React. Kinet. Catal. Lett., Vol. 19, No. 3–4, 307–310 (1982)

DETERMINATION OF ACID SITES ON CARBON SURFACE

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Received November 23, 1981
Accepted December 16, 1981

Pyridine chemisorbed on acid sites of active carbon was displaced by n-butylamine and the displaced amount was measured spectrophotometrically. This amount, supposed to be proportional to the surface concentration of carboxy groups, depends on the chemical pretreatment of active carbon.

Пиридин, хемосорбированный на кислых центрах активного угля, был измерен спектрофотометрически. Это количество, которое должно быть пропорционально концентрации карбоксильных групп на поверхности, зависит от предварительной химической обработки активного угля.

Various chemical reactions have been suggested to determine the chemical structure of acid groups occurring on the surface of active carbon. Carboxy, carbonyl, and phenol groups have been identified as acid sites, the first being the strongest one. A method based on the titration of acid groups with sodium carbonate, hydroxide and methoxide was proposed by Boehm /1/ to distinguish between these sites. Using this method, valuable information about the acidity changes caused by surface oxidation and reduction has been obtained /1, 2/.

The surface acidity has an important effect on the sorption properties of active carbon. This acidity may influence the activity of supported catalysts if active carbon is used as the catalyst carrier. It has been shown that the catalytic activity of palladium on carbon used in the synthesis of vinyl acetate decreases with increasing concentration of the surface carboxy groups. The number and size of palladium microcrystallites depend upon the number of cation-exchange sites /2/.

Recently, we have described a novel method for the determination of the surface acidity of porous solids /3/. This method, which is feasible for white as well as deeply colored samples, is based on the displacement of an aromatic base by a stronger aliphatic base from the acid sites. We used the displacement of pyridine by n-butylamine, because the amount of pyridine is determined easily by means of a UV-spectrophotometer.

The aim of the present work has been to apply the displacement method to the determination of the surface acidity of active carbon. In order to change this activity in a known manner, samples of active carbon were treated with nitric acid and hydrogen.

EXPERIMENTAL

Active carbons. Several samples of commercial active carbons (Norit, N. V. Amsterdam, The Netherlands; Chemviron, Zürich, Switzerland; Slovak Chemical Works, Hnústa, Czechoslovakia) denoted as samples I–VIII were boiled with distilled water, dried and crushed. The fractions of 30–70 μm were used throughout all experiments. All samples were dried in a stream of nitrogen (flow rate 20 ml/min) at 150 °C for 1 h.

Acidity measurement. The apparatus as well as the experimental procedure have been described earlier /3/. The apparatus was equipped with a stainless steel cell, which makes it possible to dry the samples in a proper atmosphere (N_2 or H_2) up to 500 °C. This cell consists of a tube 50 mm long (I. D. 4 mm) and two Swagelok type units. Solutions of pyridine (2.5 mmol/l) and n-butylamine (50 mmol/l) in dry cyclohexane ware used for the preadsorption and the displacement, respectively.

RESULTS

The amounts of pyridine consumed during preadsorption and liberated during displacement are given in Table 1. The differences between various commercial carbons are apparent. The greatest acidity is exhibited by sample VI, impregnated with phosphoric acid /4/.

The oxidation of a carbon surface with nitric acid leads to an increase in the surface acidity /1, 5/. On the other hand, the heating of active carbon in an atmosphere of hydrogen decreases the number of acid sites. It has been observed that in the course of such a reduction or oxidation the number of carboxy groups changes markedly /5, 6/.

Therefore, the apparent changes in the amount of displaced pyridine due to surface oxidation and reduction (Table 1) led us to the conclusion that pyridine is displaced only from the carboxy groups. This is in good agreement with our previous experiments with alumina, documenting that pyridine adsorbed on very weak

Table 1
Amounts of preadsorbed and displaced pyridine referred to unit surface area of carbon

Sample	Surface area[a] (m^2/g)	Pyridine ($\mu mol/m^2$) Preadsorbed	Pyridine ($\mu mol/m^2$) Displaced	Code
I	990	0.26	0.07	GA-1[b]
II[c]	990	0.34	0.13	–
III[d]	990	0.25	0.09	–
IV	970	0.15	0.01	CAL 12 x 40[e]
V	740	0.32	0.08	–[f]
VI	540	1.00	0.19	DEZOREX FB-4[b]
VII	1513	0.16	0.01	Supersorbon H83[g]

[a] Determined by the BET method.
[b] Slovak Chemical Works, Hnúšta, Czechoslovakia.
[c] Prepared by oxidizing Sample I with boiling HNO_3 for 1 h.
[d] Sample II heated in hydrogen at 350 °C for 1 h.
[e] Chemviron, Zürich, Switzerland.
[f] Norit N. V., Amsterdam, The Netherlands.
[g] Degussa, Frankfurt a.M., FRG.

acid sites of alumina ($pK_a > 6$) can be eluted with dry cyclohexane. Thus, the difference between the preadsorbed and the displaced amount of pyridine given in Table 1 may be due to the chemisorption of pyridine on weakly acid phenol or carbonyl groups and to physical adsorption.

Some of the active carbons examined were used in the preparation of supported platinum catalysts for the oxidation of hydroxymethyl to carboxy groups /7/. It is worth mentioning that the oxidation activity of these catalysts prepared according to Zelinsky and Glinka /8/ decreased with increasing acidity of the carbon carrier /9/. This observation demonstrates the effect of the chemical nature of carbon surface on the reduction of adsorbed chloroplatinic acid, which is carried out by formaldehyde in an alkaline aqueous medium. An opposite effect of carboxyl concentration upon palladium-on-carbon catalysts prepared by reduction of palladium chloride with hydrogen has been reported by Siedlewski and Smiegel /2/.

The main advantage of the above method proposed for acidity determination lies in its applicability to a broad range of solids. Moreover, its good accuracy enables to observe even the slightest changes in the surface acidity. The results lead us to the conclusion that the method can be useful in the characterization of different catalysts and sorbents. Its improvement is a subject of further investigation.

REFERENCES

1. H. P. Boehm: Advan. Catal., *16,* 179 (1966).
2. J. Siedlevski, W. Smigiel: Chem. Stos., *20,* 455 (1979).
3. Z. Vít, L. Nondek, J. Málek: React. Kinet. Catal. Lett., *14,* 459 (1980).
4. Catalogue of Active Carbons, Slovak Chemical Works, Hnústa, Czechoslovakia, 1978.
5. J. Siedlewski, W. Smigiel: Chem. Stos., *21,* 509 (1977).
6. J. Siedlewski, W. Smigiel: Chem. Stos., *20,* 443 (1976).
7. L. Nondek, D. Zdárová, J. Málek, V. Chvalovský: Collect. Czech. Chem. Commun. (in press).
8. N. Zelinsky, N. Glinka: Ber. Deut. Chem. Ges., *44,* 2305 (1911).
9. L. Nondek, J. Málek, unpublished results.