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Microcalorimetric and IR-spectroscopic study of the room temperature adsorption of CO_2 on pure and sulphated t-ZrO_2

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Abstract

The room temperature adsorption of CO_2 on pure and sulphated tetragonal ZrO_2 (t-ZrO_2) was studied, in order to assess how and to what extent the acid–base properties of ZrO_2 are modified by the presence of surface sulphate groups. The formation of different species, as well as their stability upon outgassing, was monitored by IR spectroscopy (2000–1000 and 2400–2300 cm^{-1} regions), whereas the population and the distribution of sites of different kind was quantitatively and energetically characterised by adsorption microcalorimetry. The formation of carbonate-like species was found to be a highly energetic ($q_{ads} > 100$ kJ/mol) and irreversible process, occurring only on the (at least partially) dehydrated surface of pure t-ZrO_2. Bicarbonate-like (hydrogen-carbonate) species (either of stable type) were found to form on both pure and sulphated t-ZrO_2 specimens, and to be accompanied by a heat of adsorption variable in the 100–40 kJ/mol range. The presence at the surface of sulphate groups causes the basicity of the t-ZrO_2 matrix to be dramatically depressed, the most basic OH^- and/or coordinatively unsaturated (CUS) O^{2-} ions being preferentially consumed by the sulphation process. Linear coordinated CO_2 complexes were also found to form on CUS Zr^{4+} cations, the acidic strength of which increases with the extent of surface dehydration and as a consequence of the presence of charge-withdrawing surface sulphate groups. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Sulphated zirconia (SZ) has been reported to exhibit an unusually high acidic strength and unexpected high catalytic activity, e.g. in the low temperature isomerisation of short-chain *n*-alkanes [1,2]. For this reason, these systems have been extensively studied in the last two decades, mostly with respect to their peculiar acidic properties [3–8]. In contrast, very little is known on the residual basic properties of the ZrO_2 matrix after the sulphation process.

Aim of this work is to study the adsorption of CO_2 on pure and sulphated tetragonal ZrO_2 (t-ZrO_2), by coupling IR spectroscopy and adsorption microcalorimetry, in order to assess how and to what extent the acid–base properties of t-ZrO_2 are modified by the presence of surface sulphate groups. The pure parent t-ZrO_2 system was a phase-stabilised preparation, so that crystalline form and morphology of the two

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ZrO_2 samples were the same and did not represent a variable of the system [9]. The catalytic activity (standard reaction: the low-temperature isomerisation of *n*-butane) of the sulphated ZrO_2 specimen dealt with in the present work was also checked [10].

Carbon dioxide is a suitable probe to reveal and characterise the surface basicity of metal oxidic systems. Indeed, in the 2000–1000 cm^{-1} spectral region are visible the features of carbonate-like species, formed by the "side-on" coordination of CO_2 molecules on pairs of coordinatively unsaturated (CUS) O^{2-}–M^{n+} ions. Unfortunately, the relevant absorptions are complicated by a number of factors, among which the natural breadth of the bands, the presence for each kind of carbonate of band pairs (due to the anti-symmetric and symmetric stretching of O–C–O groups [11]), and the large variety of species formed. Within the vast category of carbonate-like species, on hydrated surfaces CO_2 is able to interact with suitably located OH groups, yielding bicarbonate-like (hydrogen-carbonate) species characterised, besides the O–C–O stretching modes pair, also by the presence of rather narrow peaks at ~3610 and ~1230 cm^{-1}, due to OH stretching (ν_{OH}) and bending (δ_{OH}) vibrations. The formation of bicarbonate-like species upon CO_2 adsorption is therefore, often visible also through the perturbation of the surface OH stretching pattern in the high-frequency region of the IR spectrum.

CO_2 is also a soft Lewis base, and can reversibly form weak σ-coordinated species on CUS cations (CUS Zr^{4+} in the present case). CO_2 uptake at room temperature can thus reveal also the strongest fraction of Lewis acidic sites present at the surface of metal oxides. The formation of linearly coordinated ("end-on") CO_2 complexes is witnessed by the appearance of strong IR bands located in the 2400–2300 cm^{-1} spectral region. The spectral position of linear CO_2 complexes can be taken as an indication of the acidic strength of the surface CUS cations, and can be roughly correlated to the heat of adsorption, i.e. to the energy of the acid–base interaction.

In the present contribution, the nature of the various surface species formed upon CO_2 adsorption, as well as their stability upon outgassing, was monitored by in situ IR spectroscopy, and was correlated to the activation temperature of the sample (i.e. the hydration state of the surface). The population and the distribution of the different types of sites was quantitatively and energetically characterised by room temperature adsorption microcalorimetry.

2. Experimental

2.1. Materials

(i) A crystallographically pure t-ZrO_2 preparation was obtained via a sol–gel method, and was stabilised by the insertion of 3 mol% Y_2O_3, as described elsewhere [12]. After calcination at 873 K, the t-ZrO_2 preparation has a BET surface area of 71 m^2/g. (ii) The sulphated t-ZrO_2 sample was obtained by direct sulphation with H_2SO_4 of the pure t-ZrO_2 preparation. After calcination at 923 K, the sulphated t-ZrO_2 preparation has ~3.0 SO_4 groups/nm^2 and a BET area of 80 m^2/g [13]. All samples were dehydrated in vacuo and oxidised with O_2 at various temperatures (303, 473 and 673 K) prior to any adsorption experiment. The samples will be hereafter referred to as TO3 (pure t-ZrO_2) and TO3S (sulphated/calcined t-ZrO_2). The symbols are followed by a numeral indicating the outgassing temperature (K), e.g. TO3S-673 stands for a sulphated t-ZrO_2 specimen, vacuum outgassed at 673 K. CO_2 specpure from Matheson was employed.

2.2. Methods

2.2.1. Microcalorimetry

Microcalorimetry was used to measure the heat of adsorption of CO_2 at 303 K. A heat-flow microcalorimeter (Tian-Calvet, Setaram, F) was employed, following a well established stepwise procedure, described elsewhere [14,15]. The calorimeter was connected to a high vacuum volumetric apparatus (residual $p \leq 10^{-5}$ Torr, 1 Torr = 133.3 N/m^2), which enabled to determine simultaneously the adsorbed amounts and the heat evolved at increasing equilibrium pressures for small increments of the adsorptive. A first adsorption run was performed on the activated samples (primary isotherms), and a second one after pumping off the reversible phase (secondary isotherms), in order to evaluate the irreversible component of the process. The pressure was measured by means of a transducer gauge (Barocell, Edwards, 0–100 Torr).

2.2.2. *IR spectroscopy*

IR spectra of adsorbed CO_2 were run at $2\,cm^{-1}$ resolution on a Bruker FT-IR spectrometer (Mod. 113v), equipped with a MCT detector. The nominal adsorption–desorption temperature was ~300 K, but some sample heating under the IR beam should be considered. Spectral patterns were run in a strictly in situ configuration, allowing reliable spectral ratioing and background subtractions. In particular, the contribution of the gas phase was computer subtracted from all spectra. Band resolutions were carried out on unsmoothed segments of the absorbance spectra, using a commercial program by Bruker (FIT) in which one only sets the number of spectral components and the desired accuracy. The equilibrium pressure of CO_2 was measured by means of a Pirani gauge ($p_{eq} < 2$ Torr) or a Hg manometer ($p_{eq} > 2$ Torr).

3. Results and discussion

3.1. *IR spectroscopy*

Figs. 1 and 2 show the IR spectra of CO_2 adsorbed on pure (TO3) and sulphated (TO3S) zirconia samples, outgassed at various temperatures (~303, 473 and 673 K). Section A of the two figures reports the spectral features observed in the low-frequency range $2000–1000\,cm^{-1}$, where both surface bicarbonate- and carbonate-like species form upon contact with CO_2. Section B of the two figures reports the higher frequency region ($2400–2300\,cm^{-1}$), where appear the spectral features of the end-on linear complexes that CO_2 forms with surface CUS Zr^{4+} cations.

In section A, for each sample in any dehydration step three curves are shown: the lowest one refers to the surface before CO_2 contact (background), the

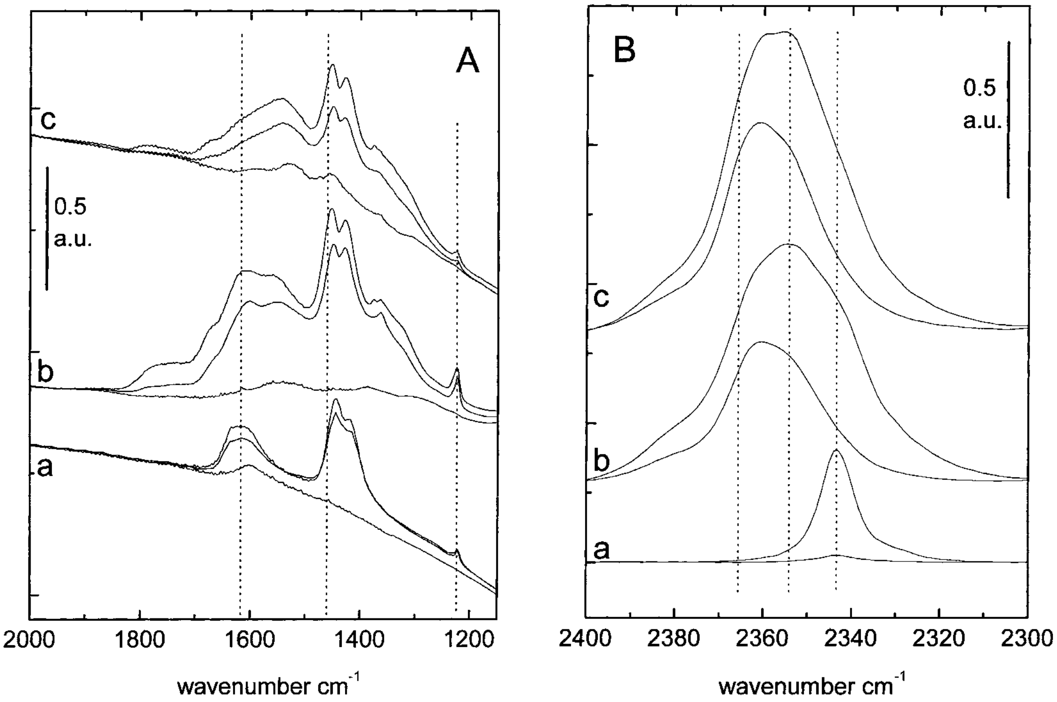

Fig. 1. Section A: IR absorbance spectra in bicarbonate and carbonate-like species spectral region ($2000–1000\,cm^{-1}$), obtained for TO3-300 (curves a), TO3-473 (curves b), and TO3-673 (curves c), before and after contact with some 25 Torr of CO_2, and subsequent evacuation at room temperature for 15 min. Dotted-line vertical traces indicate the position of the three low-frequency modes of bicarbonate-like species. Section B: IR differential spectra in the Σ_u^+ mode region ($2400–2300\,cm^{-1}$), relative to linear CO_2 complexes, obtained upon contact with CO_2 (~25 and 2.5 Torr, respectively) on TO3-300 (curves a), TO3-473 (curves b), and TO3-673 (curves c). Dotted-line vertical traces indicate the position of the three major spectral components giving the overall absorption.

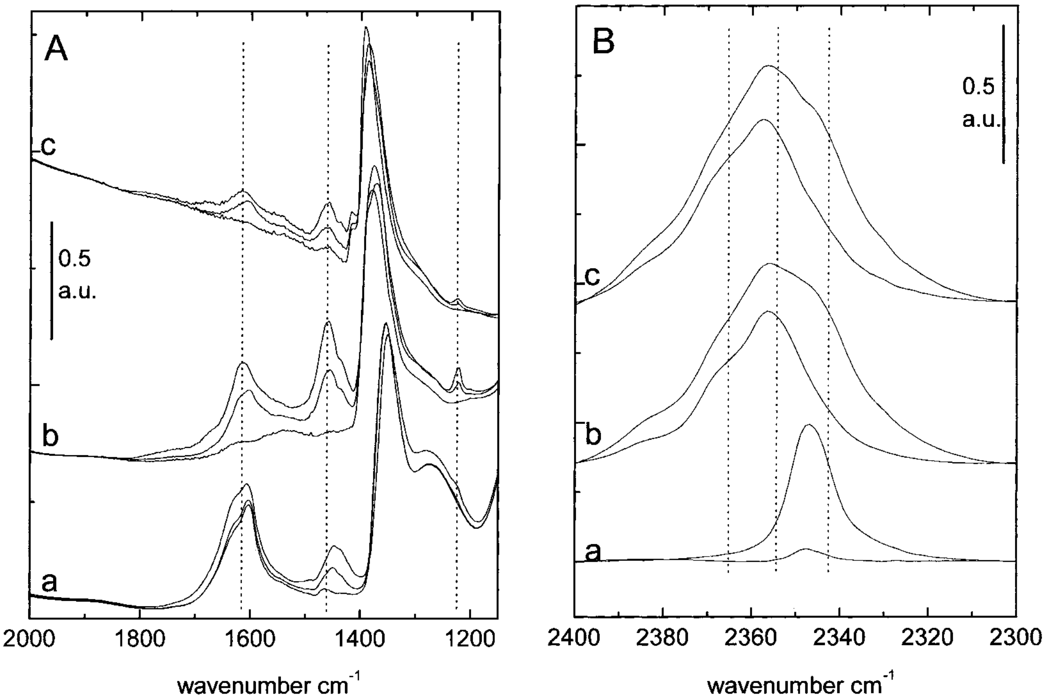

Fig. 2. Section A: IR absorbance spectra in bicarbonate- and carbonate-like species spectral region (2000–1000 cm^{-1}), obtained for TO3S-300 (curves a), TO3S-473 (curves b), and TO3S-673 (curves c), before and after contact with some 25 Torr of CO_2, and subsequent evacuation at room temperature for 15 min. Dotted-line segments indicate the position of the three low-frequency modes of bicarbonate-like species. Section B: IR differential spectra in $\Sigma_u{}^+$ mode region (2400–2300 cm^{-1}), relative to linear CO_2 complexes, obtained upon contact with CO_2 (~25 and 2.5 Torr, respectively) on TO3S-300 (curves a), TO3S-473 (curves b), and TO3S-673 (curves c). The dotted-line vertical traces indicate the position of the three major spectral components giving the overall absorption in the case of the non-sulphated parent TO3 system.

highest one to the sample in presence of some 25 Torr of CO_2 (maximum coverage attained), and the intermediate one to the sample outgassed 15 min after contact with CO_2. The latter spectra are of great interest, in that allow the stability of the species formed upon contact with CO_2 to be evaluated. As for section B, two curves are shown, relative to the maximum coverage (25 Torr) and to a medium-low coverage (~2.5 Torr); linear CO_2 surface complexes are fully reversible upon evacuation at beam temperature.

3.2. The TO3-T system

In Fig. 1A, curves a are relative to the TO3-300 sample, which bears a virtually fully hydrated surface. Indeed, in the background spectrum a broad absorption band located at ≈1630 cm^{-1}, due to the "scissor" bending mode of molecular water, is still appreciably evident. This band corresponds to water molecules coordinated on some of the surface CUS Zr^{4+} cations. By contacting the sample with CO_2, a rather complex spectrum is obtained: a weak δ_{OH} band at 1230 cm^{-1} indicates the formation of few bicarbonate-like species, whose O–C–O stretching bands are visible at ~1620 cm^{-1} (overlapped to the ~1630 cm^{-1} band of coordinated water) and 1450 cm^{-1}. Further to this, two other bands located at ~1430 and ~1460 cm^{-1} (overlapped to the high-frequency O–C–O mode of bicarbonate species) indicate the formation of some monodentate carbonate species, identified by the very small spectral separation between the two modes of the O–C–O coupled oscillators ($\Delta\nu \sim 20\ cm^{-1}$). It is recalled that, in the case of zirconia, this peculiar monodentate species forms only in the tetragonal form of the oxide, as previously reported [16].

By increasing the activation temperature (i.e. the surface dehydration degree), the complexity of the bands in this region is greatly enhanced. The bands of bicarbonate species increase in intensity on TO3-473 (curves b) with respect to TO3-300: indeed the progressive elimination of the surface hydrated layer increases the availability of surface OH species free from H-bonding, and thus, capable of forming bicarbonate species. At the same time, the formation of bidentate carbonates (bands at ~1550 and ~1330 cm^{-1} [11]) and, in minor extent, of the so-called bridged or "organic" carbonates (bands at ~1750 and ~1270 cm^{-1}) becomes more important.

By increasing the activation temperature up to 673 K, major changes are observed in the spectrum (curves c). The peculiar monodentate species are still clearly visible, but the bands typical of organic and bidentate carbonates exhibit lower intensity, as do the bands of the bicarbonate-like species.

Anticipating some of the quantitative data to be reported in the next section, the apparent decrease of adsorbing capacity of TO3-673 suggested by the spectra of Fig. 1A must be considered as an artifact, mainly due to a drastic decrease of the bands of bicarbonate species and, possibly, to changes of bands extinction coefficient with the surface hydration degree of the adsorbing system. The stability of all the carbonate-like species towards a room temperature outgassing is comparable. In fact, by pumping off the TO3 samples for some 15 min, the intensity of all spectral components decreases to the same extent, as witnessed by the spectra shown in Fig. 1A (see the intermediate curves in the spectral sets a, b and c).

In section B of Fig. 1, the spectral response in the 2400–2300 cm^{-1} interval, typical of linearly coordinated CO_2, is shown for the three TO3-T samples. In the case of the (virtually) fully hydrated sample (TO3-300, curves a), only a weak and symmetrical band centred at ~2345 cm^{-1} is observed in the presence of the highest CO_2 pressure. By partially pumping off CO_2 at beam temperature (down to 2.5 Torr), the band completely disappears, indicating that the linear CO_2 species formed on a highly hydrated surface are extremely labile. Unlike that, a very different situation is observed in the case of TO3-473 (curves b), as a complex absorption band, centred at ~2355 cm^{-1} and with components both at higher and lower frequency, forms upon CO_2 uptake. The spectral position of the overall band, located at higher frequency with respect to TO3-300, indicates that the CUS Zr^{4+} cations present on this sample, and able to coordinate CO_2 at room temperature, possess a higher Lewis acidic strength. The far larger intensity of the band (with respect to TO3-300) indicates that the populations of sites increases with increasing outgassing temperature, as expected, owing to the enhanced dehydration of the surface. The CO_2 adducts formed on TO3-473 are more stable than the ones formed on TO3-300, in that the ~2355 cm^{-1} band is still largely visible under an equilibrium pressure of ~2.5 Torr. The only component totally absent in the low-pressure conditions is the low-frequency one located at ~2345 cm^{-1}, and due to very labile (quasi-physisorbed) species. Outgassing at 473 K eliminates all the residual molecular water coordinated onto CUS Zr^{4+} cations and, possibly, a first fraction of surface OH groups. This allows Lewis acidic sites to become free to interact with CO_2: in this case, CO_2 turns out to be a good probe for testing the Lewis acidity of the surface brought about by the onset of the surface dehydration process.

In the case of TO3-673 (curves c), the overall intensity of the $\Sigma_u{}^+$ mode band increases further with respect to the TO3 samples outgassed at lower temperatures, suggesting an increased population of Lewis acidic sites. In particular, the relative intensity of the high-frequency components of the band is greatly enhanced, indicating that the outgassing at 673 K allows CUS cationic species of higher acidic strength to be created. Indeed, the activation at high temperature brings about the gradual elimination of surface OH species. The stability too of the CO_2 species formed on the highly acidic cations present on the TO3-673 surface is enhanced with respect to the samples outgassed at lower temperature, in that the CO_2 adducts are still abundantly present at an equilibrium pressure as low as ~2.5 Torr. These species are hardly eliminated upon a prolonged outgassing at room temperature, and mostly the high-frequency species.

3.3. *The TO3S-T system*

Let us turn now to the effects induced by the presence of sulphate groups at the surface of t-ZrO_2. Fig. 2A reports the spectral response in the low-frequency 2000–1000 cm^{-1} region of CO_2 adsorbed on TO3S outgassed at 303, 473 and 673 K. As in the case of the parent TO3 samples, three curves for each sample in any dehydration step are shown. By comparing this figure with the correspondent one relative to pure TO3 (see Fig. 1A), major differences are observed. In any case, the spectra of TO3S-T samples are dominated by a strong band at $\sim$1350–1390 cm^{-1}, due to the S=O stretching vibration of surface sulphates. It is worthnoting that this band is slightly perturbed, in both frequency and intensity, in the presence of adsorbed CO_2 and that a prolonged outgassing, that gets rid of the reversible fraction of adsorbed CO_2, does not bring the S=O band to the starting condition, meaning that the non-reversible fraction of adsorbed CO_2 is mainly responsible for the perturbation of surface sulphates. As for the bands of carbonate-like species forming upon contact with CO_2, in this case, they turn out to be definitely much weaker and far less complex than in the case of pure TO3. On the various TO3S-T samples, bands of variable intensity form at 1230 cm^{-1} (δ_{OH}), at 1450 and 1620 cm^{-1} (bicarbonate O–C–O anti-symmetric and symmetric stretching modes), whereas there is little evidence (if any) of the formation of either bidentate or "organic" bridging carbonates. Note that the sample activated at $\sim$300 K still shows an appreciable band at 1630 cm^{-1}, relative to the scissor mode of coordinated molecular water, and a sharp peak at $\approx$1600 cm^{-1}, due to H_3O^+ species formed in the presence of non-interacting bisulphato groups [17]. On this highly hydrated surface, the contact with CO_2 only produces a very small amount of bicarbonate species, as a consequence of the scarce availability of OH species free from H-bonding and of CUS surface cations on which the first coordination of CO_2 occurs [18,19]. Also, the stability of bicarbonate species is very low, in that even a short outgassing is sufficient to suppress almost completely all the spectral features of these species. Increasing the activation temperature up to 473 K, it is possible to observe the maximum amount of bicarbonates that may form upon CO_2 contact (as witnessed by the intensity of the δ_{OH} band at $\sim$1230 cm^{-1}). It is not surprising that the sulphation process, leading to the formation at the surface of acidic sulphate groups, suppresses almost completely the basic properties of zirconium dioxide. Somewhat surprising is, on the contrary, the fact that the only residual basicity of sulphated t-ZrO_2 is due to some OH groups, responsible for the formation of some bicarbonate species [16]. The surface population of these OH species, absorbing at $\sim$3760 cm^{-1} and ascribed to terminal (mono-coordinated) hydroxyls, is either unchanged or even increased by the sulphation process.

In section B of Fig. 2, the spectral range of linearly coordinated CO_2 (2400–2300 cm^{-1}) is shown for the three TO3S-T samples. Let us consider first the virtually fully hydrated TO3S-300 system (curves a): the spectrum is quite similar, in shape and intensity, to that obtained with the corresponding unsulphated system, as on the highly hydrated surface only a band located at $\sim$2345 cm^{-1}, due to an extremely labile (quasi-physisorbed) species is present. The only difference is that the spectral position of the weak linear CO_2 species is some 5 cm^{-1} higher than in the case of the non-sulphated system, due to inductive effects caused by charge-withdrawing surface sulphate groups. For this reason, it is rather unlikely that this low-frequency linear CO_2 band is due to a merely physisorbed species. Similarly to what observed for the non-sulphated sample, in the case of more highly dehydrated surfaces, such as TO3S-473 (curves b) and TO3S-673 (curves c), a significant shift of the overall CO_2 band towards higher frequency, as well as a dramatic increase in the intensity of the band itself, is observed. These results indicate that on both TO3S-473 and $-$673 the uptake of end-on CO_2 is much higher than on TO3S-300, as more and more acidic CUS Zr^{4+} cations are involved in the formation of linear CO_2 complexes. By comparing the spectral position of the band of linearly coordinated CO_2 formed on sulphated and unsulphated samples, it is worthnoting that, in all cases, all components of the band (including the low-frequency one) are somehow shifted towards higher frequencies. As anticipated for the low-frequency species, this upwards-shift of Lewis coordinated species is an effect typical of sulphated systems: the presence of electron-acceptor groups as sulphate groups, increases the Lewis acidic strength (i.e. the electron-withdrawing capacity) of the CUS cationic sites. As a consequence, the spectral position grows, and the lability of the adsorbed species decreases. In fact, in the case of TO3S-673, the linear CO_2 complexes were so resistant to an outgassing at beam temperature that a prolonged ($\sim$30 min) evacuation was needed to achieve a complete elimination of the relevant band.

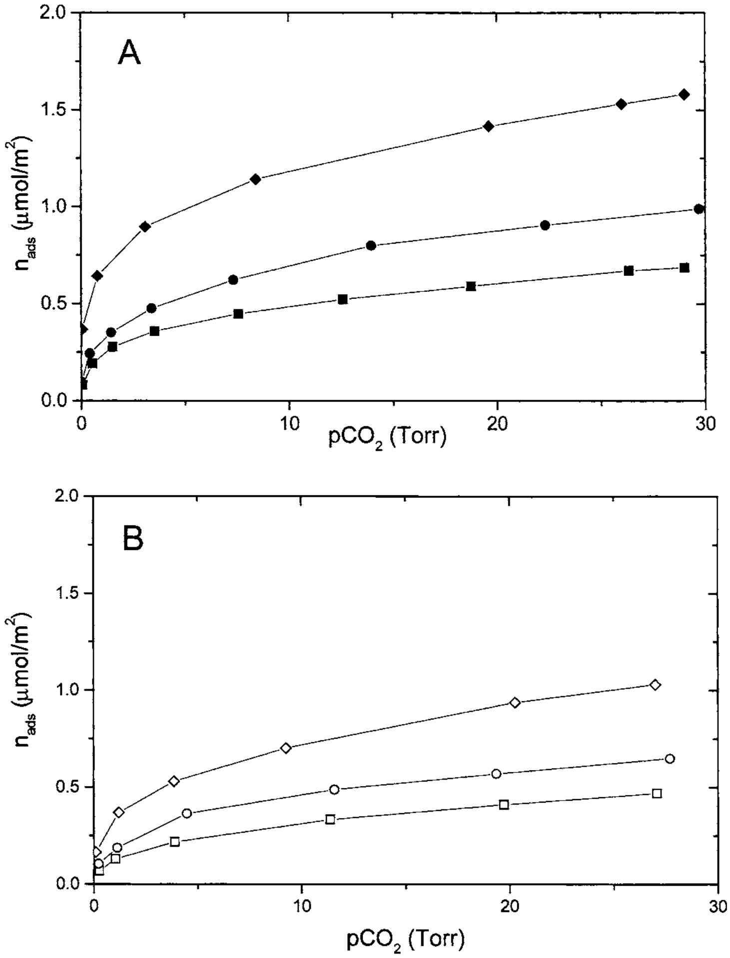

Fig. 3. Section A: volumetric isotherms (adsorbed amounts vs. equilibrium pressure: first run) of CO_2 on pure ZrO_2 (TO3) outgassed at $T = 303$ K (square); 473 K (circle); 673 K (diamond). Section B: the same as in section A, but second run adsorption isotherms (open symbols). $T_{ads} = 303$ K.

3.4. Adsorption microcalorimetry

In Fig. 3, the volumetric isotherms (n_{ads} versus p, adsorbed amounts as a function of equilibrium pressure) of CO_2 adsorbed on TO3-T samples are reported. Section A refers to the primary adsorption isotherms (total uptake), whereas sections B to the secondary ones (reversible uptake). It is clearly evident that the adsorbed amounts per unit surface area increase as the outgassing temperature increases, according to the fact that the number of surface sites able to interact with CO_2 increases with the progressive surface dehydration. By comparing primary and secondary volumetric isotherms, it appears that the interaction is only partially reversible (in the adopted conditions: outgassing at 303 K at $p \sim 10^{-5}$ Torr). For instance, at $p = 25$ Torr and for each activation temperature, ~33% of the total amounts adsorbed in the primary run remains irreversibly held at the surface. The calorimetric isotherms (Q^{int} versus p_{CO_2}, integral heat evolved as a function of equilibrium pressure: not reported for the sake of brevity) exhibit a similar trend. By subtracting the second run curves from the first one, the amounts of the irreversible component of the process are obtained. Table 1 reports, for all TO3-T samples, the quantitative and

Table 1
Quantitative (n_{ads}: adsorbed amounts, (μmol/m^2)) and energetic data (Q^{int}: integral heat evolved (J/m^2); $q_p = (Q^{int}/n_{ads})_p$ kJ/mol: molar heat of adsorption at $p_{CO_2} = p$) for CO_2 adsorbed on pure (TO3-T) and sulphated (TO3S-T) ZrO_2 at low and high CO_2 pressure

n_{ads} (μmol/m^2)	μmol/m^2 (first run) at $p = 2.5$ Torr	μmol/m^2 (first run) at $p = 25$ Torr	μmol/m^2 (second run) at $p = 2.5$ Torr	μmol/m^2 (second run) at $p = 25$ Torr	μmol/m^2 (first to second run) at $p = 2.5$ Torr	μmol/m^2 (first to second run) at $p = 25$ Torr
TO3-303	0.314	0.667	0.176	0.451	0.138	0.216
TO3-473	0.422	0.941	0.271	0.628	0.151	0.313
TO3-673	0.843	1.529	0.451	1.020	0.392	0.509
TO3-S-303	0.031	0.232	0.031	0.186	–	0.046
TO3-S-473	0.248	0.682	0.217	0.651	0.031	0.031
TO3-S-673	0.604	1.116	0.589	1.085	0.015	0.031
Q^{int}(J/m^2 × 10^2)	J/m^2 × 10^2 (first run) at $p = 2.5$ Torr	J/m^2 × 10^2 (first run) at $p = 25$ Torr	J/m^2 × 10^2 (second run) at $p = 2.5$ Torr	J/m^2 × 10^2 (second run) at $p = 25$ Torr		
TO3-303	2.16	3.11	1.08	1.89		
TO3-473	2.97	4.32	1.62	2.97		
TO3-673	6.08	8.65	3.16	6.22		
TO3-S-303	0.155	0.698	0.155	0.465		
TO3-S-473	1.55	3.26	1.40	3.02		
TO3-S-673	3.95	6.28	3.80	6.05		
$q_p = (Q^{int}/n_{ads})_p$ (kJ/mol)	kJ/mol (first run) at $p = 2.5$ Torr	kJ/mol (first run) at $p = 25$ Torr	kJ/mol (second run) at $p = 2.5$ Torr	kJ/mol (second run) at $p = 25$ Torr		
TO3-303	69	47	38	42		
TO3-473	70	46	60	47		
TO3-673	72	57	70	61		
TO3-S-303	50	30	50	25		
TO3-S-473	63	48	65	46		
TO3-S-673	65	56	65	56		

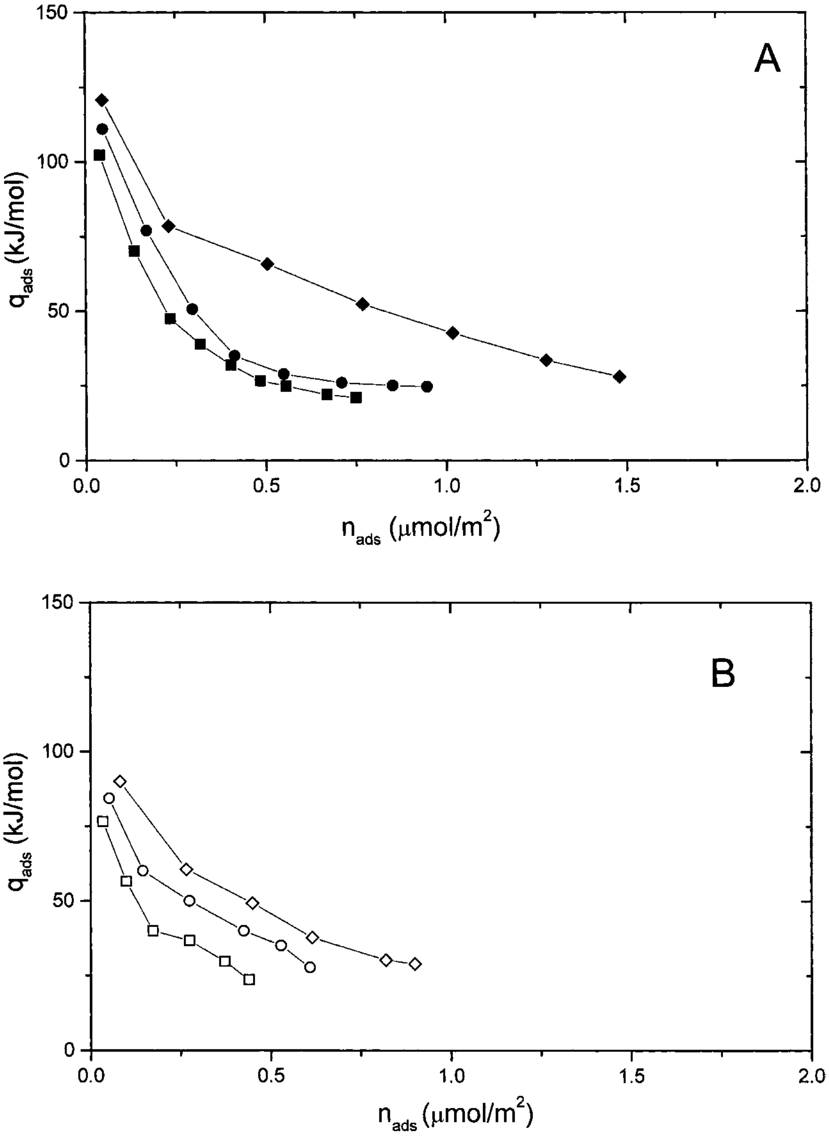

Fig. 4. Section A: heat of adsorption of CO_2 as a function of coverage (first run) on pure ZrO_2 (TO3) outgassed at $T = 303$ K (square); 473 K (circle); 673 K (diamond). Section B: the same as in section A, but second run of adsorption (open symbols). $T_{ads} = 303$ K.

energetic adsorption data (total, reversible and irreversible components) at low (2.5 Torr) and high (25 Torr) pressure of CO_2.

In Fig. 4, the (differential) heat of adsorption of CO_2 on TO3-T samples are reported for the first run (section A) and the second run (section B). In all cases the trend of the curves of Fig. 4A is typical of highly heterogeneous surfaces, in that the heat values decrease from an initial high value down to quite low values, i.e. ~25 kJ/mol. However, the various curves decrease in a significantly different way. In particular, the curves of TO3-303 and TO3-473 decrease quite rapidly from an initial q_0 value (heat of adsorption extrapolated to zero coverage) of ~125 and 110 kJ/mol, respectively, whereas the TO3-673 curve, that exhibits a q_0 value only slightly higher (~130 kJ/mol), decreases much more smoothly than the other two. This particular trend indicates the presence on TO3-673 of a large family of sites interacting with CO_2 with a heat of adsorption in the 100–40 kJ/mol interval, likely due to the far more severe surface dehydration attained. Part of these sites are likely to be pairs of CUS Zr^{4+}–O^{2-} sites giving rise, upon interaction with CO_2, to strongly adsorbed carbonate-like species responsible for the IR bands observed in the 2000–1000 cm^{-1} region, as seen in Fig. 1A. In Fig. 4B, the secondary run curves are shown. For any outgassing temperature, the extrapolated q_0 values are lower than in the first run: slightly below 100 kJ/mol for TO3-303 and TO3-473 and slightly above 100 kJ/mol in the case of TO3-673. The observed trends indicate that, as expected, the reversible interaction of CO_2 with the surface is less energetic than the total interaction (reversible plus irreversible adsorption). Indeed, bicarbonate species are only partially reversible upon outgassing at 303 K, and carbonate-like species are not reversible at all, as already indicated by the IR spectra. The shape of the curves is similar in all cases, but for the higher heat values in the curves obtained for higher outgassing temperature. At the final equilibrium pressure reached during our experiments ($p \sim 25$ Torr) the heat of adsorption approaches a plateau at ~25 kJ/mol. This low heat of adsorption can be reasonably associated with the formation of the very labile (quasi-physisorbed) linear CO_2 species observed at ~2345 cm^{-1} (see Fig. 1B).

In Fig. 5, the volumetric isotherms of CO_2 adsorbed on TO3S-T samples are reported. Unlike what observed for the pure TO3-T specimen, in this case, it is clearly evident that the adsorbed amounts per unit surface area during the first and secondary adsorption runs are very close, suggesting that the interaction between CO_2 and the sulphated t-ZrO_2 samples is almost totally reversible. This is in quite good agreement with what observed in the IR spectra, shown in Fig. 2. In the TO3S-473 and −673 the irreversible component is <5% of the total adsorption. In Table 1, the quantitative and energetic data obtained for CO_2 adsorbed on TO3S-T systems are reported and compared with data obtained for the unsulphated TO3-T samples.

By comparing the volumetric isotherms obtained for sulphated and non-sulphated systems, it appears clearly that (for any activation temperature), the presence at the surface of sulphates depresses the amount of CO_2 adsorbed. The calorimetric isotherms (not reported) do exhibit a similar trend, indicating that also the integral heat evolved during the adsorption process is depressed by the surface sulphate groups. This datum is not surprising, in that the sulphation process is actually expected to get rid of the strongest surface basic sites, able to bind irreversibly CO_2. At the opposite, the sites able to bind CO_2 molecules reversibly are not dramatically decreased by the surface sulphation process, as witnessed by the similarity

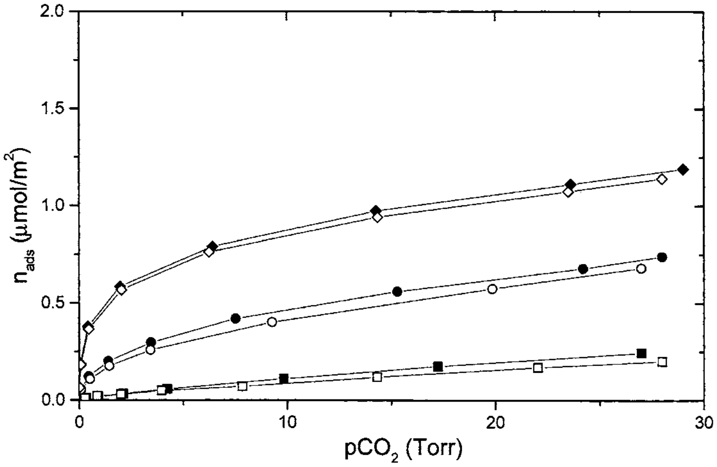

Fig. 5. Volumetric isotherms (adsorbed amounts vs. equilibrium pressure) of CO_2 on sulphated ZrO_2 (TO3S) outgassed at $T = 303$ K (square); 473 K (circle); 673 K (diamond). Solid symbols: first run; open symbols: second run. $T_{ads} = 303$ K.

of the amounts adsorbed (per unit surface area) in the secondary adsorption run of the pure TO3 and the primary/secondary adsorption runs on TO3S, especially on samples activated at medium-high temperatures. To better illustrate the different population of the various species formed on pure TO3 and sulphated TO3S samples, the total amounts (first run) as well as the reversible (second run) and the irreversible (first minus second runs) ones are shown as a function of the activation temperature in Fig. 6 (section A reports data for pure TO3-T samples and section B for the sulphated TO3S-T ones). The difference in the quality of the interaction of CO_2 with the two different samples is quite striking. In fact: (i) the irreversible component is rather important for the basic surface of pure t-ZrO_2, whereas it is virtually null in the case of the surface of t-ZrO_2 modified by the sulphation process; (ii) in the case of sulphated samples the total amount adsorbed (at $p = 25$ Torr) are lowered by some 30% with respect to the pure (basic) TO3 system; (iii) the total amounts adsorbed per unit surface area on the sulphated TO3S system increase linearly with activation temperature, whereas in the case of pure TO3 we note that, for activation $T \geq 473$ K, the adsorbed amounts increase more rapidly than at lower activation temperature.

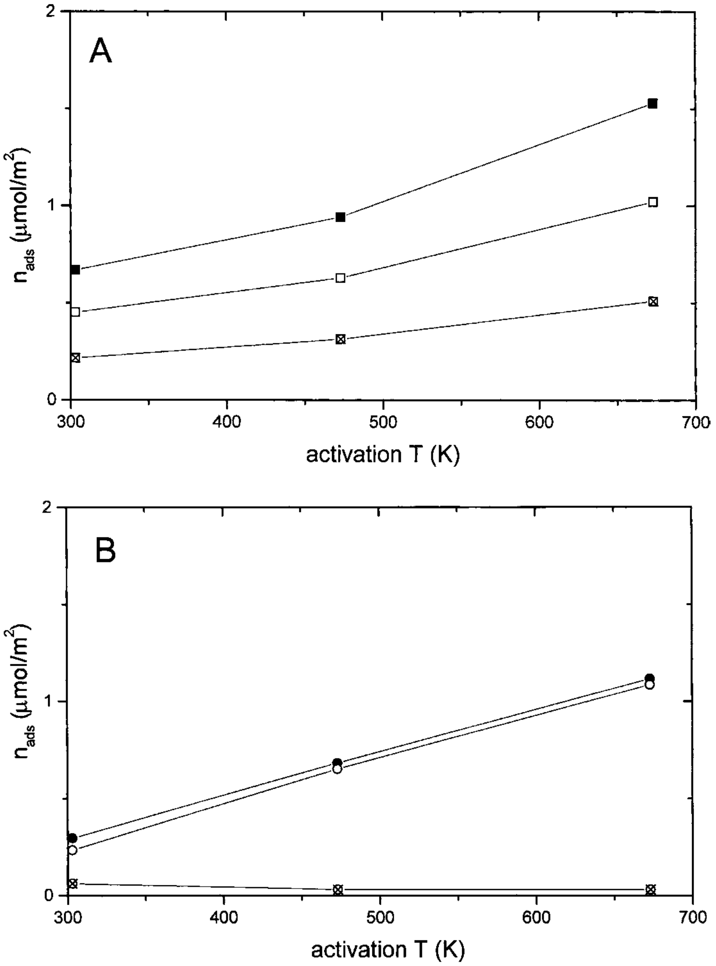

Fig. 6. Section A: amounts of CO_2 adsorbed at $p = 25$ Torr on pure ZrO_2 (TO3) as a function of the activation temperature. Solid symbols: total adsorption (first run); open symbols: reversible adsorption (second run); crossed symbols: irreversible component (first to second run). Section B: the same as in section A, but for CO_2 adsorption on sulphated ZrO_2 (TO3S).

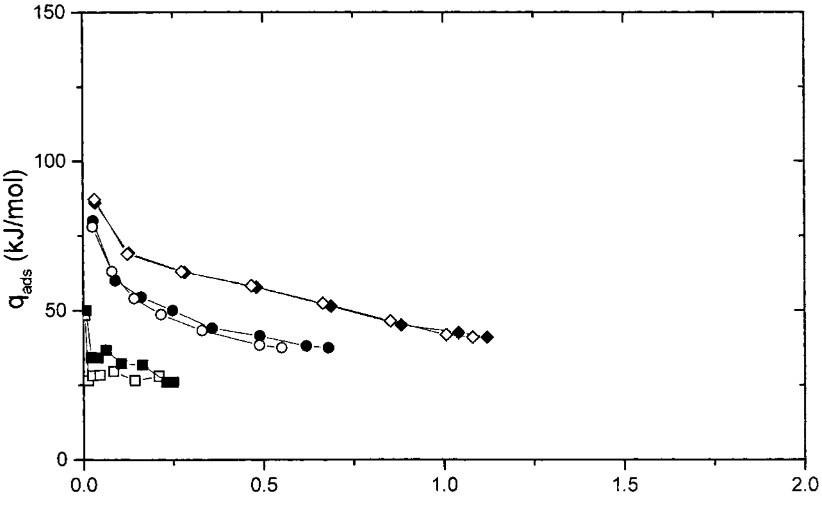

Fig. 7. Heat of adsorption of CO_2 as a function of coverage on sulphated ZrO_2 (TO3S) outgassed at $T = 303$ K (square); 473 K (circle); 673 K (diamond). Solid symbols: first run; open symbols: second run. $T_{ads} = 303$ K.

It is worthnoting that the latter effect is due to a fair increase of both reversible and irreversible components.

In Fig. 7, the (differential) heats of adsorption on the sulphated TO3S-T samples are reported as a function of the adsorbed amounts. Major differences are observed in the spectrum of heat values of sulphated samples in comparison with the unsulphated ones. Apart from the virtually total reversibility of the interaction (i.e. virtual coincidence of first and second runs) both q_0 values and shape of the heat versus coverage plots are completely different from those of the pure specimens. In particular, the adsorption heat values of TO3S-303 are quite low and almost constant (~25 kJ/mol), in agreement with the IR-spectroscopic indication that, on this sample, only very labile quasi-physisorbed species are formed upon contact with the highest CO_2 pressure (Fig. 2). All adsorption heat values of TO3S-473 and −673 are higher than those of TO3S-303, the q_0 values are slightly below 100 kJ/mol and decrease smoothly down to 45 and 50 kJ/mol, respectively. The heat versus coverage plot of TO3S-673 lies above that of TO3S-473 in the whole coverage interval examined. By comparing the first/second runs curves of the reversible uptake on TO3S-T with the intrinsically reversible secondary run curve of unsulphated TO3-T systems, it is worthnoting that for the samples activated at 473 and 673 K the q_0 value is comparable (~100 kJ/mol), but the curves of TO3 decrease with increasing coverage more rapidly than those of TO3S. The limit heat value for TO3 is ~25 kJ/mol, whereas for TO3S-473 and 673 it is ~40 kJ/mol. As for the TO3S-303 system, the measured heats are quite low, but this is not surprising if we consider that the small regions of the surface free from sulphates are (virtually) completely hydrated, and thus, possess very few sites available for the interaction with CO_2. Consistently, the heat values of TO3S-303 are lower than those of for the pure TO3 sample.

In order to illustrate better the proportions of the various species created upon contact with CO_2 at the surface of TO3 and TO3S, three different domains can be singled out in the heat versus coverage plots: (i) species formed with a heat higher than 100 kJ/mol; (ii) species formed with a heat comprised in the 100–40 kJ/mol interval; (iii) species formed with a heat lower than 40 kJ/mol. The reasons for this quite arbitrary (though reasonable) choice stems on the fact that species formed with $q > 100$ kJ/mol are irreversibly formed only on the pure TO3 system, in that neither in the case of the secondary adsorption isotherms on TO3 nor in the case of all isotherms on TO3S heat values higher than 100 kJ/mol were ever measured. These species are identified as carbonate-like species, as indicated by the IR spectra of Fig. 1A. At high coverage (equilibrium pressure of ~25 Torr), the heat versus coverage plots of TO3S-T tend to a plateau of ~40 kJ/mol, whereas in the case of TO3-T samples the plots tend to a plateau of only ~25 kJ/mol. We consider that, at the highest coverage reached ($p \sim 25$ Torr) CO_2 species linearly coordinated on CUS Zr^{4+} cations prevail: the surface presence of charge-withdrawing sulphate species was explained above to increase the acidity of coordinatively unsaturated cations, and this is the reason why the heat of formation of these species is appreciably higher on TO3S than on TO3 case. This observation is in agreement with the spectroscopic evidence of an upwards frequency shift of linearly coordinated CO_2 species formed on TO3S-T samples. On the basis of the IR-spectroscopic evidence, it is also possible to assign the heat values in the 100–40 kJ/mol interval to bicarbonate-like species (of both stable and labile nature) and to the strongest (but still reversible) coordinated CO_2 species.

In Fig. 8, the amounts adsorbed within a particular interval of heat values are reported as a function of the activation temperature. Section A refers to pure

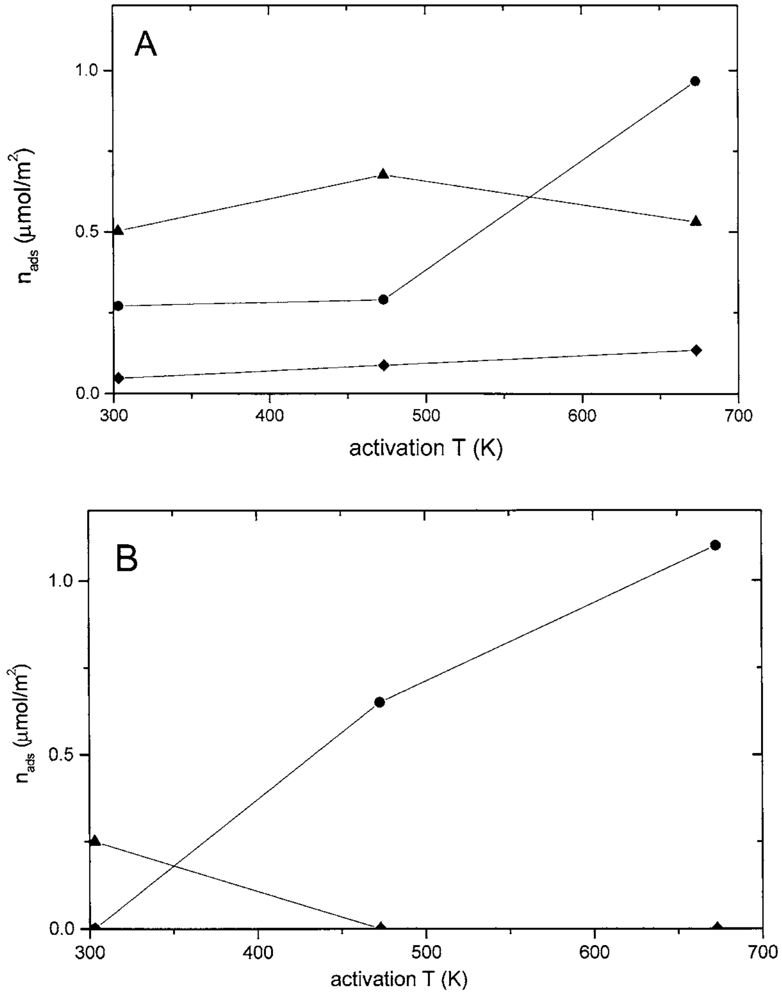

Fig. 8. Section A: total amounts (first run) of CO_2 adsorbed on pure ZrO_2 (TO3) as a function of the activation temperature. Diamond symbols: high energetic species ($q_{ads} > 100$ kJ/mol); circle symbols: medium-energetic species ($100 < q_{ads} < 40$ kJ/mol); triangle symbols: low-energetic species ($q_{ads} < 40$ kJ/mol). Section B: the same as in section A, but for CO_2 adsorption on sulphated ZrO_2 (TO3S).

TO3, whereas section B to TO3S. In the case of pure TO3 (first run), highly energetic sites ($q > 100$ kJ/mol) are only a minor component of the process, but their number increases linearly with increasing activation temperature. Medium-energetic sites ($100 < q < 40$ kJ/mol interval) are definitely more abundant than the most energetic ones, and are almost constant for TO3-303 and TO3-473 whereas on TO3-673 the amount of this species increases significantly. Low-energetic sites ($q < 40$ kJ/mol) are the most abundant ones, but their number tends to decrease somewhat for activation at $T \geq 473$ K. In the case of TO3S samples, the sites distribution is dramatically different from that of non-sulphated systems: highly energetic sites (in our model, the sites capable to form carbonate-like species) are virtually absent, irrespective of the outgassing temperature. Low energetic sites ($q < 40$ kJ/mol) are present only in the low-temperature activated TO3S-303 specimen, whereas medium-energetic sites are virtually the only species responsible for the interaction of CO_2 with TO3S-473 and TO3S-673. The relevant adsorbed CO_2 species are mainly labile bicarbonate-like ones and "end-on" $Zr^{4+} \leftarrow CO_2$ adducts.

4. Conclusions

The combined use of adsorption microcalorimetry and IR spectroscopy allowed to describe the evolution of basic sites present at the surface of a pure tetragonal form of ZrO_2, variously activated, by using CO_2 as a molecular probe. Different surface species were found to form upon contact with CO_2, following the extent of surface dehydration brought about by vacuum thermal treatments in the ~300–673 K interval. In the analytical spectral region, 2000–1000 cm^{-1}, the "side-on" coordination of CO_2 on CUS O^{2-}–Zr^{4+} pairs leads to the formation of carbonate-like species together with bicarbonate-like species. The latter form on available terminal OH groups, present on partially dehydrated surfaces. Being CO_2 also a soft Lewis base, "end-on" coordination of CO_2 leads to the formation of several species at acidic CUS Zr^{4+} cationic sites, revealed in the 2400–2300 cm^{-1} spectral region, whose presence at the surface is a consequence of the dehydration process. The overall ZrO_2/CO_2 interaction was found to be largely irreversible, in that even a prolonged evacuation at ambient temperature allows only a labile fraction of bicarbonate species and all of the linearly coordinated CO_2 to be desorbed.

The same pure tetragonal form of ZrO_2 surface modified by the addition of sulphates (and calcined at a proper temperature, in order to obtaining a strongly acidic catalyst active in the low temperature isomerisation of *n*-butane) was found to behave quite differently towards CO_2. In fact, the basic properties of pure t-ZrO_2 were found to be dramatically depressed in the sulphated specimens, though not suppressed. CO_2 uptake on sulphated t-ZrO_2 was found to lead to few species that are almost completely reversible, but for a small fraction of bicarbonate-like species. As for the energetic aspects of CO_2 adsorptive, it was observed that the heat of adsorption is quite high (q_{ads}>100 kJ/mol) in the case of strong and irreversibly held carbonate-like species, whereas it is comprised in the 100–25 kJ/mol for both bicarbonate-like species (either stable or labile upon evacuation) and linearly coordinated CO_2. The low limit-value of ~25 kJ/mol, measured at the highest coverage attained with pure t-ZrO_2 is associated with the formation of a very labile (quasi-physisorbed) linear species, identified by a sharp band located at ~2345 cm^{-1}, the only component present in that spectral region on t-ZrO_2 activated at room temperature. In the case of sulphated t-ZrO_2, the low limit-value is still ~25 kJ/mol only for the (virtually) fully hydrated samples. In the case of samples outgassed at a temperature sufficiently high to make available some the acidic CUS Zr^{4+} sites, the low limit-value for the heat of adsorption is significantly higher than ~25 kJ/mol (~40 kJ/mol). In addition, all the linear CO_2 complexes formed on sulphated t-ZrO_2 samples are shifted towards higher frequencies, indicating that the relevant CO_2 species formed at CUS Zr^{4+} cations are more strongly bound. The acidic strength of surface CUS cations turns out to be enhanced, by inductive effect, in the presence of strong charge-withdrawing surface sulphate groups.

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