01	18.0

Table 5
Acidity profile (distribution of sites according to acidity strength) recorded by NH_3-TPD /ISE for H-ZSM-5 samples with different SiO_2/Al_2O_3

SiO_2/Al_2O_3 ratio of H-ZSM-5	Peak temperature (°C)		Amount of desorbed NH_3 (mmol g_{cat}^{-1})		
	I	II	I	II	Total
29	216	395	0.563	0.488	1.05
59	295	416	0.150	0.337	0.488
102	355	449	0.113	0.230	0.345
400	N.P.[(a)]				
1000	N.P.[(a)]				

N.P.[(a)]: It was not possible to determine the acidity profile for these very low acidity samples, since the acidity variations are below the detection limit.
(): distribution in %.

by AA, these data were all acceptable with some higher accuracy for the ISE method. Table 8 and figure 2 show the distribution curves of the acid strength (strength profiles) of these zeolites, which comprised of three peaks corresponding to three strength categories (weak, medium and strong acid sites). As expected, the acid sites of the H-mordenite were generally stronger than the H-Y zeolite (higher desorption temperatures), although the total acidity of the former zeolite is much lower (higher SiO_2/Al_2O_3 ratio, tables 6–8). In particular, the proportion of strong acid sites of the H-mordenite was much more important than that of the H-Y (Table 8).

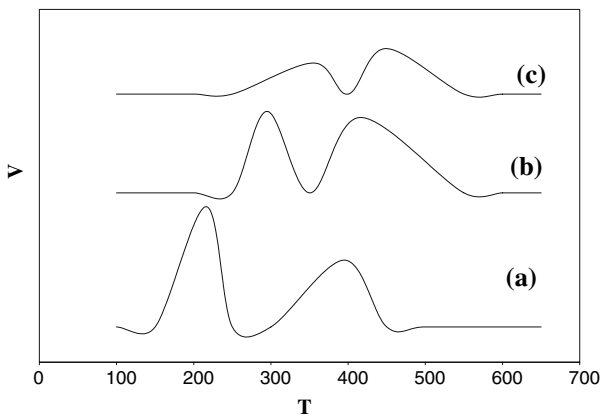

Figure 1. (Acidity) strength profile obtained by NH_3-TPD/ISE method for H-ZSM-5 zeolites with different SiO_2/Al_2O_3 ratios: (a) 29, (b) 59, and (c) 102 (v being expressed as millimoles of desorbed NH_3 by g of catalyst and by °C; T : temperature in °C).

Regarding the ultrastable Y zeolite (H-USY), the values of total acidity given by the back-titration and the ISE methods were much lower than that calculated from the Al content of the material (tables 7 and 8). This is well understood because the special treatment of the Y zeolite to finally result in USY material includes several steps (steam treatment at high temperature [1,16]), which extract several Al atoms from their tetrahedral coordination. Not only the structure of the zeolite is stabilized, but also the activity of catalytic cracking is considerably enhanced. In this context, the dislodgement of several Al atoms from the framework of Y

Table 6
Acid sites density of zeolites other than H-ZSM-5, obtained by NH_3-TPD/back-titration

Sample	SiO_2/Al_2O_3 ratio	Calculated [Al] concentration ($mmolg_{cat}^{-1}$)	Acid sites density ($mmolg_{cat}^{-1}$) determined by back-titration method	Difference (%)
H-Y	6.28	4.021	3.45 ± 0.17	14.0
H-USY	5.47	4.463	1.58 ± 0.19	65.0
H-Mordenite	29.5	1.057	1.23 ± 0.07	15.0

Table 7
Acid sites density of zeolites other than H-ZSM-5, obtained by NH_3-TPD/ISE

Sample	SiO_2/Al_2O_3 ratio	Calculated [Al] concentration ($mmolg_{cat}^{-1}$)	Acid sites density ($mmolg_{cat}^{-1}$) determined by ISE method	Difference (%)
H-Y	6.28	4.021	3.64 ± 0.23	9.50
H-USY	5.47	4.463	1.63 ± 0.07	63.5
H-Mordenite	29.5	1.057	1.16 ± 0.08	10.0

Table 8
Acidity profile (distribution of sites according to acidity strength) recorded by NH_3-TPD/ISE for zeolites other than H-ZSM-5

Zeolite	Peak temperature (°C)			Amount of desorbed NH_3 ($mmolg_{cat}^{-1}$)			
	I	II	III	I	II	III	Total
H-Y	213	321	445	1.73 (48)	1.46 (40)	0.450 (12)	3.64
H-USY	285	365	485	0.563 (34)	1.02 (60)	0.107 (6)	1.69
H-Mordenite	325	405	475	0.225 (20)	0.338 (29)	0.597 (51)	1.16

():distribution in %.

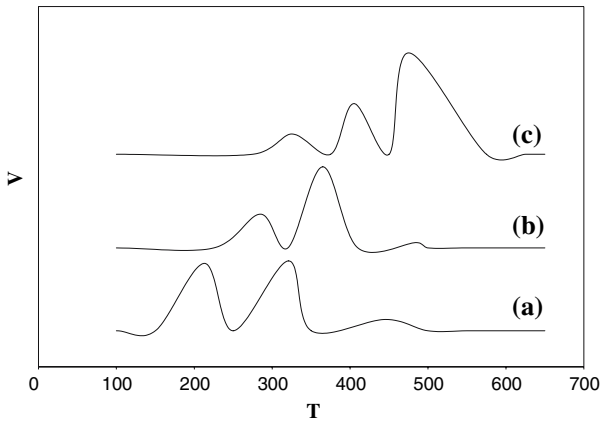

Figure 2. (Acidity) strength profile obtained by NH_3-TPD/ISE method for the following types of zeolite; (a) H-Y, (b) H-USY, and (c) H-Mordenite (v being expressed as millimoles of desorbed NH_3 by g of catalyst and by °C; *T*: temperature in °C).

zeolite leads to a lower total acidity in the USY zeolite (in general, the extra-framework Al are not very acidic). As pointed out by ref. [16], high catalytic properties are observed. In our case, two observations on the H-USY could be made (when compared to the H-Y, table 8):

– desorption peaks were slightly shifted to higher temperatures, indicating a slightly stronger acidity;
– more importantly, the proportion of acid sites corresponding to a desorption temperature of >320 °C increased from 40% to 60% (table 8). These newly formed acid sites could correspond to the new kind of Brönsted sites as identified by Niwa et al. [16] using the IRMS-TPD method (IR = infrared, MS = mass spectrometry).

3.1. Conclusion

We have shown that the new method NH_3-TPD using a pH-meter equipped with an ISE to study zeolites, shows several advantages with respect to the conventional back-titration and GC-TCD techniques.

(1) It can give accurate data of acid sites density, even for materials with quite low acidity.
(2) The acid strength profile shows quite well separated desorption peaks which allow an easy assessment of the quantity of acid sites of the same strength.
(3) The technique is simple and the equipment is not expensive. No corrosion of the ISE is expected (this

is not the case for the TCD filament which may undergo corrosion because of the evolved ammonia).

(4) The analysis is rapid and the interpretation of the results, almost immediate.

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