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Application of in situ TG to characterize catalyst acidity

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Abstract

The acidity of several types of catalyst was measured by means of in situ TG, using the procedure of NH_3 adsorption–desorption, with a modified quartz furnace tube on a Du Pont 9900 Computer/Thermal Analysis System. HY and HZSM-5 zeolites were used as reference samples to test the repeatability and/or precision of this method. The total acid amount and acid strength of samples could be directly calculated from the mass change on TG–DTG curves of NH_3 adsorption–desorption. The relative standard deviation of the data which were collected from five measurements of HY is less than ±0.050. This result was examined using HZSM-5 and the data were comparable with those reported in the literature.

The relations between the acidities and the catalytic activities for Pt/MgO-cross linked montmorillonite (Pt/MgO-CLM) and β zeolite catalysts are also discussed.

INTRODUCTION

A series of acid catalytic reactions, such as catalytic cracking, isomerization, alkylation, reforming and so on, have a close correlation with the acidity of the catalysts in petrochemical processing procedures. Catalyst acidity is one of the criteria used to evaluate catalytic activity. Characterization of catalyst acidity assumed an important role in the preparation and development of catalysts. Furthermore, the development of methods of measuring acidity has attracted a great deal of attention for the characterization of solid surface acidity. So far, the methods of acidity determination have not been very sensitive.

Tanabe introduced various methods concerned with solid surface acidity measurement [1]. Forni [2] systematically summarized the methods for determining solid surface acidity and compared the main merits and demerits in application. Microcalorimetry was used to characterize catalyst acidity by Auroux et al. [3] and modified flow microcalorimetry [4] has also been utilized to measure catalyst acidity. Stone and Rase [5] used thermal analysis techniques to measure heat change, which is an indication of acid

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strength, accompanying adsorption of bases such as piperidine and NH_3 on a solid catalyst, and by means of DTA examined the correlation between catalytic activity and acid site strength of solid samples. Shirasaki et al [6] measured, by means of a DTA–TG combination technique, the acid amount and acid strength of silica–alumina using pyridine, *n*-butylamine and acetone as adsorbate. Ghosh and Curthoys used simultaneous DTA and TGA to determine the acidity of hydrogen mordenites (HM) and dealuminated HM zeolites and compared the data with those determined by other methods. Aboul-Gheit et al. [8] carried out desorption experiments with preadsorbed NH_3 on the samples or samples which had been immersed in triethylamine using DSC and obtained results concerning the distribution of acid site strength of amorphous silica–alumina, γ-Al_2O_3 and Na-type, H-type mordenites. Liu et al. [9] used the TG–temperature programmed desorption (TPD) method, with ethylamine as adsorbate, to examine the acidity of ZSM-5 catalysts modified with phosphorus and magnesium compounds and obtained data about their acid amount and acid strength; they then achieved satisfactory results concerning the relationship between catalyst acidity and catalyst activity. Recently papers concerning acidity determination from TPD techniques have been published [9–14].

This paper describes a method of in situ TG with NH_3 adsorption–desorption, which could quantitatively measure acid amount and acid strength of the zeolites and catalysts, by means of a modified quartz furnace tube on the TG module of a Du Pont 9900 Computer/Thermal Analysis System. The data repeatability was very good and their precision is comparable with those of refs. 9, 11, 12 and 14. It was shown that catalyst acidity is closely related to activity for example, in the cases of Pt/MgO-CLM and H-β zeolite catalysts.

EXPERIMENTAL

Materials

Samples

HY and HZSM-5 zeolite as well as β zeolite catalysts were provided by Group 2202 and Group 402 respectively at the Research Institute of Petroleum Processing, Beijing. The Pt/Mg-CLM was prepared by Dr. Da Zhijian.

Gases

N_2 carrier (or purge gas, purity 99.999%) and NH_3 adsorbate (purity 99.999%) were produced by the Beijing Oxygen Factory.

Instrumentation

A 951-TGA (thermogravimetric analyzer) of a Du Pont 9900 Computer/Thermal Analysis System and a quartz furnace tube (QFT) modified by the authors were employed.

Procedures

The apparatus is shown schematically in Fig. 1. The QFT is inserted into the TGA furnace and the purge gas line and adsorbate line are connected to their inlets. The sample (about 10 mg) is put in the platinum basket and spread out carefully in an even thin layer. The desired experimental limit (initial equilibration temperature, heating rate, pretreat terminal temperature, isothermal time or TPD limited temperature) is then set using the TA program of the computer.

After completing the above procedures, the run program of the computer is started and the experimental operation is run according to the instructions from the computer program. During the experiment the introduction and stop for adsorbate NH_3 was manually controlled. When the run is complete, data processing is carried out by means of a specific data analysis program in the computer and the amount of NH_3 desorbed (a measure of the amount of acid of samples) and its desorption temperature (i.e. acid strength) could be obtained from the TG and DTG curves, respectively.

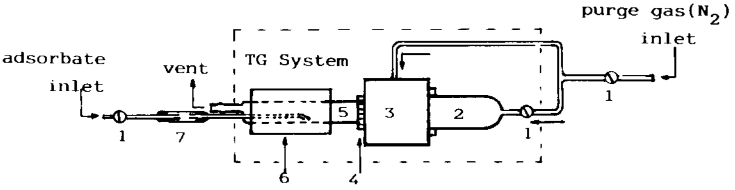

Fig. 1. Schematic diagram of the in situ TG apparatus for NH_3 adsorption–desorption experiments. 1, stop valve; 2, glass envelope; 3, balance assembly; 4, furnace tube retaining ring; 5, modified quartz furnace tube (QFT); 6, furnace assembly; 7, connector.

RESULTS AND DISCUSSION

Examination of the repeatability of the acidity data

HY zeolite was used as the reference sample. The repeatability experiments were carried out by means of NH_3 adsorption–desorption in situ TG on a Du Pont 9900 Computer/Thermal Analysis System. The relative standard deviation of the data, which were collected from 5 runs, was less than ±0.050. The complete run was scanned and the results are shown in Fig. 2.

In Fig. 2, the curve A is the complete TG curve, in which the sample mass changes with increase of time. The curve can be divided into the following segments: a–b is the pretreatment stage; b–c is an isothermal stage at 500°C; c–d is a decrease in temperature from 500 to 150°C and constant mass stage; d–f is NH_3 adsorption under isothermal conditions at 150°C; at point f NH_3 is entered manually; at f–g physically adsorbed NH_3 is purged

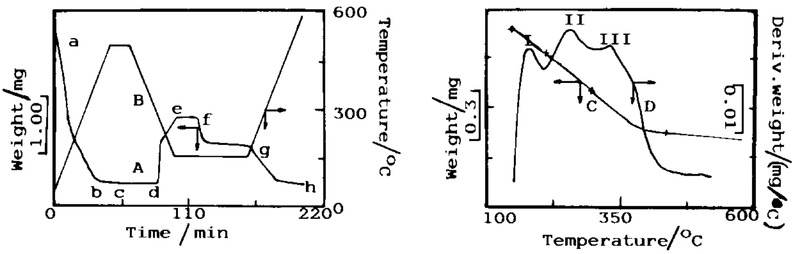

Fig. 2. NH_3 adsorption and desorption curves on HY zeolite. Curve A, complete NH_3 adsorption–desorption TG curve; curve B, programmed temperature curve; curve C, NH_3 desorption TG integral curve; curve D, NH_3 desorption DTG differential curve.

and the sample mass should become constant; g–h is the TPD stage at a heating rate of 10°C min^{-1} from 150 to 500°C.

Curve B in Fig. 2 represents the track of the temperature program and the response of each stage to the changed temperature situation. Curves C and D are, respectively, the TG integral curve and DTG differential curve for NH_3 desorption from 150°C to 500°C.

The DTG curve (curve D in Fig. 2) has three peaks (I, II and III) corresponding to three stages for NH_3 desorption; the temperatures of the peak maxima could provide a measure of the strength of NH_3 adsorption on HY zeolite (i.e. the acid strength of HY). The troughs of the curves could indicate the start and/or stop point of each peak. Hence the amount of NH_3 desorbed for each stage could be calculated from the mass change between two points on the TG curve. The results are listed in Table 1.

The data in Table 1 indicate that the relative standard deviation, which was calculated from five measurements of the amount of NH_3 chemically adsorbed at 150°C and of NH_3 desorbed from 150 to 500°C TPD for HY, was less than ±0.050. The repeatability of the desorption peak temperature of NH_3 in the three stages, taken as a measure of the adsorption strength of NH_3, was also good; the relative standard deviations of the amount of NH_3 desorbed in stages I, II and III were ±0.130, ±0.154 and ±0.106, respectively.

From our knowledge of the structure of Y-faujaste, it was deduced that the three acid sites mentioned above probably corresponded to three cation positions in the HY cage. However, the exact attribution of relations between acid sites and cation positions still needs to be confirmed by means of other techniques.

Examination of validity of the acidity data

In order to test the validity (or reliability) of acidity data measured using the situ TG, we have taken HZSM-5 zeolite as a reference sample and measured its acidity, as it has been commonly used by other catalysis

TABLE 1

Data repeatability for five measurements of NH_3 adsorption–desorption of HY by in situ TG

Test order	Amount of NH_3 adsorbed/ mmol g^{-1}	Total amount of NH_3 desorbed/ mmol g^{-1}	TPD from 150 to 500°C					
			Stage I		Stage III		Stage III	
			Amount of NH_3 desorbed/ mmol g^{-1}	Peak/°C	Amount of NH_3 desorbed/ mmol g^{-1}	Peak/°c	Amount of NH_3 desorbed/ mmol g^{-1}	Peak/°C
1	5.224	5.173	1.156	181	1.763	264	2.100	332
2	5.140	5.039	1.217	181	1.549	259	2.273	302
3	5.181	4.965	1.156	181	1.347	261	2.462	335
4	4.666	4.608	0.840	187	1.637	251	2.131	314
5	4.855	4.916	1.039	182	2.039	258	1.839	327
$\bar{X}$ [a,c]	5.013	4.940	1.082	182	1.667	258.6	2.161	322
S [b,c]	0.242	0.210	0.150	2.6	0.257	4.8	0.230	13.8
$S/\bar{X}$ [d]	0.048	0.042	0.130	0.040	0.154	0.019	0.106	0.043

[a] $\bar{X} = \sum_{i=1}^{n} X_i/n$. [b] $S = \sqrt{\sum_{i=1}^{n} (X_i^2 - n\bar{X}^2)/(n-1)}$. [c] $\bar{X}$, mean value of n time measurements; n, test time number; i, a given time; X_i, value of one arbitrary measurement. [d] $S/\bar{X}$, Relative standard deviation.

researchers to characterise acidity. The results are listed in Table 2. The acidity data for three measurements of HZSM-5 zeolite are compared with those obtained from other workers [9, 11, 12, 14].

The data in Table 2 show that the repeabability of three measurements with an HZSM-5 zeolite sample in which the SiO_2/Al_2O_3 ratio was 53 was good, the relative standard deviation being less than ±0.030. The acidity results approach those obtained from other techniques for HZSM-5 zeolite which had similar SiO_2/Al_2O_3 ratios and their peak temperatures of adsorbate desorption were close to each other. Therefore the method of NH_3 adsorption–desorption measured using in situ TG is valid and reliable for measurement of the solid catalyst surface acidity.

Catalysts' acidity and activity

Relationship between the acid amount of the Pt/MgO-CLM catalysts and the hydrocracking activity for cumene

The activity evaluation experiment was carried out using a pressure microreactor. Test conditions were as follows: Pt in sample, is 0.6 mass%; hydrogen pressure, 1.96 MPa; hydrogen flow rate, 60 ml min^{-1}; amount of catalyst, 100 mg; the reaction temperature, 300°C; cumene dose, 0.2 μl.

TABLE 2

Comparison of acidity data for HZSM-5 measured by different methods

Sample SiO_2/Al_2O_3	Carrier gas	Adsorbate	Adsorption temp./°C	Acid amount [a]		Acid strength distribution		Ref.
				mmol g^{-1}	Sites × 10^{20} g^{-1}	Peak I/°C	Peak II/°C	
53	N_2	NH_3	150	0.7304	4.40	203	425	This work
				0.6928	4.17	202	376	This work
				0.7016	4.27	201	416	This work
$S/\bar{X}$ [b]				0.028	0.027	0.005	0.060	This work
48	He	Ethylamine	150	0.7248	4.38	225	425	9
52	He	NH_3	150	0.7706	4.64	230	435	11
47.3	He	NH_3	150	0.7505	4.52	194	405	12
49.5	He	NH_3	70	0.7803	4.70	200	480	14

[a] Units of some data have been converted in order to allow comparison with results presented here.

[b] $S/\bar{X}$, Relative standard deviation.

TABLE 3

Relationship between the acid amount of the Pt/MgO-CLM catalysts and their activity

Sample no.	MgO/ mass%	Acid amount mmol g^{-1}	Hdrocracking activity for cumene/mass%			
			Total conversion	$<C_3$	$<C_9$	i-C_A [a]
1	0.5	0.4890	8.11	5.97	0.56	1.58
2	1.0	0.4415	5.36	3.12	0.65	1.60
3	3.0	0.3831	3.76	1.72	0.51	1.54

[a] Isoaromatic hydrocarbons

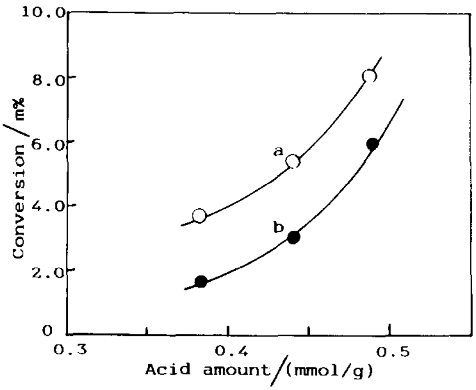

Fig. 3. Relation between the cumene hydrocracking activities and the acidities of Pt/MgO-CLM catalysts: curve a, total conversion; curve b, $<C_3$ yield.

The results are listed in Table 3 and shown in Fig. 3. The data showed that the acid amount of catalysts was closely related to the MgO component of the samples. The acid amount decreased with increase of the amount of MgO in the catalysts; it was obvious that some of the acid sites had been poisoned by basic MgO. However, the total conversion and $<C_3$ yield of the hydrocracking reaction on those catalysts for cumene depended on the acid amount of the samples.

It is well known that the acid function of the catalysts had an essential effect on hydrocracking activity for cumene, and their hydrogenation function was provided by the platinum in the samples. The platinum of all samples was 0.6 mass%, so the yields of $<C_3$ hydrocarbons and iso-aromatics (i-C_A) in the reaction generally remained constant.

Relation between the acid amount of H-β zeolite catalysts and their α values for cracking reaction of n*-hexane*

The H-β zeolite catalysts were prepared as follows: The Na-β zeolites were exchanged using $(NH_4)_2SO_4$ solution according to conventional procedures to obtain NH_4-β zeolites (with different SiO_2/Al_2O_3 ratios)

TABLE 4

Test results of physicochemical properties of β zeolite samples

Sample no.	Crystal/%	Na_2O/ mass%	SiO_2/Al_2O_3	α	Acid amount/ mmol g^{-1}	Distribution of acid strength/mmol g^{-1}		
						150–250°C	250–350°C	350–500°C
1	80	0.015	21.9	512.0	0.9905	0.3076	0.3778	0.3014
2	80	0.012	38.8	441.0	0.6755	0.2252	0.2815	0.1689
3	>100	0.045	57.1	273.4	0.3710	0.2254	0.1484	0.1072

which were subjected sequentially to washing, filtration, extrusion, drying at 120°C and calcination at 540°C for 4 h to give H-β zeolites which were then crushed to 18–36 mesh for use in tests.

The α values of samples was measured according to the method described in ref. 15, employing an SQ-204 gas chromatograph and a micro reactor system. The definition of α is

$$\alpha = K_{\text{samp.}}/K_{\text{ref.}}$$

where $K_{\text{samp.}}$ and $K_{\text{ref.}}$ are the first order velocity constants (s^{-1}) of reaction for n-hexane on the given sample and amorphous SiO_2–Al_2O_3 (as reference), respectively.

The acidities of three H-β zeolite samples were determined by the in situ TG method. As before, the total acid amount of the samples could be calculated from TG mass loss curve. The distribution of their acid strengths could also be obtained from the mass changes that corresponded to three desorption stages, i.e. three temperature ranges (150–250°C, 250–350°C and 350–500°C) on TG during TPD.

The test data listed in Table 4 show that samples are all more than 80%

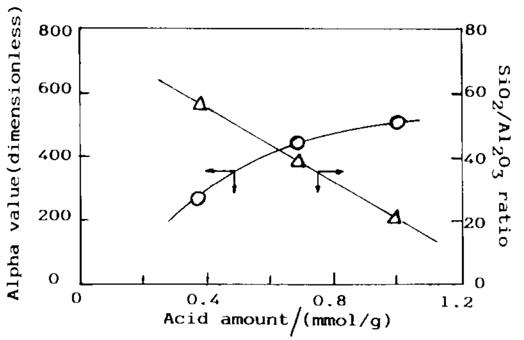

Fig. 4. Relationship between acid amount of H-β zeolites with different SiO_2/Al_2O ratios and α for n-hexane on H-β zeolite catalysts.

crystalline with less than 0.050% Na_2O. The total acid amount decreased with increase of the SiO_2/Al_2O_3 ratios in zeolite samples and the α value of catalysts simultaneously diminished. The changes of acid amount with SiO_2/Al_2O_3 ratios appeared to be a straight line with uniform slope; however the changes of acid amount with α value were a smooth curve, these results are clearly exhibited in Fig. 4. It is obvious that the α value, which is a measure of cracking activities of catalysts, is closely related to their acidities.

CONCLUSIONS

Solid catalyst surface acidity could be measured by means of NH_3 adsorption–desorption with in situ TG using a Du Pont 9900 Computer/Thermal Analysis System. The repeatability of the acidity data collected from five test runs for the HY sample is very good and the relative standard deviation is less than ±0.050. The test results for HZSM-5 are in close agreement with those of references.

The acidities of Pt/MgO-CLM and the β zeolite catalysts, measured by means of in situ TG were closely related to the catalytic activities of the samples.

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