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Determination of the Structural Water of Catalysts with Potassium Vapour

I. Investigation of the Thermal Dehydration of Silica Gel

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An experimental method for investigating the structural water of adsorbents and catalyst by treatment with potassium vapours has been developed. Measurement of the hydrogen evolved showed a reproducibility of each experiment of the order of 5–6%. Within the range of 400–700°C, investigation of thermally dehydrated silica gel by treatment with potassium vapours showed values which were twice as low as those obtained gravimetrically; at 800–900°C, both methods gave equal values.

INTRODUCTION

The surface acidity of adsorbents and catalysts prepared on the basis of SiO_2, Al_2O_3, Cr_2O_3 etc. is of great importance for their activity. This fact has been the reason for many investigations aiming at the qualitative and quantitative determination of the acidity of solid surfaces. Two types of acidities are known: protonic (determined by the presence of OH groups) and nonprotonic (due to Lewis centers). This problem has been studied mostly by chemical methods. They are based on the interaction between a given reagent and the surface OH groups of the adsorbent or catalyst. The interactions of diborane (*1–6*), methyl-magnesium iodide and methyl-lithium (*7–10*), diazomethane (*11, 12*), primary alcohols (*13, 14*), trimethylchlorsilan (*15, 16*), thionyl chloride (*11, 17, 18*), deuterium or heavy water (*19–22*) with the surface OH groups have been studied. In the literature, there are also data on some ion-exchange reactions carried out with aluminum chloride (*23*), basic aluminum chloride (*24, 25*), and calcium hydroxide (*26–28*). The decrease in catalytic activity as a result of ion exchange can also give an estimate of acidity (*29*). Volumetric methods using potassium methylate (*30, 31*) and butylamine (*32, 33*) as titrators have also been developed. Another way of estimating surface acidity is that of using adsorption of ammonia (*34–38*), pyridine (*39*) etc.

The chemical methods used for the determination of surface acidity have some weak points. Above all, in most cases, the reactions do not take place quantitatively. Moreover, the effect of molecular water cannot be eliminated. On the other hand, the results lack a definite sense due to the inaccuracy of distinguishing between chemisorption and physical adsorption. In some cases, diffusion interferes or the results depend on the dimensions of the reagent molecules. For that reason, most of the methods have an empirical character and their application is rather a comparative test for the samples investigated.

Significant information gives the study of surface acidity by some physical methods. Among these, infrared spectroscopy gives more detailed and systematical results (*10, 40–47*). Some authors determine the OH groups/molecular water ratio (*45*).

The purpose of the present paper is to

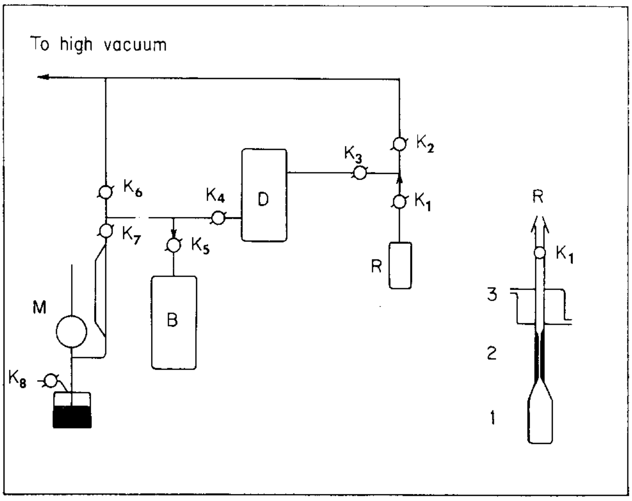


FIG. 1. Apparatus for the determination of OH groups using potassium vapours: B, balloon, V, diffusion pump, M, McLeod gauge, R, reactor; 1. reactor space; 2. capillary; 3. condenser.

propose a new method for the determination of the structural water of catalysts and adsorbents as well as to use this method for studying the changes occuring on the surface of these bodies.

EXPERIMENTAL

The method proposed in the present work is based on the interaction of the catalyst surface with potassium vapours. The presence of both bound and molecular water is expected to result in hydrogen evolution. Measurement of its amount would enable us to estimate the surface protonic acidity. At the same time, there arise difficulties due to diffusion and the incomplete proceeding of the reaction. Moreover, the result must not be influenced by accompanying adsorption phenomena as well as by other processes affecting the sample. Another substantial difficulty can arise if the formation of potassium hydride is not prevented. In order to establish the optimum conditions of the reaction, preliminary experiments were carried out, an ampoule containing potassium and a silica gel sample (treated under vacuum at 250°C) being heated at various temperatures. The change in pressure was measured by a glass membrane manometer. It was established that the gas evolution took place with a high rate and reached saturated values at temperatures about 400°C (the dissociation pressure of potassium hydride at 411°C is 760 mm Hg).

The apparatus used had to satisfy the following conditions: 1) to allow treatment of the sample under vacuum and during heating; 2) to ensure removal of the hydrogen evolved during the reaction; 3) to ensure measurement of this hydrogen. For this purpose, we used an apparatus which was connected with a standard vacuum equipment fitted with a mercury diffusion pump. Figure 1 shows the scheme of our apparatus. The reactor given separately consists of reaction space (1) having a volume of 3 cm^3, a 0.05×30 mm capillary (2) and a condenser (3).

The sample and an ampoule containing potassium under vacuum were placed in the reaction space, heated under vacuum for 6 hr at 250°C, then the ampoule containing potassium was broken (stopcock K_1 remaining closed) and the temperature raised to 400°C. The hydrogen evolved during the reaction was pumped off through the capillary and collected in balloon B which was attached to the measuring part of the apparatus. Stopcocks K_1 and K_3 were then closed and the pressure in the apparatus measured by a McLeod gauge (M). The low pressure of the vapours of potassium under the reaction conditions and its much greater atomic weight facilitate the hydrogen to come out mainly through the capillary. The small amounts of potassium crept into the capillary are quickly cooled by the walls of the condenser, which decreases the possibility of the formation of potassium hydride. The latter is formed at temperatures above 200°C.

Investigation of Thermally Dehydrated Silica Gel and Discussion of the Results

Commercial silica gel of medium porosity was used for the initial sample. It was treated several times with hydrochloric acid (A.R.) and washed with twice distilled water until no more chlorine ions were present. Definite amounts of this silica gel were heated in air at temperatures of 400, 500, 600, 700, 800 and 900°C for 48 hr. These conditions are believed to ensure a constant content of structural water at each temperature (*48*). The structural water was determined for each sample by heating at 1100°C. The partially dehydrated samples thus prepared were treated with potassium vapours in the way described above. Each determination was carried out 3–5 times. The results obtained as well as the results of thermal treatment are given in Fig. 2. The course of the dehydration curve (I) is similar to that observed by other authors (*48*). In the range between 400 and 700°C, curve II (obtained by treatment of the samples with potassium vapours) shows values which are twice as low as those given by curve I, whereas at 800 and 900°C both curves coincide.

Let us discuss the possible reactions in the system under consideration. In the presence of molecular water, the following process will take place:

$$K + H_2O = KOH + \tfrac{1}{2}H_2 \qquad (1)$$

The OH groups will also take part in reaction (2):

$$K + HO\!-\!\underset{|}{\overset{|}{Si}}\!- = KO\!-\!\underset{|}{\overset{|}{Si}}\!- + \tfrac{1}{2}H_2 \qquad (2)$$

Under these conditions, a partial reduction of SiO_2 is also possible, whereas the interaction of K_2O with SiO_2 may result in a silicate.

As is evident from reactions (1) and

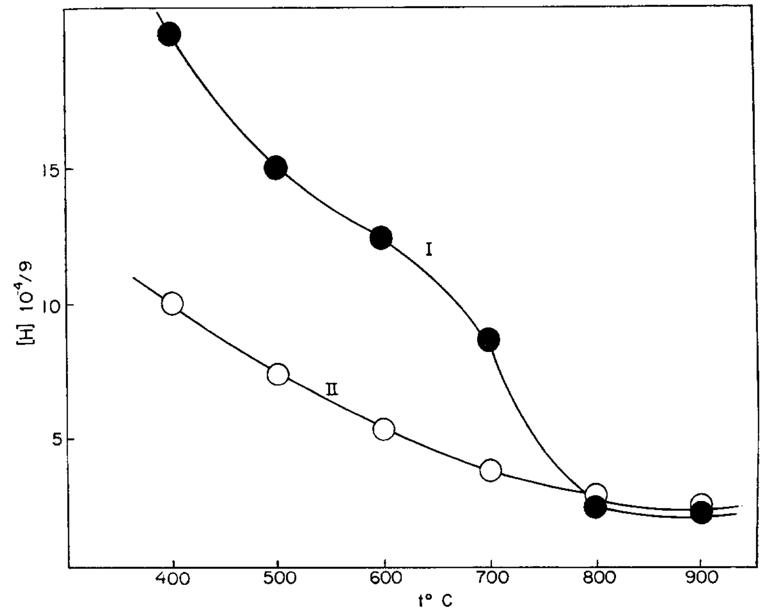
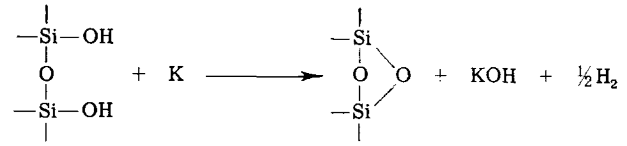


Fig. 2. Curve I, hydrogen content according to the dehydration curve; Curve II, hydrogen evolved during treatment with potassium vapours.

(2), when molecular water is present, the amount of hydrogen evolved is twice as low as in the case when one molecule of water is in the form of two OH groups. To determine the conditions under which one or the other process may prevail, we shall consider some data obtained from the IR spectra on the nature of water present in silica gel. According to Baverez and Bastik (*45*), at 240°C the molecular water should be removed. Fraissard and Imelik (*47*) have found that at 1640 cm^{-1}, the line of bending vibration of the water molecules disappears altogether in the spectra of samples dehydrated at 600°C, which indicates the presence of molecular water up to this temperature. The same authors show that after dehydration at temperatures up to 800°C, the OH groups interact with each other by means of hydrogen bonds. Above this temperature, free OH groups are observed. On the basis of this picture, we suggest the following explanation of the results obtained. For samples dehydrated at temperatures below 800°C, the amount of hydrogen evolved (curve II) is twice as small as that determined gravimetrically, due to reactions (1) and (3) taking place:



For samples prepared at higher temperatures, reaction (2) should be valid.

It is interesting to mention that according to the comparison made by Boehm (*49*), the number of OH groups in aerosil (nonporous silica gel) determined by chemical methods (interaction with thionyl chloride, titration with sodium base, reaction with boron trichloride, methylation, adsorption on aluminum chloride, basic aluminum chloride etc.), is twice as low as that obtained gravimetrically, by deuterium exchange and infrared spectroscopy. In our investigations, one and the same chemical method leads to a ratio of 1:2 or 1:1 depending on the state of the OH groups.

REFERENCES

1. SHAPIRO, I., AND WEISS, H. G., *J. Phys. Chem.* **57**, 49 (1953).
2. WEISS, H. G., KNIGHT, J. A., AND SHAPIRO, I., *J. Am. Chem. Soc.* **81**, 182 (1953).
3. STOBER, W., *Kolloid. Z.* **145**, 17 (1956).
4. NACCACHE, C., FRANCOIS-ROSSETTI, J., AND IMELIK, B., *Bull. Soc. chim. France* **2**, 404 (1959).
5. BAVEREZ, M., AND BASTICK, J., *Bull. Soc. chim. France* **12**, 3226 (1964).
6. NACCACHE, C., AND IMELIK, B., *Compt. rend. Acad. Sci.* **250**, 2019 (1960).
7. DEUEL, H., AND HUBER, G., *Helv. chim. Acta* **34**, 1697 (1951).
8. UYTTERHOEVEN, J., *Bull. groupe franc. argiles* **13**, 69 (1962).
9. UYTTERHOEVEN, J., HELLINCKS, E., AND FRIPIAT, J. J., *Silicates ind.* **28**, 241 (1963).
10. UYTTERHOEVEN, J., AND FRIPIAT, J. J., *Bull. Soc. chim. France* **4**, 788 (1962).
11. BOEHM, H. P., AND SCHNEIDER, M., *Z. anorg. Chem.* **301**, 326 (1959).
12. EBERT, K. H., *Mh. Chem.* **88**, 275 (1957).
13. STÖBER, W., BAUER, G., AND THOMAS, K., *Ann. chem* **604**, 104 (1957).
14. BAUER, G., AND STÖBER, W., *Kolloid. Z.* **160**, 142 (1958).
15. STÖBER, W., *Kolloid. Z.* **149**, 39 (1956).
16. KOHLSCHÜTTER, H. W., BEST, P., AND WIRZING, G., *Z. anorg. Chem.* **285**, 236 (1956).
17. BREMER, H., JANIAK, F., AND STACH, H., *Wiss. Z. Techn. Hochschule Chem.*, Leuna-Merseburg **8**, 105 (1966).
18. UYTTERHOEVEN, J., AND NAVEAU, H., *Bull. Soc. chim. France* **1**, 27 (1962).
19. HALDEMAN, R. G., AND EMMET, P. H., *J. Am. Chem. Soc.* **78**, 2917 (1956).
20. LEE, J. K., AND WELLER, S. W., *Anal. chem.* **30**, 1057 (1958).
21. HALL, W. K., LEETIN, K. H., CHELSEKE, F. I., AND O'REILLY, *J. Catalysis* **2**, 506 (1963).
22. ZHURAVLEV, L. T., KISSELEV, V. F., NAYDINA, V. P., AND POLYAKOV, A. L., *Zh. Fiz. Khim* **37**, 2054 (1963) (Russian, *J. Physical Chemistry*).
23. BOEHM, H. P., SCHNEIDER, M., AND ARENDT, F., *Z. anorg. Chem.* **320**, 43 (1963).
24. KÖHLSCHÜTTER, H. W., GETROST, H., AND

Miedtank, S., *Z. anorg. Chem.* **308,** 190 (1961).

25. Boehm, H. P., and Schneider, M., *Z. anorg. Chem.* **316,** 128 (1962).
26. Greenberg, S. A., *J. Phys. Chem.* **60,** 325 (1956).
27. Greenberg, S. A., *J. Phys. Chem.* **65,** 12 (1961).
28. Plachinda, A. S., Chertov, V. Kh., and Neimark, I. E., *Ukr. chim. J.* **31,** 567 (1965), Russian.
29. Topchieva, K. V., and Moskovskaya, I. R., *Dan SSSR* **123,** 891 (1958), Russian.
30. Münzing, E., Blume, H., and Rost, H., *Z. Chem.* **9,** 257 (1961).
31. Strich, E. K., Becker, K., Blume, H., and Hille, J., *Chem. Techn.* **17,** 489 (1965).
32. Hammet, L., and Deyrup, A., *J. Am. Chem. Soc.* **54,** 2721 (1932).
33. Walling, C., *J. Am. Chem. Soc.* **72,** 1164 (1950).
34. Tamele, M. W., *Disc. Far. Soc.* **8,** 270 (1950).
35. Webb, A. M., *Ind. Eng. Chem.* **49,** 261 (1951).
36. Barth, R. T., Ballon, E. V., *Anal. Chem.* **33,** 1080 (1961).
37. Dzis'ko, V. A., *III Int. Congr. Cat. Amsterdam 1964,* vol. 1, p. 422.
38. Mirschler, A. E., *J. Catalysis* **6, 1** (1966).
39. Bosaček, V., Polak, R., Kučera, E., and Daneš, V., *Coll. Czechosl. Chem. Commun.* **27,** 2575 (1962).
40. Mapes, J. E., and Eishens, R. P., *J. Phys. Chem.* **58,** 1059 (1954).
41. Kotov, E. I., *Optika i spectroscopia* **3, 115** (1957).
42. Fripiat, J. J., and Uytterhoeven, J., *J. Phys. Chem.* **5,** 800 (1962).
43. Anderson, J. A., Jr., and Wickersheim, K. A., *Surface Sci.* **2,** 252 (1964).
44. Akshinskaya, N. V., Davydov, V. Ya., Zhuravlev, L. T., Kertoys, D., Kisselev, A. V., Kuznetsov, B. V., Nikitin, Yu. S., and Rybina, V., *Colloid. J.* **26,** 529 (1964). (Russian)
45. Baverez, M., and Bastick, J., *Compt. rend. Acad. Sci.* **260,** 3939 (1965).
46. Barthmeuf, D., Perrin, M., and Trambouse, J., *Bull. Soc. chim. France* **2,** 605 (1966).
47. Fraissard, J., and Imelik, B., *Bull. soc. chim. France* 1710 (1963).
48. Egorov, M. M., Krassil'nikov, K. G., and Kisselev, V. F., *Zh. Fiz. Khim.* **32, 2448** (1958). (Russian, *J. Phys. Chem.*)
49. Boehm, H. P., *Adv. Catalysis* **16,** 179 (1966).