MICROCALORIMETRIC STUDY OF ARGON, OXYGEN, NITROGEN AND CARBON MONOXIDE ADSORPTION ON CRYSTALLINE ZIRCONIA

M. R. Alvarez[1], M. J. Torralvo[2], Y. Grillet[3], F. Rouquerol[2] and J. Rouquerol[3]

[1]DEPARTAMENTO DE QUÍMICA INORGÁNICA. FACULTAD DE CIENCIAS. UNIVERSIDAD COMPLUTENSE. 28040-MADRID, SPAIN
[2]UNIVERSITÉ DE PROVENCE, PLACE VICTOR HUGO, 13331-MARSEILLE CEDEX 3, FRANCE
[3]CENTRE DE THERMODYNAMIQUE ET DE MICROCALORIMÉTRIE DU CNRS, 26 RUE DU 141ème R.I.A., 13003-MARSEILLE, FRANCE

The adsorption of argon, oxygen, nitrogen and carbon monoxide at 77 K on crystalline zirconia and microporous zirconia gels has been studied by adsorption volumetry and isothermal microcalorimetry.

The microporous structure of the zirconia gel may explain the higher enthalpy of adsorption obtained for argon. Both crystalline samples are mesoporous and in each case, the polar sites on the surface give specific interactions with dipolar (CO) or quadrupolar (N₂, O₂) molecules, which can be deduced from the adsorption isotherms and the corresponding differential enthalpy curves.

Keywords: adsorption of gases, crystalline zirconia

Introduction

Due to the utility of ZrO_2 as both, catalyst and support, ion exchanger and precursor for ceramic materials, a great deal of work has been devoted to analyze the influence of the preparation conditions on the textural properties of zirconia and the thermal stability of the different crystalline phases [1, 2].

Zirconia gels obtained by hydrolysis from zirconium salt solutions are microporous and thermal treatment of these gels up to 670–720 K produces a progressive decrease of the micropore volume [3], which can be explained in terms of a reduction of the micropore size [4]. By heating at temperatures higher than 720 K, the amorphous zirconia crystallizes to the tetragonal phase, which with

an increase in temperature, progressively transformes to the more stable mono-clinic phase [2].

Amorphous, tetragonal and monoclinic zirconia differ in their surface chemi-cal properties [5], a fact which merits further study in the surface characteriza-tion of amorphous and crystalline zirconia, in respect to their applications.

In this paper we report the results obtained in the study of the adsorption of argon, oxygen, nitrogen and carbon monoxide on amorphous and crystalline zir-conia. We have selected adsorbates with different molecular polarity, and we have benefited from the sensibility of microcalorimetric techniques to obtain in-formation of both, the microporous texture and 'specific nature' of the surface.

Experimental

Samples

The starting material was a zirconia gel obtained by hydrolysis of a solution of zirconium oxychloride with ammonia in water. The product was filtered, washed with water, dried over $CaCl_2$ and then treated at 383 K in air for 6 hours (sample C(383/6h)). Crystalline zirconia was prepared by heating zirconia gel in air at 723 K for 20 hours (sample C(723/20h)) and 30 days (C(723/30d)). Each sample was a two-phase mixture of the tetragonal and monoclinic form. Prior to the adsorption, the samples were outgassed under vacuum at ambient tempera-ture.

Experimental techniques and methods

The adsorption isotherms of Ar, O_2, N_2 and CO at 77 K and their correspond-ing differential enthalpy curves, were obtained from simultaneous volumetric and microcalorimetric adsorption measurements applying a slow and continuous introduction of the adsorptive [6]. For each sample, complete adsorption-desorp-tion isotherms of nitrogen were determined by the conventional static procedure.

Analysis of the adsorption isotherms was made by the BET equation (BET area was obtained with the assumption of a molecular cross-sectional area of $0.138 \, nm^2$ for argon, $0.141 \, nm^2$ for oxygen, $0.162 \, nm^2$ for nitrogen and $0.162 \, nm^2$ for carbon monoxide) and the α_s method using standard N_2/silica and Ar/silica isotherms given by Sing [7] for the construction of the α_s-plots.

Pore size distributions were obtained on the basis of the Kelvin equation using a cilindrical pore model [8].

Results and discussion

In Fig. 1a the adsorption-desorption isotherms of nitrogen at 77 K are plotted for the three samples. Pore size distribution curves, calculated from both, adsorption and desorption branches (Fig. 1b), show a progressive increase in pore size with the time of treatment.

The continuous recorded adsorption isotherms of several adsorbates on the crystalline samples are drawn in Fig. 2a and 3a, and the corresponding curves of differential enthalpy of adsorption ($|\Delta_{ads} h|$) as a function of coverage (V/V_m) are plotted in Fig. 2b and 3b. In Fig. 2b the curves of differential enthalpy of adsorption of argon and nitrogen on the zirconia gel are also plotted.
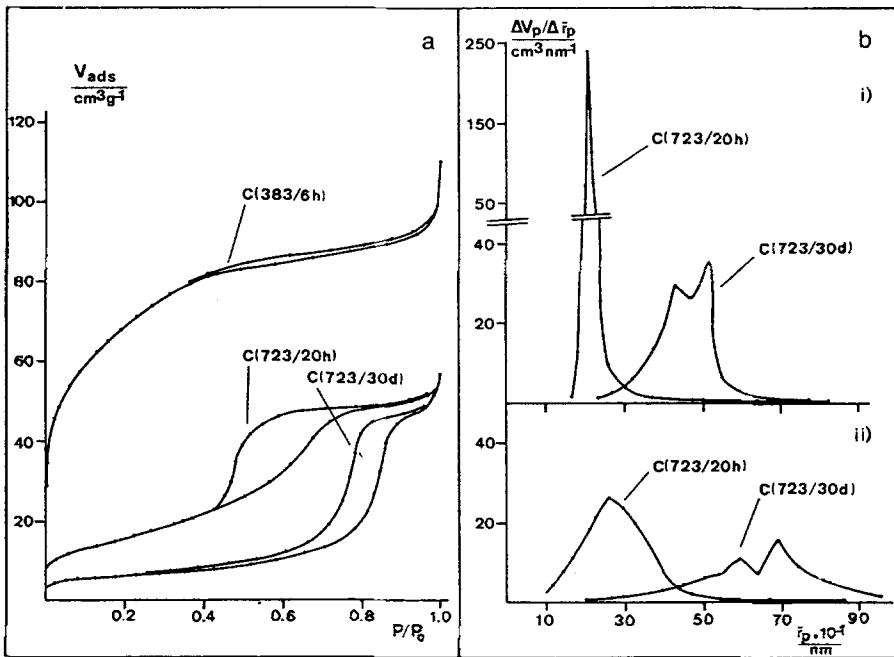

Fig. 1 Adsorption of nitrogen at 77 K on zirconia gel (C(383/6h)) and crystalline zirconia (C(723/20h), C(723/30d)) a) Adsorption-desorption isotherms b) Pore size distributions (i) desorption branch, ii) adsorption branch)

From the adsorption isotherms, several quantitites have been calculated and collected in Table 1. These include the BET monolayer capacity (V_m), the BET surface area (S_{BET}), the BET C value and the ratio of the monolayer capacities for adsorbed nitrogen and argon ($V_{m (N_2)} / V_{m (Ar)}$). The values of the external surface are (S_{α_s}) and micropore volume (V_o, using the density of the liquid adsor-

bates at 77 K), have been calculated from the α_s-plots (Fig. 2c) and also collected in Table 1.
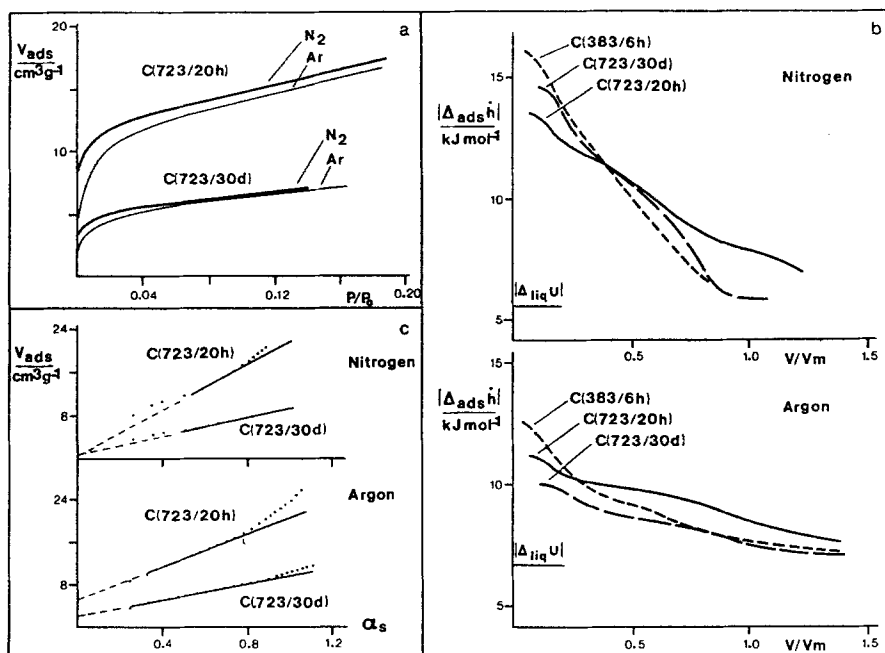

Fig. 2 Argon and nitrogen adsorption at 77 K on zirconia gel (C(383/6h)) and crystalline zirconia (C(723/20h), C(723/30d)) a) Adsorption isotherms. b) Differential enthalpy of adsorption as a function of coverage c) α_s-plots

The adsorption of argon and nitrogen on the mesoporous samples shows that:

In both cases, the ratio of the monolayer capacities ($V_{m\,(N_2)} / V_{m\,(Ar)}$) is higher than that calculated from the molar volumes of these adsorbates at the three-dimensional liquid state (Table 1).

Table 1 Adsorption parameters concerning crystalline zirconia

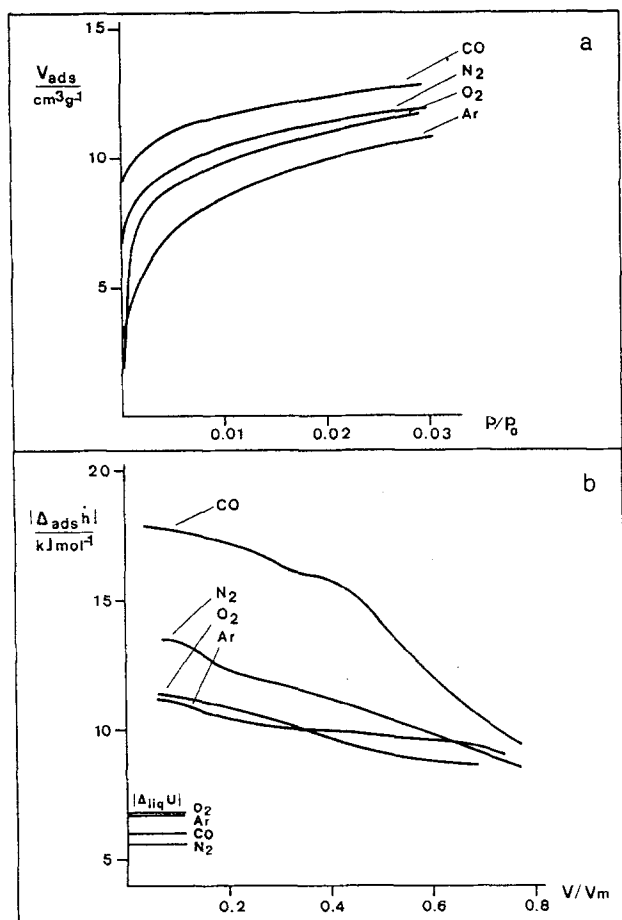| Sample	C(723/20h)				C(723/30d)	
Adsorbate	Ar	N$_2$	O$_2$	CO	Ar	N$_2$
V_m / cm^3·g^{-1}	15.0	15.7	16.9	16.1	6.5	6.6
S_{BET} / m^2·g^{-1}	55.5	68.5	64.0	70.0	24.2	28.7
C	46	47	41	70	82	87
$V_{m\,(N_2)} / V_{m\,(Ar)}$	1.05				0.01	
S_{α_s} / m^2·g^{-1}	38.1	63.5			18.2	26.2
V_o / cm^3·g^{-1}	0.006	0.0			0.003	0.001

Fig. 3 Adsorption of Ar, O_2, N_2 and CO at 77 K on sample C(723/20h) a) Adsorption isotherms b) Differential enthalpy of adsorption as a function of coverage

The differential enthalpy of adsorption of nitrogen is higher than that of argon at low surface coverage and its decrease during the progressive formation of the monolayer is larger and more sudden than for argon (Fig. 2b).

For argon adsorption, the enthalpy curves show at low surface coverage a decrease with increasing temperature (383 K to 723 K) and time (20 hours to 30 days) of treatment. However, in the case of nitrogen adsorption although the enthalpy values are higher for the microporous gel, these values increase when the time of treatment at 723 K is raised from 20 hours to 30 days.

For nitrogen adsorption, the α_s-plots (Fig. 2c) show a marked departure from linearity in the low coverage region.

From these results we can deduce several points of interest concerning these three samples:

The features that we can observe in the curves of differential enthalpy of adsorption of argon on these three samples, together with the α_s-plots, show that the higher differential enthalpy at low surface coverage for the gel is due to, its microporous structure, as previously shown [4].

In the case of the crystalline samples, both the values of the $(V_{m(N_2)} / V_{m(Ar)})$ ratio and the differences in the differential enthalpy of adsorption of nitrogen and argon, can be understood in terms of a specific interaction of the quadrupolar N_2 molecules with the polar sites of the surface, as previously shown in the case of hydroxylated silicas [9]. If so, some degree of localization of the molecules in the monolayer, can explain the departure from the linearity observed in the nitrogen α_s-plot at low coverage [10].

Concerning this point it is interesting to see Fig. 3. In the low pressure region the adsorption isotherms of Ar, O_2, N_2 and CO are shifted with respect to each other is such a way, that the higher the polarity of the adsorbate molecule, the higher the amount adsorbed. The differences in the BET area calculated from the isotherms (Table 1) can be explained in the same way that when comparing argon and nitrogen adsorption. With the assumption, as in the case of nitrogen adsorption [9], that the electrical field of the surface has an orientating effect on dipolar (CO) and quadrupolar (O_2) molecules, the mean cross-sectional are of these molecules is likely to be smaller than that obtained from the densities of the liquid adsorbates. If we take for the argon molecule a cross-sectional are of 0.138 nm^2, the values of 0.122, 0.131 and 0.129 nm^2 for O_2, N_2 and CO molecules respectively, provide agreement to the BET areas obtained. Calorimetric results are in accordance with the above interpretation; the differential enthalpy curves (Fig. 3b) show a clear relation between the adsorption enthalpy and the polarity of the adsorbate molecule. Polar sites in crystalline zirconia may be hydroxyl groups, coordinatively unsaturated Zr(IV) atoms, [11], and/or Zr(III) atoms because tetragonal zirconia has a noticeable stoichiometry range [12].

These results, seem also to indicate that in crystalline zirconia a long thermal treatment at 723 K produces a widening of the pores, responsible for the decrease in the argon-surface interaction and, at the same time, an increase in the specific interaction.

*   *   *

References

1 H. T. Rintjen, Physical and Chemical Aspects of Adsorbents and Catalysts, Academic Press, New York 1977, p. 316.
2 R. N. Patil and E. C. Subbarao, Acta Crystallogr., A26 (1970) 535.
3 M. J. Torralvo-Fernández and M. A. Alario-Franco, J. Colloid Interf. Sci., 77 (1980) 29.
4 M. J. Torralvo, Y. Grillet, F. Rouquerol and J. Rouquerol, J. Chim. Phys., 77 (1980) 125.
5 W. Hertl, Langmuir, 5 (1989) 96.
6 Y. Grillet, F. Rouquerol and J. Rouquerol, J. Chim. Phys., 2 (1977) 179 and 7–8 (1977) 778.
7 J. D. Carruthers, P. A. Cutting, R. E. Day, M. R. Harris, S. A. Mitchell and K. S. W. Sing, Chem. and Ind., (1968) 1772.
   D. A. Payne, K. S. W. Sing and D. H. Turk, J. Colloid Interf. Sci., 43 (1973) 287.
8 C. Pierce, J. Phys. Chem., 57 (1953) 149.
9 J. Rouquerol, F. Rouquerol, C. Pérès, Y. Grillet and M. Boudellal, Characterization of Porous Solids, Soc. Chem. Ind., London 1979, p. 107.
10 J. D. Carruthers, D. A. Payne, K. S. W. Sing and L. J. Stryker, J. Colloid Interf. Sci., 36 (1971) 205.
11 C. Morterra, R. Aschieri and M. Volante, Mater. Chem. Phys., 20 (1988) 539.
12 S. J. Aronson, Electrochem. Soc., 108 (1961) 312.

Zusammenfassung — Mittels Adsorptionsvolumetrie und isothermer Mikrokalorimetrie wurde bei 77 K die Adsorption von Argon, Sauerstoff, Stickstoff und Kohlenmonoxid an kristallinem Zirkoniumdioxid und an mikroporösen Zirkoniumdioxidgelen untersucht.

Die Mikroporenstruktur von Zirkoniumdioxidgel kann als Erklärung der höheren Adsorptionsenthalpie für Argon angesehen werden. Beide kristallinen Proben sind mesoporös und die polaren Stellen an der Oberfläche führen in jedem Falle zu spezifischen Wechselwirkungen mit dipolaren (CO) oder quadrupolaren (N_2, O_2) Molekülen, worauf man aus den Adsorptionsisothermen und den korrespondierenden differentialen Enthalpiekurven schließen kann.