

DETERMINATION OF BASIC SITES ON THE SURFACE
OF METAL OXIDE CATALYSTS
BY DESORPTION OF BENZOIC ACID

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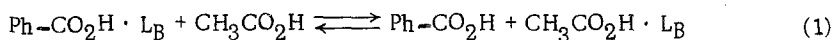
A method has been developed for the determination of the concentration of basic sites on white and deeply colored solid porous materials, which is based on the displacement of adsorbed benzoic acid by acetic acid. The determination is rapid and gives results comparable with those obtained by the titration with benzoic acid using thymolphthalein as indicator.

Был разработан метод определения концентрации основных центров на белых и глубоко окрашенных твердых пористых материалах. Метод основан на замещении адсорбированной бензойной кислоты уксусной кислотой. Определение является быстрым и дает результаты, подобные результатам, полученным титрованием бензойной кислоты, используя тимолфталейн в качестве индикатора.

The surface concentration of basic sites on a solid catalyst can be determined by several methods /1/. The standard procedure is based upon adsorption of an indicator on basic sites and titration with benzoic acid /2/. Non-polar hydrocarbons, such as isooctane or benzene, are used as solvents and a wide range of indicators is recommended for end-point determination /1/. The titration may be conducted also in an aqueous medium; for instance, the concentration of strongly basic sites on the silica surface saturated with sodium hydroxide was determined by titrating a suspension of silica in water with a solution of sulfuric acid /3/. All titration methods using adsorbed indicators fail when applied to colored or black solid materials. In such cases, a back titration /4/ may be car-

ried out, but the results are influenced by physical adsorption of the acid used. The surface concentration of basic sites has been determined also by measuring the amount of carbon dioxide or boron trifluoride adsorbed from the gas phase /5, 6/ and by calorimetric titration /7/. Both methods have been applied with success also to colored samples; the large sample consumption, amounting to several grams for one determination is, however, a great disadvantage of the latter procedure.

The method reported in this communication is based upon the adsorption of benzoic acid on basic sites and displacement of the adsorbed acid by an excess of acetic acid, eq. (1), using a flow-through-arrangement.



The amount of desorbed benzoic acid is determined by means of a differential UV analyzer. A comparison with the titration method developed by Tanabe and Yamaguchi /2/ is given.

EXPERIMENTAL

Methanol and benzoic acid, both analytical reagent grade chemicals (Lachema, Brno, Czechoslovakia), were used as obtained. Acetic acid was purified by distillation from KMnO_4 to remove substances exhibiting absorbance at 254 nm. Chromium(III) oxide was prepared by calcination of chromium(III) hydroxide at 600 °C. Samples of alumina (Brockman's II for TLC; Reanal, Hungary), iron(III) oxide (Girdler G-3B) and cerium(IV) oxide (pract. pure, Fluka A. G., Switzerland) were obtained by grinding and sieving of commercial materials. Fractions containing particles ≤ 0.07 mm in diameter were used for all determinations.

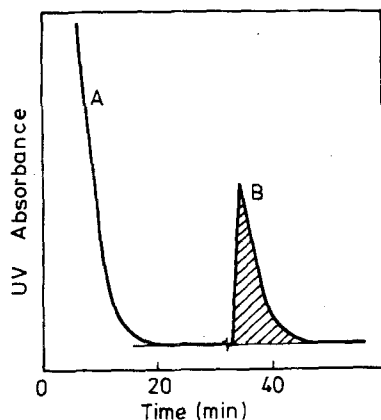


Fig. 1. Elution (A) of unadsorbed benzoic acid by methanol (flow rate 0.5 ml/min) and displacement (B) of adsorbed benzoic acid by an excess of acetic acid (0.05M solution in methanol; flow rate 0.5 ml/min) from alumina (32 mg; see Table 1, No. 1)

In a typical experiment, a sample of a metal oxide (20–50 mg) was charged into a short glass column (I. D. 3.5 mm) between two layers of glass ballotini (particle size 0.05–0.1 mm) and the column was terminated by low-volume fittings. A 0.5M solution of benzoic acid in methanol was passed through the sample to cover all basic sites by benzoic acid. The unadsorbed benzoic acid was eluted with pure methanol which was passed up the column at a flow rate of 0.5 ml/min with a syringe pump; the time necessary for this operation was 30 min. Pure methanol was replaced by a 0.05M solution of acetic acid in methanol introduced onto the column at a flow rate of 0.5 ml/min. The amount of desorbed benzoic acid was monitored continuously by means of a double-beam UV analyzer (Development Works, Czechoslovak Academy of Sciences, Prague) measuring the absorbance at 254 nm, connected to a TZ 21S linear recorder (Laboratory Instruments, Prague); a time vs. concentration curve pertaining to desorbed benzoic acid was recorded (Fig. 1). The experiments using a column packed with

Table 1
Surface concentrations of basic sites ($pK \geq 9.7$) on
various metal oxides

No.	Metal oxide	Calcination temperature ($^{\circ}C$)	Surface area ^a (m^2/g)	Concentration ($\mu mol/m^2$)	
				desorption	titration ^b
1	Al_2O_3	450	82	1.58	1.46
2	Al_2O_3	650	76	1.67	1.58
3	Al_2O_3	850	41	1.10	1.46
4	Cr_2O_3	600	8.5	2.35	-
5	Fe_2O_3	200	65	1.77	-
6	CeO_2	200	15.5	2.25	-

^a Measured by the BET method;

^b Determined by titration with benzoic acid, using thymolphthalein as indicator

glass ballotini only, gave a zero value. The amount of desorbed benzoic acid was calculated with the aid of calibration and by integrating the time vs. concentration curve. Under standard conditions, the relative error did not exceed 5%.

The titration of basic sites on samples of alumina was carried out according to the known procedure using thymolphthalein as indicator ($pK = 9.7$) /2/. The equilibrium was attained after 24 hrs and the color change at the end point was rather indistinct.

RESULTS

The surface concentrations of basic sites found for different samples of alumina are summarized in Table 1. This oxide was chosen for a comparison be-

tween the standard titration method /2/ and that based on the displacement of adsorbed benzoic acid by acetic acid.

It is evident that a good agreement exists between both methods, indicating that the surface concentration of basic sites ($pK \geq 9.7$) can be satisfactorily determined using our method. The results of basicity measurements carried out with several colored metal oxides are listed in Table 1. In summary, the method described is more rapid (2 hrs) and more sensitive than the known procedures and requires only negligible amounts (20–50 mg) of a sample for one determination. The method has been used by us with success for determining the relationship between the surface concentration of basic sites and the catalytic activity of various metal oxides in aldolisation reactions.

REFERENCES

1. K. Tanabe: *Solid Acids and Bases*, Chapter 3, Kodansha, Tokyo 1970.
2. K. Tanabe, T. Yamaguchi: *J. Res. Inst. Catalysis, Hokkaido Univ.*, 11, 179 (1963).
3. S. Malinowski, S. Sczepanska: *J. Catal.*, 2, 310 (1963).
4. K. Shibata, T. Kioura, K. Tanabe: *J. Res. Inst. Catalysis, Hokkaido Univ.*, 18, 189 (1970).
5. G. M. Schwab, H. Kral: *Proc. IIIrd Intern. Congr. Catalysis, Amsterdam*, Vol. I, No. 20, North-Holland Publishing Co., Amsterdam, 1964.
6. S. Malinowski, S. Sczepanska, J. Sloczynski: *J. Catal.*, 7, 68 (1964).
7. K. Tanabe, T. Yamaguchi: *J. Res. Inst. Catalysis, Hokkaido Univ.*, 14, 93 (1966).