Journal of Thermal Analysis, Vol. 7 (1975) 119—124

AN APPARATUS FOR SIMULTANEOUS DETERMINATION OF ELECTRICAL CONDUCTIVITY AND THERMOGRAVIMETRIC CURVES OF SOLID SYSTEMS

N. JURANIĆ, D. KARAULIĆ and D. VUČELIĆ

Department of Physical Chemistry, Faculty of Sciences; Institute for Chemistry, Technology and Metrology, Belgrade, Yugoslavia

(Received February 8, 1973; in revised form July 13, 1973)

A new apparatus for measurement of electrical conductivity during thermogravimetric analysis is described. Results of an investigation of the water-zeolite system in the interval $-200°$ up to $+450°$ prove the suitability of this apparatus in the investigation of gas-solid interaction mechanisms.

Measurement of electrical conductivity during phase changes or chemical reactions in solids can in certain cases provide useful information on the reaction mechanism. Very good results have been obtained for gas-solid systems, and especially for the water-zeolite system, which has been the subject of numerous investigations [1—7].

In general, the electrical conductivity of zeolites can be given in the form:

$$\sigma = f(\Theta, T)$$

where: σ is the electroconductivity; θ the degree of coverage of the surface by sorbed water; and T the absolute temperature.

The degree of coverage by physisorption changes with the temperature and when an exact measurement of electrical conductivity has to be made, both parameter changes have to be followed simultaneously. However, in all the papers mentioned the electrical conductivity was determined as a function of only one parameter, while the influence of the other parameter was calculated indirectly. Samples are usually prepared with different degrees of coverage and are afterwards transferred to the apparatus for measurement of electrical conductivity. The changes due to contact with the air during transfer are usually disregarded. In the case of measurement of the temperature-dependence of the conductivity, the change of the degree of coverage is either disregarded or indirectly corrected via known TG curves. Probably as a consequence of different experimental conditions, various results have been obtained, although in all cases an identical water-zeolite system was treated.

It is evident that it is possible to obtain the most exact results only when the electroconductivity is measured simultaneously as a function of both parameters. A simple apparatus enabling such a measurement is described below. This apparatus permits combined TG and CE (electrical conductivity) analyses.

Apparatus

Basically, the apparatus consists of two metallic spirals connected to the sample to be tested. The spirals perform a dual function: they serve at the same time as a microbalance and as the electrical connections of the sample to the bridge for the resistance measurement. The general view is shown in Fig. 1.

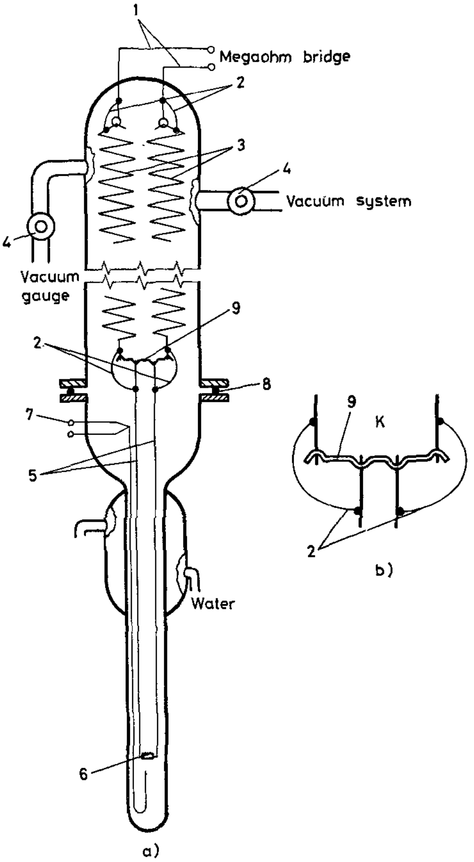

Fig. 1. Apparatus for simultaneous measurement of thermogravimetric and electrical changes in solids

a — General schematic view; 1 — Leads with hooks for fixing of spirals, 2 — Leads, 3 — Metallic spirals, 4 — Teflon valves, 5 — Electrode leads, 6 — Sample, 7 — Thermocouple, 8 — Point with "O"-ring, 9 — Quartz beam "K"; b — Enlarged view of the beam 9

The glass part is made of pyrex glass and consists of two main sections: the upper section is a fixed tube 100 mm in diameter, where metallic spirals, electrical outlets and teflon valves for sorption gas inlet and evacuation are located. The lower tube is of considerably smaller size (20 mm in diameter) with the aim of decreasing the temperature difference between the tube and the sample. The smaller tube is removable to permit easy access to the sample. Lubrication is avoided by using teflon valves and joints sealed by a rubber O-ring. Teflon valves were made by the Ace Glass Co., and are suitable for vacuum systems up to 10^{-6} torr. O-rings are protected from overheating by a water cooler.

Microbalance and metallic parts

The microbalance consists of the two metallic spirals Fe – W alloy wire guage 0.20 mm, each with 120 coils, 18 mm core diameter. The metallic spirals are located in the upper glass tube, 5 cm apart. They are suspended by Ni – W hooks melted into the glass, which serve as outler electrodes. On the lower end, the spirals are connected by a quartz beam "K". From the beam two wires support the sample; these two wires are connected to the spirals by very thin connections, as shown in Fig. 1, detail "b". It is evident that the only connection of the spirals is the quartz beam, and therefore the apparatus is suitable for measurements of resistance up to 10^6 Ohm, which represents the quartz beam resistance. The spirals exhibit linear elongation up to 600 mg weight. In this range, the balance sensitivity was 200 ± 5 μm/mg.

Sample

The sample was prepared from 13X zeolite powder, made by Union Carbide Co. The powder was pressed under a pressure of 10 000 psi, and cut to a block shape of $10 \times 5 \times 2$ mm. It was connected by its smallest surfaces to the electrodes, with colloidal silver. After the sample had been subjected to degassing at 400 – 450° for a period of 12 hours at 10^{-6} torr, gases and vapours were sorbed on it up to the desired degree of coverage. Electrical conductivity was then measured either as a function of the degree of coverage or both.

Measurement of the conductivity

Pure zeolite and zeolite with sorbed gases have much lower resistances than 10^6 Ohm throughout the whole temperature range, and these resistances can be determined. The resistance is measured with an alternating current having a frequency of 1 kHz. No dependence of the conductivity on frequency was found within the measured range. The capacity impedance originates from the leads and coils and is lower than 5 per cent of the resistance impedance. Immediately before reading of the elongation of the spirals, the latter are put into short circuit in order to avoid the influence of electrostatic forces. For elongation measurement a KM-8 cathetometer, made in the USSR, was used.

Experimental results

This combination of TG and CE analyses was applied to investigations of the system zeolite 13X-water.

Electroconductivity vs. degree of coverage is shown in Fig. 2. As evident from curve 1, starting with a degree of coverage $\Theta \sim 0.82$, the zeolite conductivity increases exponentially. Curve 2 shows the conductivity on a larger scale. It is evident that the increase of the conductivity appears at about $\theta \sim 0.82$, corresponding to an intermolecular distance of about 2.7 Å, quite close to the hydrogen bond distance. This fact leads to the hypothesis of the participation of the protons of the sorbed molecules, in the mechanism of the conductivity, beginning with the monolayer and so on.

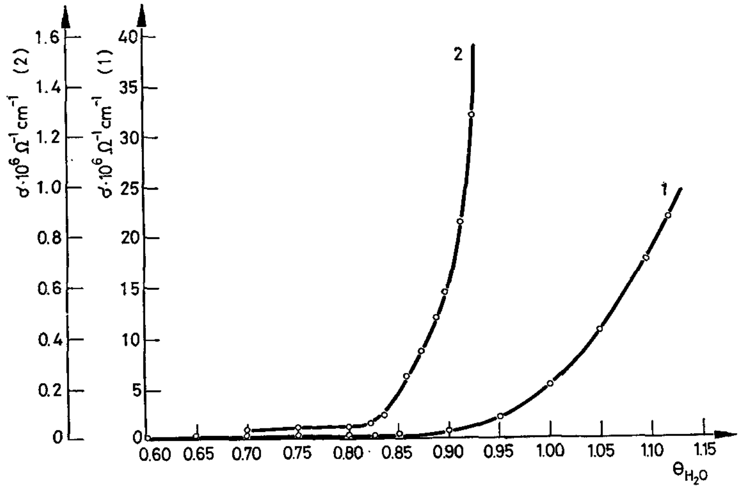

Fig. 2. Electrical conductivity vs. degree of coverage for the system water — zeolite 13X it was adopted that $\Theta \sim 1 = 200$ mg/g

Simultaneous TG and CE analyses, results of which are shown in Fig. 3, confirm these conclusions. At temperatures higher than 260°, where the degree of coverage is lower than 0.1 (curve 2), the electrical conductivity increases exponentially, due to the Na^+ ions of the zeolite (curve 1). In the interval 80 – 260°, as in curve 2, the water quantity remains below a degree of coverage 0.9, and as the results from Fig. 2 should not considerably affect the conductivity. The conductivity within this interval (curve 1, Fig. 2) conforms with these assumptions.

At temperatures lower than 60°, the degree of coverage exceeds 0.9, causing a considerable increase of the conductivity. At about 5°, completely unexpectedly, both curves decrease with temperature decrease. For the conductivity curve this could be explained by the water freezing at about 0°C, although such an assumption is contrary to the results of NMR measurements [8], which show that the freezing point of the sorbed water is about 173 K. However, water desorption for curve 2 cannot be easily explained by some occurrence of solid-gas interaction. It seems that the desorption takes place because the glass walls are at a lower temperature than the sample and the water condenses and freezes on them, because the vapour pressure of the ice is lower than that of the sorbed water for $\theta > 1$. Hence some kind of "distillation" of the water occurs from the sample onto the walls. This desorption is also followed by a drop of the electrical conductivity to the value characteristic for zeolite at the particular temperature.

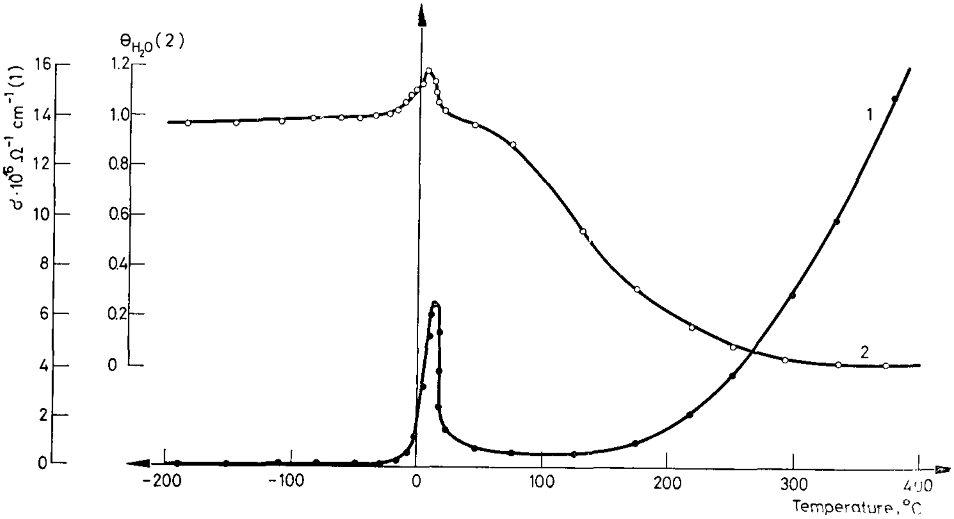

Fig. 3. Thermogravimetric analysis and electrical conductivity vs. temperature for system water — zeolite 13X. Curve 1 — electrical conductivity; Curve 2 — TG curve

References

1. H. E. Rabinowitsch and W. C. Wood, Electrochem., 39 (1933) 562.
2. I. R. Beattie, Trans. Faraday Soc., 50 (1954) 581; ibid. 51 (1955) 712.
3. B. A. Glazun, M. M. Dubinin et al., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1964) 1939; ibid. (1966) 393, 1129, 1249, 1253, 1668; ibid. (1967) 977, 982, 987.
4. R. M. Barrer and E. A. Saxon-Napier, Trans. Faraday Soc., 58 (1962) 156.
5. R. M. Barrer and L. V. Rees, Trans. Faraday Soc., 56 (1960) 709.
6. D. C. Freeman and D. N. Stamires, J. Chem. Phys., 35 (1961) 799.
7. D. N. Stamires, J. Chem. Phys., 36 (1962) 3174.
8. D. Vučelić, Unpublished.

Résumé — On décrit un nouvel appareil pour la mesure de la conductivité électrique au cours de l'analyse thermogravimétrique. Les résultats des études effectuées sur des systèmes eau-zéolithe entre —200 et +450° ont prouvé que l'appareil se prête aux études de mécanisme d'interaction gaz-solide.

Zusammenfassung — Eine neue Vorrichtung zur Messung der elektrischen Leitfähigkeit während der thermogravimetrischen Analyse wird beschrieben. Die Ergebnisse von an Wasser-Zeolyt-Systemen im Bereich von $-200°$ bis $+450°$ durchgeführten Untersuchungen bestätigen die Eignung des Apparates zum Studium des Mechanismus von Wechselwirkungen zwischen fester und Gas- Phase.

Резюме— Описан новый прибор для измерения электропроводности при проведении термогравиметрического анализа. Результаты исследования системы вода-цеолит, проведенного в области температур — 200° + 450° С, показали пригодность прибора для исследования механизма газ — твердое вещество.