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Characterization of acid catalysts by thermometric titration

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Thermometric titration as a method suitable for the characterization of the acidity of catalysts is presented. The determination of the acid strength, the end point of titration and the total heat of neutralization by thermometric titration is tested using samples of benzoic acid, zeolite NaHY and unsupported and supported (TiO_2, SiO_2, $SiO_2{\cdot}Al_2O_3$) tungstosilicic acid. The determination of the end point of titration acidity is discussed. The method is recommended for the determination of the total neutralization enthalpy as well as the enthalpy of the neutralization of the strongest acid centers in solid catalysts.

KEY WORDS: thermometric titration; acidic properties; acid catalysts; hetropoly compounds; 12-tungstosilicic acid; oxide supports.

1. Introduction

From the catalytic point of view the determination of the acidity of a catalyst presents an important but complicated problem. It has been tackled by many investigators. In 1935 the acid strength of catalysts was characterized by Hammett [1], who was using colored indicators. This method has two shortcomings: it is not applicable for colored and dark samples and the acid strength is characterized only by a certain pH interval. Apart from the acid strength measurements, the number of acid sites was first determined by Tamele [2] in 1950. He titrated with *n*-butylamine a solid catalyst suspended in benzene and used the Hammett indicator. This method was also limited to white samples. Trambouze *et al.* [3] in 1954 developed thermometric titration. They titrated with dioxane a silica–alumina sample suspended in benzene and controlled the changes of temperature using a thermocouple connected to a galvanometer. Topchieva *et al.* [4] in 1964 replaced the fast titration applied in [3] by slow titration. Tanabe and Yamaguchi [5] in 1970 and also Bakashi and Gavalas [6] in 1975 replaced the thermistor by a Beckman thermometer and dioxane by *n*-butylamine.

However, the latter authors used thermometric titration for determination of the differential heat of acid-site neutralization, not being interested in the determination by this method of the total concentration of the acid sites.

Since that time laboratory techniques have made distinct progress in the precision of temperature measurements and registration. The aim of the present research was to verify the application of improved thermometric titration methods based on the use of a precise thermistor thermometer and computerized registration of the results.

2. Experimental

Four series of samples were used: (1) benzoic acid, (2) NaHY zeolite ($Na_{6.44}H_{49.56}(AlO_2)_{51.9}(SiO_2)_{140.1}$, cation exchange 88.5%), (3) dodecatungstosilicic acid $H_4SiW_{12}O_{40}{\cdot}23.6H_2O$ (HSiW) (p.a. Fluka), (4) catalysts: HSiW supported on TiO_2, SiO_2, $SiO_2{\cdot}Al_2O_3$ obtained as described in [7]. The coverage of the catalyst's surface with HSiW corresponded to 0.25 monolayer. Before thermometric titration all samples were dehydrated and transferred immediately into the titration apparatus. Zeolite NaHY was activated in vacuum by heating for 1 h at 393 K and subsequently 4 h at 773 K. HSiW was dehydrated by heating for 4 h at 373 K. After such pretreatment, heteropolyacid contained only constitutional water (2 mol of water per 1 mol of HSiW) controlled by DTG. *n*-Butylamine (p.a. Aldrich) was distilled before experiments. A solution of *n*-butylamine (1.0 M) used for thermometric titration was prepared by dissolving a known amount of amine in toluene.

The titration was carried out in a Dewar vacuum flask equipped with a thermistor and filled with 100 ml of toluene, Teflon stirrer and microburette with 1.0 M *n*-butylamine solution in toluene [8]. The changes of temperature were measured with an accuracy of ±0.015 °C. The heat capacity for this system was determined electrically and hence the heats of reaction of our catalysts with *n*-butylamine could be computed. After thermometric titration an excess of amine solution was added to the Dewar. In order to determine the amount of amine not reacting a chemical analysis was done. 10 ml of solution was titrated with aqueous solution of hydrochloric acid (0.2 mol/dm^3) in the

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presence of bromothymol blue as the indicator. In the course of titration the vessel containing non-mixed liquids was intensively agitated.

In addition, in the case of NaHY zeolite the acidity was determined by thermometric titration with *n*-butylamine dissolved in benzene using Hammett indicators ($H_0 \leq 0.8$ and $H_0 \leq 4.8$) as described in [5].

3. Results

Figure 1 shows the thermometric titration curve of benzoic acid, which easily dissolves in toluene. The consecutive portions of amine were introduced to the system at 5 min intervals and temperature was continuously registered. It is seen that after the addition of each portion of amine after a short time a constant temperature level was reached. Such constant level temperatures are shown in figure 2 as a function of the amount of *n*-butylamine introduced into the system. An analogous curve presenting the results of the titration of the sample of NaHY zeolite is shown in figure 3.

4. Discussion

The following data may be in principle obtained from the thermometric titration of an acid solid catalyst: the concentration of the acid sites calculated from the end point of the titration, the enthalpy of neutralization ΔH_1 of the strongest acid centers, the total sorption (neutralization) enthalpy ΔH_T and also differential sorption enthalpies ΔH_d being calculated from the particular temperature increments or the slope of the linear sections of the graph.

Figure 2 shows that in the case of titration of benzoic acid dissolved in toluene the temperature *versus* volume of 1 M *n*-butylamine plot ($T-V$ plot) is composed of two linear sections and the end point of titration can be easily read from their intersection point P. In three consecutive determinations, 7.88 ± 0.40 mmol of *n*-butylamine were used per 1 g of the dissolved acid as compared with the value 8.196 known from the stoichiometry. It should be observed here that the linearity of the $T-V$ plot is due to the fact that all acid molecules had the same acid strength and hence the same neutralization heat.

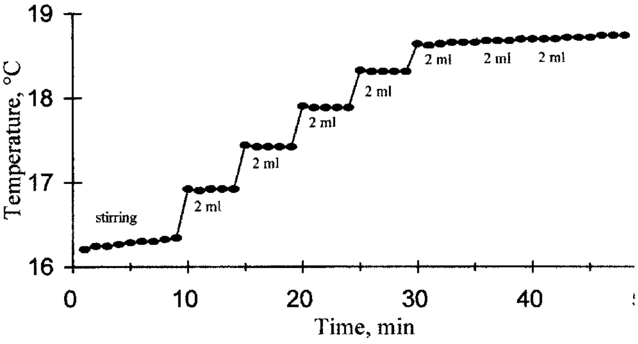

Figure 1. Slow thermometric titration of benzoic acid dissolved in toluene (2 ml of *n*-butylamine solution in toluene added at intervals of 5 min).

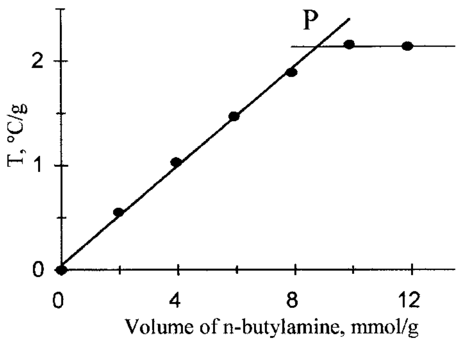

Figure 2. Thermometric titration curve of benzoic acid with *n*-butylamine.

However, the situation is not as simple as that if we titrate solids containing acid centers of different strength. In such a case the thermal effect corresponding to the consecutive portions of *n*-butylamine decrease with increasing number of titrant portions and the unequivocal determination of the final point of titration is difficult.

Trambouze *et al.* [3] used point A (figure 3), the intersection point of the extrapolation of the initial linear section and the line corresponding to the final constant temperature independent of further addition of *n*-butylamine. Topchieva *et al.* [4] on the other hand used the first point on the constant temperature line, *i.e.* point B.

Table 1 presents the data for NaHY characterizing the reproducibility of the values corresponding to the particular points. The standard deviation of points A and B was respectively 3.7% and 5%. However, there is a distinct difference between the total acidity values calculated from the positions of points A and B. In such a situation the additional point C was introduced.

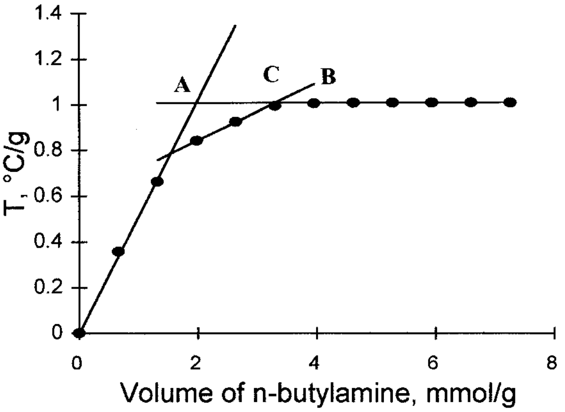

Figure 3. Thermometric titration of NaHY suspended in toluene (1 ml of *n*-butylamine solution added at different intervals).

Table 1
Total acidity of NaHY (mmol/g)

Point A	Point B	Point C	Hammett titration	
			$H_0 \leq 0.8$	$H_0 \leq 4.8$
2.15 ± 0.08	4.00 ± 0.2	3.33 ± 0.3	2.57 ± 0.17	2.88 ± 0.1

Point C is the intersection of the regression line taken over the last points of titration and the constant temperature line was assumed as the end point of titration. The result obtained for this latter point was comparable with the total content of acid sites determined by the Hammett method ($H_0 \leq 4.8$). However, the reproducibility of the results was worse.

Hence the thermometric determination of the total number of acid sites by the thermometric titration with *n*-butylamine cannot be recommended for such catalysts in which the values obtained from points A, B and C disagree. In fact, in the case of titration of benzoic acid all three points merge into a single point P.

It should be here observed that in the case of the series of HSiW-supported catalysts the point C determinations of the total content of acid sites corresponded quite satisfactorily with the value obtained by chemical analysis (table 2). Consequently, despite all the difficulties in determining the final point of thermometric titration we would rather recommend the C-point calculation of the total acidity.

Another detail which can be obtained from thermometric titration is total neutralization heat ΔH_T, which is *n*-butylamine sorption calculated either per mass unit of the catalyst or per mole of *n*-butylamine used. The latter value, which is in fact the heat, enables better comparison of the catalysts in one series.

In the case of NaHY zeolite the total neutralization enthalpy was -0.31 ± 0.01 kJ per g of catalyst, which corresponded to -96.6 ± 3.03 kJ per mole of used *n*-butylamine (calculated from point C). Also, in the case of silica-supported HSiW, the total neutralization enthalpy calculated per catalyst's mass, -0.29 ± 0.02 kJ, reached quite satisfactory precision. From the latter value the average neutralization enthalpy was -40.9 ± 5.8 kJ per *n*-butylamine mole. The values obtained for the series of supported HSiW catalysts are given in table 2.

Table 2
Total acidity and acid strength of catalysts containing dodecatungstosilicic acid $H_4SiW_{12}O_{40}$ on different supports

Catalyst	Point C (mmol/g)	Chemical analysis (mmol/g)	$-\Delta H_1$ (kJ/mol)	$-\Delta H_T$ (kJ/mol)
$HSiW/TiO_2$	3.8	3.8	112	56.7
$HSiW/SiO_2$	1.6	1.5	102	40.9
$HSiW/SiO_2{\cdot}Al_2O_3$	1.9	1.8	76	36.6
HSiW	2.9	3.1	120	77.2

In the latter series of catalysts the initial part of the $T-V$ graph was linear and from its slope the enthalpy of neutralization of the strongest acid centers, ΔH_1, was calculated. In the case $HSiW/SiO_2$ it was -102 ± 1.1 kJ/mol. On the other hand the analogous value obtained from the titration of unsupported $H_4SiW_{12}O_{40}$ was -120 ± 3 kJ/mol. The comparison of both values indicates that the acid strength of HSiW decreased on the support.

It should be observed here that in the case of titration of unsupported heteropolyacid the amount of used *n*-butylamine corresponded to roughly 4 *n*-butylamine per proton in HSiW. This was due to the penetration of polar amine into the bulk of dehydrated heteropolyacid and consecutive formation of monoprotonated amine and subsequently protonated dimers, trimers and tetramers. The formation of such protonated clusters was described, *e.g.* by Misono *et al.* [9]. Sorption of *n*-butylamine from the gas phase and also from the solution is very fast even at room temperature. In our case the initial sorption enthalpy, 120 kJ per mole of amine, corresponded to the formation of protonated monomer.

The values of both the average neutralization enthalpy and the neutralization enthalpy of the strongest acid sites considered to be determining the catalytic activity changed in the following sequence:

$$\text{HSiW unsupported} > HSiW/TiO_2 > HSiW/SiO_2 > HSiW/SiO_2{\cdot}Al_2O_3$$

This corresponded well to sequence of the activities:

$$\text{HSiW unsupported} > HSiW/TiO_2 > HSiW/SiO_2 > HSiW/SiO_2{\cdot}Al_2O_3$$

of the same series of catalysts in the gas-phase formation of methyl–*tert*-butyl ether at 40 °C.

This indicates that the method of thermometric determinations of both enthalpies can be recommended as a simple and inexpensive method of characterizing the acidity of the catalysts.

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