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CHARACTERIZATION OF ALUMINIUM OXIDE SAMPLES BY MEANS OF SPECIAL THERMAL ANALYSIS TECHNIQUES

M. Planda and P. Staszczuk

Chemistry Faculty, Maria Curie-Skłodowska University, M. Curie-Skłodowska Sq. 3
20-031 Lublin, Poland

Abstract

Thermodesorption of benzene and water from alumina samples saturated in vacuum dessicator were studied under quasi-isothermal conditions. The Q-TG and Q-DTG curves show multi-step mass losses associated with the evaporation of liquids from pores and physisorbed liquid films from active sites with different energies. The isotherms of adsorption-desorption of nitrogen on porous alumina samples were measured using sorptomatic method and pore size distribution functions have been calculated. The correlation between porosity parameters and the volume of desorbed liquids is presented. A good agreement between above data was obtained.

Keywords: adsorption of nitrogen, porous aluminas, thermodesorption of benzene and water

Introduction

Alumina is widely used in many areas of life. It encompasses all of the interesting features of a satisfactory support, selective adsorbent or catalyst. Alumina was commercially introduced in 1932 by AlCOA for water adsorption [1]. Alumina has originally been known as a desiccant to the chemical process industries [2]. Aluminas have successfully been used in the catalysis [3] and adsorption industries [4]. Recently, the variety and complexity of applications have become almost endless.

Alumina is a term used for high surface area forms of aluminium oxides produced by thermal dehydration of aluminium hydroxides or hydrated aluminas. They exist as at least five thermodynamically stable phases and many more metastable transition forms. The low temperature form of alumina known as γ-alumina, which in fact consists of a mixture of different microcrystalline forms (ρ, χ, γ, and η) is produced at dehydration temperatures up to 600°C. High temperature forms are θ and κ. With the exception of some α-aluminas (formed above 950°C) they possess surface hydroxyls which can have a certain degree of activity in adsorption. The crystallographically stable oxides are not usually considered useful since they have little porosity and low surface area [6]. The chemical activity and active adsorption sites results from the defect structure in the aluminium and oxygen lattice produced during the amorphous to crystalline transition which occurs during the thermal dehydration

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process. Since the activated materials generally fall somewhere between the amorphous and crystalline forms they are usually referred as ‘transition forms’. Most but not all transition aluminas have the defect spinel structure. The details of the spinel structure are given by Clark [7]. The complexity of the surface chemistry of the aluminas arises because the properties of the various aluminas and their defect structures are sensitive to the conditions under which the materials are dehydrated.

The alumina surface is amphoteric, containing both acidic and basic sites of varying strengths and concentration. Acidity results from the presence of the coordinately unsaturated Al^{3+} ions and acidic hydroxyls while the basic sites arise from the presence of O^{2-} ions and basic hydroxyls. Among the earliest detailed studies of the surface are those of Peri [8] and Peri and Hannan [9] who developed a model for the progressive dehydroxylation of alumina surface which could account for the presence of five different types of acidic and basic hydroxyl groups observed by infrared spectroscopy.

The surface structure of alumina essentially determines its adsorptive characteristics, an understanding of the surface chemistry of alumina is necessary to comprehend selective adsorption properties. There are presented the results of studies carried out to determine adsorption and porosity characteristics of three commercial aluminium oxide samples.

Results and discussion

Thermodesorption measurements

Measurements of programmed thermodesorption of water and benzene from the surface of studied aluminium oxides samples from Aluminium Co. of America marked below as Al-19, Al-30 and Al-39 under the quasi-static (quasi-isothermal, quasi-isobaric) conditions were made by means of the derivatograph Q-1500 D (MOM, Budapest, Hungary). In this technique the type of a specially shaped sample crucible was used [10]. The apparatus was connected with the computer via the interface equipped with a suitable program Derivat (Medson, Paczkowo, Poland) to register the sample mass loss curves as a function of temperature and/or time and to determine the differential Q-DTG curves with respect to temperature and/or time. The mass-loss Q-TG curves were measured over a temperature range 20–250°C with the furnace heating rate of 6°C min^{-1} [11].

The changes of mass loss Q-TG and differential mass loss Q-DTG curves with respect to temperature of benzene and water thermodesorption from alumina oxide samples are shown in Figs 1–6.

It follows from Figs 1 and 2 that presented curves are characterized by 2–3 inflections (on Q-TG curves) and peaks (on Q-DTG curves) resulting from successive stages of evaporation of benzene and water being at different energetical stages on alumina surfaces.

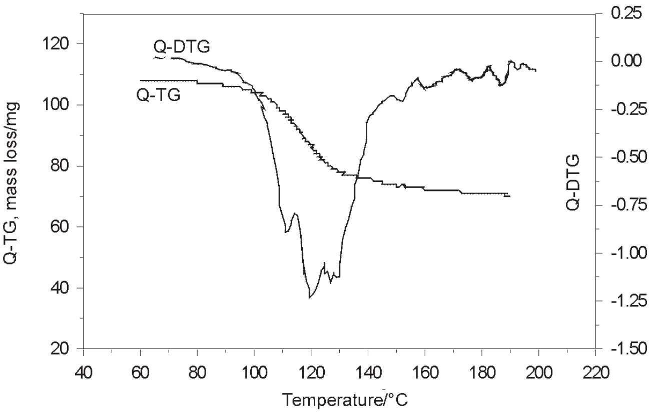

Fig. 1 Q-TG and Q-DTG curves for desorption of benzene from Al-19 alumina sample

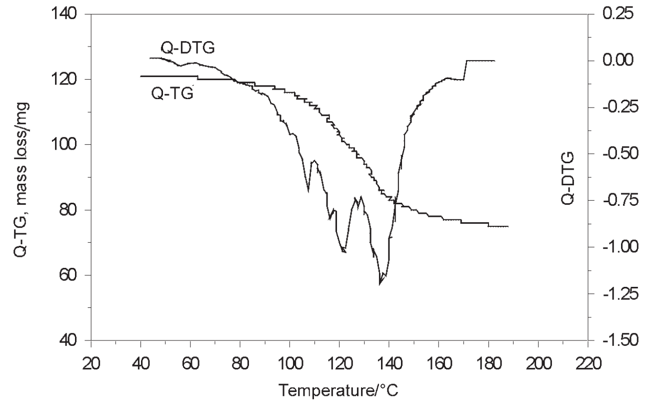

Fig. 2 Q-TG and Q-DTG curves for water desorption from Al-19 alumina sample

The thickness of the adsorbed layer can be controlled by altering the mode of immersion of the samples. Thus, immersion in benzene and water vapors in a desiccator with $p/p_0=1$ saturates all adsorption sites as well as surface and capillary forces. Under such conditions the surface and capillary forces are compensated as in the McBain balance adsorption method. Samples prepared in this way do not contain excess bulk liquid, which would affect the kinetics and mechanism of thermodesorption by lateral interactions between molecules. The Q-DTG curves are characteristic 'spectrum' of the thermodesorption process and reflect an energetic state of benzene and water molecules on the surface of alumina with various heterogeneous properties. The shape of Q-DTG curves result from the discontinuous properties of adsorbed layers and disruption of the adsorbate–adsorbate and adsorbate–adsorbent bonds. The adsorption energies of benzene and water result from dispersive and non-dispersive interactions, respectively. Benzene molecules interact with the alumina surfaces by means of π-electrons of different densities. The water/alumina interactions are realized by stronger hydrogen bonds which are caused by the large bonding energy in the ice-like structures of water films close to surfaces.

The interpretation of the thermodesorption of benzene and water from alumina surfaces can be explained as follows.The first stage is the evaporation of liquids from capillaries (desorption of the liquids film in the region of capillary condensation on isotherm adsorption). During the next stages, the thermodesorption of liquids takes place from mesopores and finally from the surface and active sites of the samples. On the basis of the water mass loss Q-TG curves the number of individual hydroxyl groups present on the adsorbent surfaces can be calculated [12].

Moreover, using single Q-DTG curve, it is possible to determine the total heterogeneity (energetical and geometrical) of the sample studied: the energy distribution and pore size distribution functions [13].

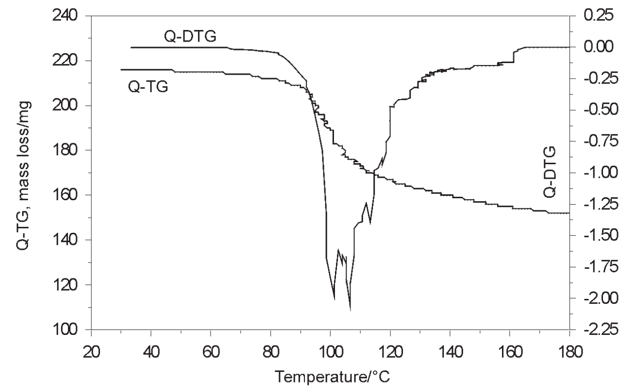

Fig. 3 Q-TG and Q-DTG curves for benzene desorption from Al-30 alumina sample

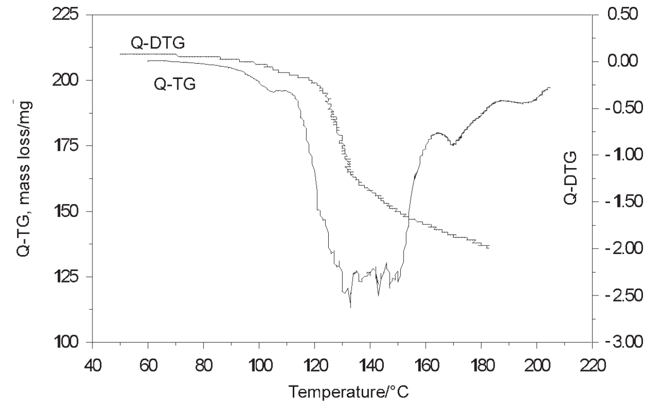

Fig. 4 Q-TG and Q-DTG curves for water desorption from Al-30 alumina samples

Adsorption measurements

In order to compare the surface properties of the investigated aluminium oxides the low-temperature nitrogen adsorption–desorption isotherms at 78 K were measured using an automatic Sorptomatic 1800 apparatus (Carlo Erba, Milan).

The nitrogen adsorption–desorption isotherms provide additional information and are shown in Fig. 7. Isotherms for sample studied (type II in BET classification) have condensation parts and hysteresis loops in the 0.45–1.0 region of p/p_0 which indicate the presence of mesopores in the surfaces. The specific surface area of the samples (Table 1) was obtained on the basis of the standard Brunauer–Emmett–Teller method and ranged from 318 to 386 $m^2 g^{-1}$ with corresponding total porosity varying from 0.40 to 0.54 $cm^3 g^{-1}$. Although samples Al-19 and Al-30 had the highest total porosity, about 50% of pores exceed 10 nm. The pore size distribution was obtained by means of Barrett–Joyner–Halenda method from the desorption data in the pore size range 1–300 nm.

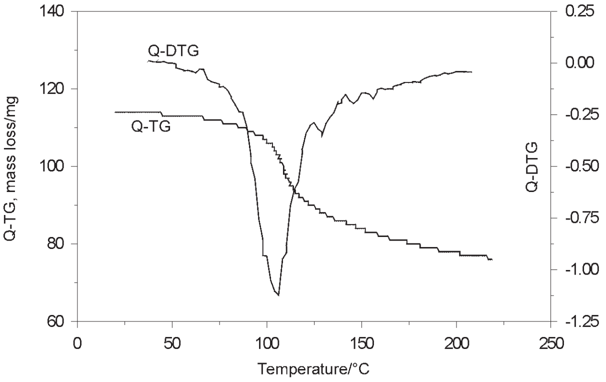

Fig. 5 Q-TG and Q-DTG curves for benzene desorption from Al-39 alumina samples

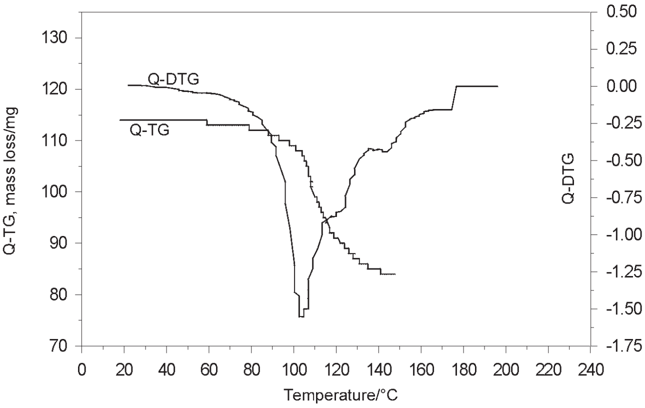

Fig. 6 Q-TG and Q-DTG curves for water desorption from Al-39 alumina samples

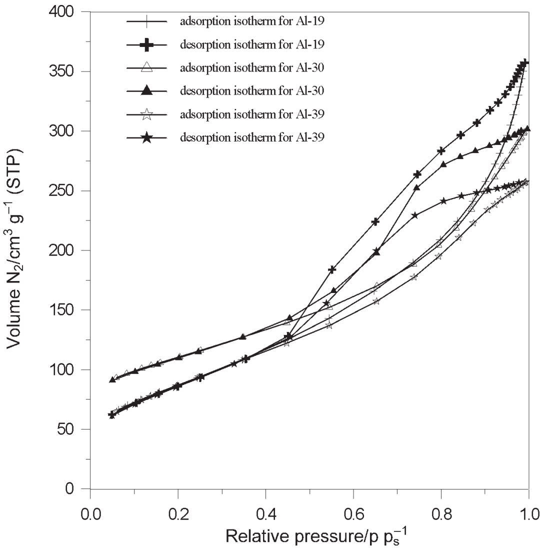

Fig. 7 Low-temperature adsorption–desorption isotherms of nitrogen for the Al-19, Al-30, and Al-39 alumina samples

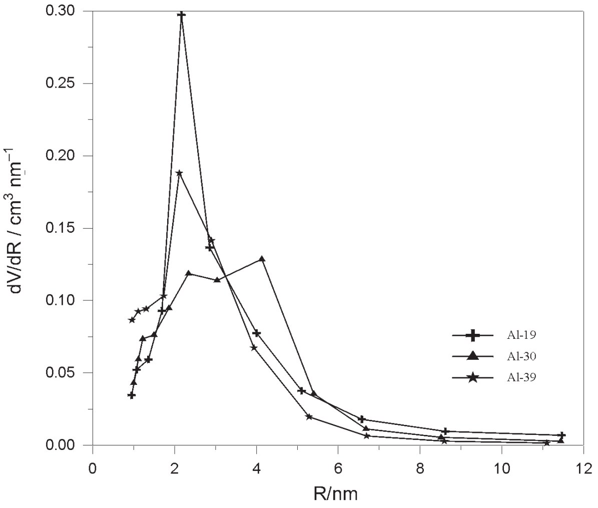

Fig. 8 Pore size distributions for the Al-19, Al-30, and Al-39 alumina samples

Pore size distribution curves (PSD) for the studied alumina samples are shown in Fig. 8. The d*V*/d*R* plots are the Gauss type for Al-19 and Al-39 (sharp peaks correspond to pore radii of ca 2 nm) and bimodal for Al-30 (two peaks correspond to pore radii of ca 2.5 and 4.5 nm) alumina samples.

The structural characteristics of the studied alumina adsorbents i.e. value of specific surface area (by BET method) S_{BET}, total pore volume $V_{total\ (sorptom.)}$, average pore diameter D, calculated from low-temperature sorptomatic adsorption–desorption isotherms of nitrogen are presented in Table 1.

Table 1 Pore structure parameters of alumina oxides calculated from sorptomatic nitrogen adsorption–desorption isotherms

Sample	S_{BET}/m^2 g^{-1}	$V_{total\ (sorptom.)}$/cm^3 g^{-1}	D/nm
Al-19	318.1	0.54	6.8
Al-30	385.8	0.46	4.8
Al-39	317.6	0.40	5.0

Table 2 Total pore volume of the alumina oxides calculated from sorptomatic and thermal analysis methods

Sample	Al-19	Al-30	Al-39
$V_{total\ (sorptom.)}$	0.54	0.46	0.397
$V_{water\ (Q\text{-}TG)}$	0.53	0.45	0.398
$V_{benzene\ (Q\text{-}TG)}$	0.51	0.41	0.395

The Q-TG plots in Figs 1–6 make the determination of the adsorption capacity, the volume of mesopores on the alumina surface and amount of liquid bonded to the surface possible. These parameters may be compared with results from independent methods, such as the McBain balance and sorptomatic data. A correlation between the porosity of sorptomatic parameters and the amount of the desorbed liquids vapors (benzene and water) from thermal analysis methods are demonstrated in Table 2. The total pore volumes of the samples calculated from Q-TG plots for benzene and water are in very good agreement with the sorption results.

References

1 I. B. Batnitt, U.S. Patent, 1 (1932) 868.
2 C. Busetto, G. Del Piero and G. Manara, J. Catal., 85 (1984) 260.
3 R. Sh. Mikhail, Th. El-Nabarawy and A. M. Youssef, Surf. Technol., 11 (1980) 279.
4 K. P. Goodboy and H. L. Fleming, Chem. Eng. Prog., 80 (1984) 63.
5 A. M. Youssef, M. A. Hamada and N. Nawar, Mater. Lett., 15 (1993) 386.
6 K. Weters and G. M. Bell, Technical Paper No. 19, Oxides and Hydroxides of Aluminium, Pittsburgh, PA 1972.
7 G. M. Clark, The Structure of Non-Molecular Solids, John Wiley & Sons, New York 1971, pp. 306–322.
8 J. B. Peri, J. Phys. Chem., 69 (1965) 220.
9 B. Peri and R. B. Hannan, J. Phys. Chem., 64 (1960) 1526.
10 F. Paulik, Special Trends in Thermal Analysis, Academic Press, J. Wiley & Sons, Chichester, 1995.

11 P. Staszczuk, J. Therm. Anal. Cal., 53 (1998) 597.
12 P. Staszczuk, Colloids and Surfaces A: Physicochem. and Eng. Aspects, 105 (1995) 291.
13 V. I. Bogillo and P. Staszczuk, J. Therm. Anal. Cal., 55 (1999) 493.