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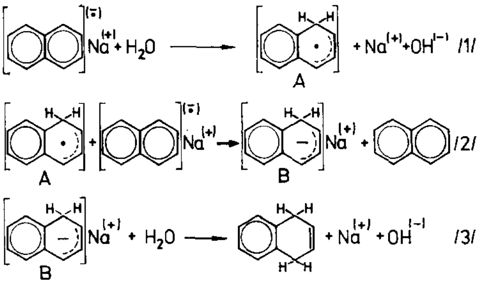
Determination of Hydroxyl Groups and Water Adsorbed on the Surface of Heterogeneous Catalysts by Titration with Alkali Metal Naphthenide Solutions

In this Note we present a method for determining the concentrations of hydroxyl groups and water adsorbed on the surfaces of heterogeneous catalysts by titrating the catalyst suspension in dry tetrahydrofuran (THF) with alkali metal naphthenide solution. The method which we propose is based on the well-known reactions of anion radicals of aromatic hydrocarbons with protons. Anion radicals derived from alkali metal naphthenides have very strong basic properties. Their basic strength H equals about 33, which means that they are able to detach a proton from molecules of compounds with $pK_a \leqslant 33$ (*1*). A mechanism of anion radical protonation was proposed by Paul *et al.* (*2*). The reaction of alkali metal naphthenides with water may be written as follows.



The first step of the reaction is the addition of a proton to the anion radical resulting in the formation of the hydronaphthyl radical (A). This radical is rapidly reduced to an anion (B) which forms 1,4-dihydronaphthalene after addition of the next proton. The slowest step is that described by Eq. (1). The rate constant of this reaction step at 20°C in a tetrahydrofuran solution is $1.0 \times 10^4\ M^{-1}\ S^{-1}$ (*1*). The electron transfer from the anion radical to the intermediate hydronaphthyl radical [Eq. (2)] is very rapid. Hoijtink *et al.* (*3*) showed that the electron affinity of the hydronaphthyl radical is higher than that of the parent molecule. The last step of the reaction, i.e., protonation of the hydronaphthyl anion, is also very fast, the conjugated carbanion being a stronger base than the anion radical (*1*).

Considering a balance of all three reaction steps one may ascertain that, as a result of the reaction with two protons (in this case from two water molecules), two molecules of sodium naphthenide have undergone decomposition, so the reaction is completely stoichiometric. The stoichiometric proceeding of the reaction of sodium naphthenide with water was demonstrated by us in the following manner. A known volume of sodium naphthenide solution in THF was decomposed with an excess amount of water; the quantity of the resulting sodium hydroxide was measured by titrating with HCl titrant using phenolophthalein as indicator. The same volume of naphthenide solution in THF was titrated with water, the end point being marked by the disappearance of the green color. We found that the amount of water consumed in sodium naphthenide titration was the same as that of the sodium hydroxide formed in the reaction of the first procedure. Thus, it may be concluded that the reaction proceeds entirely stoichiomet-

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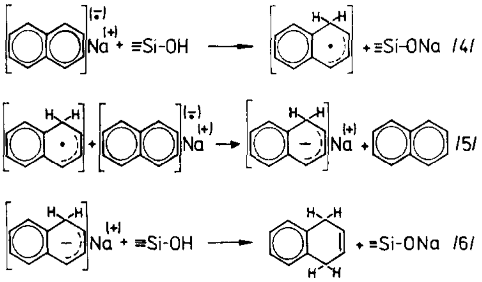
rically. The mechanism presented above also applies to the case of other proton donors, including OH groups and water adsorbed on the surfaces of heterogeneous catalysts. We suppose that, in the case of surface hydroxyl groups (e.g., on a SiO_2 surface), the reaction proceeds as follows.



Alkali metal naphthenide solutions have an intense dark-green color, which is clearly observable, even at a concentration below 0.005 *M*. Decomposition of the salt as a result of reaction with a proton is of course accompanied by disappearance of the color of the solution. Alkali metal naphthenides, therefore, are very good reagents for titration, the end point of which may be determined by noting the appearance of a nonfading dark-green color. Alkali metal naphthenides are paramagnetic in the sense of ESR spectroscopy. Naphthalene anion radical spectra obtained using the paramagnetic spin-resonance method are well defined (*4*). Titration of OH groups and adsorbed water may be also carried out by recording the ESR spectra of the catalyst suspension after adding each drop of the anion radical solution. The appearance of a nonfading ESR signal characteristic of the naphthalene anion radical marks the end of the titration. We have found that the anion radical signal occurs after addition of an excess drop of naphthenide, in the ESR spectra of both the suspension and the filtered-off catalyst.

The application of the method to hydroxyl groups and adsorbed water determination does not involve errors resulting from side reactions, as in the case of titration with the Karl Fischer reagent (*5*) or the case of gaseous diborane (*6*). The basic strength of the anion radical is so great that competing reactions of the sodium cation are not possible. Titration with alkali metal naphthenide solutions is faster and less complicated than the pulse chromatographic method proposed by Nondek (*7*). The advantage of our method lies in its high sensitivity (even at great dilution, alkali metal naphthenide solutions possess their characteristic green color) enhanced by the additional possibility of following the reaction by the ESR method. We have ascertained that our results (Table 1) are comparable to the results obtained using the chromatographic method according to Nondek (*7*). The reproducibility of the results is satisfactory, and the relative error is approximately 10%. The reaction is very fast, and, therefore, successive drops of the titrant may be added at short time intervals. An important advantage of the method is the simple apparatus and easy preparation of the titrants.

Tetrahydrofuran (Loba Chemie, for chromatography) was purified by distillation from the benzophenone–potassium system. Naphthalene (Koch–Light, puriss) was purified by sublimation. Solutions of sodium naphthenide and potassium naphthenide in THF were obtained by a method analogous to that proposed by Scott *et al.* (*8*).

The concentrations of the solutions prepared were approximately 0.50 *M* for sodium naphthenide and 0.10 *M* for potassium naphthenide. A number of two-component catalysts, characterized according to Tanabe *et al.* (*9*) by high Brønsted acidity, and also alumina and silica gel were investigated. SiO_2 and silica–alumina (8.7 : 1.3) were industrial preparations. Al_2O_3 was obtained by precipitating $Al(OH)_3$ with water from a benzene solution $Al(iso\text{-}OC_3H_7)_3$. The hydroxide was then

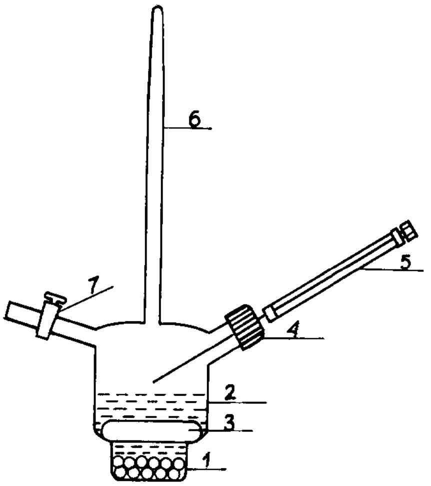


FIG. 1. Apparatus for titration with alkali metal naphthenides: (1) catalyst sample; (2) tetrahydrofuran; (3) magnetic stirrer; (4) screwthread adaptor with septum; (5) Hamilton threaded plunger syringe (87000); (6) ampoule for ESR measurements; (7) vacuum/dry-nitrogen connection.

washed with distilled water and was dried at 120°C. The resulting preparation was calcined for 24 hr at 550°C in a stream of air. All binary oxides were obtained by coprecipitation of corresponding hydroxides with aqueous ammonia: silica–magnesia (SiO_2:MgO = 8:2 and 1:9) from $Mg(NO_3)_2 \cdot 6H_2O$ and $Si(OC_2H_5)_4$ water–alcohol solutions; boria–thoria (7.8:2.2) from $Th(NO_3)_4 \cdot 6H_2O$ and H_3BO_3 solution in absolute alcohol; and thoria–alumina (2.5:7.5) from an aqueous solution of $Th(NO_3)_4 \cdot 6H_2O$ and $Al(NO_3)_3$. These hydroxides were all washed with distilled water, dried, and calcined as in the case of Al_2O_3. All catalyst samples were calcined at 550°C for 16 hr in a stream of dry deoxidized nitrogen. Catalyst fractions from 0.2 to 0.5 mm in size were used in the measurements. Titration was carried out in the apparatus shown in Fig. 1. The weight of the sample of the catalyst to be titrated was roughly 300 mg. Weighing, transferring, and all other operations were carried out under water-free and oxygen-free conditions. Absolutely dry THF, 2.5 ml, was added to the catalyst. Naphthenide solutions were added in portions of 0.01 ml. The titer of the solution was precisely determined before each measurement by titrating a measured volume of the solution with water until the green color disappeared. The titration was considered to be over with the appearance of a nonfading color of the suspension and a time-independent ESR signal originating from the naphthalene anion radical. One measurement takes approximately 40 min. ESR measurements were carried out using an X-band spectrometer (modulation: 100 kHz). Determinations of surface hydroxyl group and adsorbed water concentrations were made using the method of Nondek (7). Specific surfaces of the catalysts were determined by the BET method.

The results of measurements of surface hydroxyl group and adsorbed water con-

TABLE 1

Concentrations of Surface Hydroxyl Groups and Adsorbed Water

Catalyst	Specific surface area (m^2/g)	Determination of amounts of OH groups and adsorbed water by					
		Pulse chromatographic method		Titration with sodium naphthenide		Titration with potassium naphthenide	
		(OH/100 Å^2)	(mmole/g)	(OH/100 Å^2)	(mmole/g)	(OH/100 Å^2)	(mmole/g)
SiO_2	213.0	0.71	0.25	0.48	0.17	0.54	0.19
Al_2O_3	178.0	1.0	0.30	0.98	0.29	0.81	0.24
Al_2O_3–SiO_2 (1.3:8.7)	200.0	0.39	0.13	0.39	0.13	0.33	0.11
MgO–SiO_2 (2:8)	486.9	0.44	0.36	0.59	0.48	0.58	0.47
MgO–SiO_2 (9:1)	54.0	4.9	0.44	5.2	0.47	4.9	0.44
B_2O_3–ThO_2 (7.8:2.2)	12.1	18.0	0.36	18.5	0.37	15.0	0.30
ThO_2–Al_2O_3 (2.5:7.5)	278.4	1.5	0.67	1.4	0.65	1.3	0.63

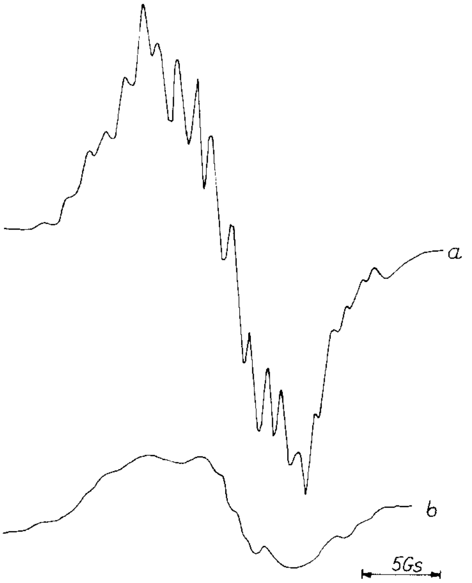


FIG. 2. Naphthalenide anion radical ESR spectra obtained after titrating reagent excess drop addition: (a) spectrum of suspension, (b) spectrum of filtered-off catalyst. Measurements were carried out at room temperature.

centrations obtained by the method of titration with alkali metal naphthenide solutions and by the pulse chromatographic method are compared in Table 1. The results are essentially consistent. Certain discrepancies may result from the completely dissimilar nature of the chemical reactions used in these methods. Figure 2 presents ESR spectra of the naphthalene anion radical registered at the end of titration for both the Al_2O_3 sample in suspension and that filtered-off after titration. The method should find general application to surface OH group and adsorbed water determinations due to the simplicity, speed, and sensitivity resulting from the high reactivity of the titrants.

REFERENCES

1. Holy, N. L., Chem. Rev. **74**, 243 (1974).
2. Paul, D. E., Lipkin, D., and Weissman, S. I., *J. Amer. Chem. Soc.* **78**, 116 (1956).
3. Hoijtink, G. J., van Schooten, J., de Boer, E., and Aalbersberg, W. Y., *Rec. Trav. Chim. Pays.-Bas* **73**, 355 (1954).
4. Lipkin, D., Paul. D. E., Townsend, J., and Weissman, S. I., *Science* **117**, 534 (1953).
5. Mitchell, J., *Anal. Chem.* **23**, 1069 (1951); Kellum, G. E., and Smith, R. C., *Anal. Chem.* **39**, 341 (1967).
6. Shapiro, I., and Weiss, H. G., *J. Phys. Chem.* **57**, 219 (1953).
7. Nondek, L., *React. Kinet. Catal. Lett.* **2**, 283 (1975).
8. Scott, N. D., Walker, J. F., and Hansley, V. L., *J. Amer. Chem. Soc.* **58**, 2442 (1936); "Methoden der Organischen Chemie" (E. Müller, Ed.), Vol. 13, p. 381. Stuttgart: Georg Thieme Verlag, 1972.
9. Tanabe, K., Sumiyoshi, T., Shibata, K., Kiyoura, T., and Kitagawa, J., *Bull. Chem. Soc. Japan* **47**, 1064 (1974).

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