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Development and Suppression of Surface Acidity on Monoclinic Zirconia: A Spectroscopic and Calorimetric Investigation

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The surface Lewis acidity of pure monoclinic ZrO_2 activated at three different temperatures (670, 870, and 1070 K) has been studied from a quantitative and energetic point of view by means of adsorption of CO at room temperature, coupling IR spectroscopy, and adsorption microcalorimetry. Two different CO adspecies are formed at the surface, whose spectral position, heat of adsorption, and relative population depend on the extent of surface dehydroxylation: a high-frequency (CO_H) species ($2192\text{--}2195\text{ cm}^{-1}$, $65\text{--}73\text{ kJ mol}^{-1}$, $0.18\text{--}0.24\text{ CO molecule nm}^{-2}$ on ZrO_2 outgassed at 670 and 870 K, respectively) and a low-frequency (CO_L) species ($2184\text{--}2187\text{ cm}^{-1}$, $44\text{--}50\text{ kJ mol}^{-1}$, $0.50\text{--}0.80\text{ CO molecule nm}^{-2}$ on ZrO_2 outgassed at 670 and 870 K, respectively). At 1070 K, the onset of the sintering causes a marked decrease in the population of the high-frequency species but does not modify the acidic strength of the two sites. The change of acidity with the extent of surface dehydroxylation has also been checked by adsorbing CO during a stepwise rehydration of the surface obtained by irreversible adsorption of H_2O . Following reconstruction of the surface-hydroxylated layer, the activity toward CO progressively declines and is eventually suppressed. There is a linear dependence of the decrease of the activity toward CO on the amount of preadsorbed water: four molecules of H_2O irreversibly held at the surface cause the elimination of one acidic site. Both spectroscopic and energetic data indicate that the rehydration pattern is far from being the plain reverse of the dehydration one.

Introduction

In recent years, zirconium dioxide has become very important in the field of high-technology ceramics, with improved mechanical properties (particularly in wear parts, i.e., engine applications).¹

The understanding of the surface behavior of the finely divided zirconia as starting material is quite important in order to characterize it as a precursor for neoceramic materials. In fact, the sintering process and the overall chemical properties of the product may be affected by the acid-base properties of the surface and by the nature of the hydrated surface layer.

The surface properties of zirconia have been studied in recent years by several authors, as ZrO_2 is also widely used in heterogeneous catalysis (methanol and hydrocarbons synthesis, alcohols dehydration, hydrogenation and hydrogen exchange²⁻⁴). The acid-base polyfunctional nature, which determines the characteristic catalytic behavior, has been studied by the adsorption of probe molecules such as CO, CO_2 , pyridine, and H_2 .⁴⁻⁸

In view of the importance of the knowledge of the surface properties of ZrO_2 in both fields of application, a

systematic investigation of the surface properties of pure laboratory samples and of different industrial specimens (variously doped with Yttria) has been undertaken. The aim is to elucidate the role played by the preparation route, the thermal history of the material, and the presence of contaminant and/or dopants upon the surface reactivity. Zirconia, in fact, is often modified by the addition of other oxides (Y_2O_3 , MgO , CaO), which stabilize the crystallographic phase and the microstructure required for a good performance as ceramic material.¹

Some preliminary information was obtained on the surface acidity of a pure monoclinic zirconia by means of the adsorption at room temperature of CO.^{9,10} Carbon monoxide, which interacts via a simple σ -coordination to coordinatively unsaturated non-d cations exposed at the surface, is in fact a suitable "soft" probe molecule, widely used for a virtually nonperturbative characterization of the surface Lewis acidity of oxides.^{11,12}

In a previous work,⁹ the presence of Lewis acidity at the surface of pure ZrO_2 was revealed by IR spectroscopy: two distinct acidic sites have been observed in the spectral range in which other authors⁶⁻⁸ reported, at low CO coverage, the presence of one CO adsorbed species only.

The sites for both CO species are formed by the vacuum thermal condensation of surface hydroxyls at $T \geq 400$ K. They have been assigned to two different Zr^{4+} cations, coordinatively unsaturated (cus), exposed either

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at different crystallographic planes or with different coordinative unsaturations. The polarizing power (i.e., acidic strength) and the relative population of the two Zr^{4+} sites strongly depend upon the thermal activation of the sample.¹⁰

In the present paper, we investigate by means of adsorption microcalorimetry and IR spectroscopy (a) the adsorption capacity and the interaction energy of CO with ZrO_2 and (b) the gradual surface rehydration of ZrO_2 and the parallel modification of its activity toward CO.

Three samples, activated in vacuo at three different temperatures (which were shown to yield different surface characteristics¹⁰) will be considered: (i) a partially hydroxylated one, which already exhibits an appreciable activity toward CO ($T_{out} = 670$ K); (ii) a completely dehydroxylated one, in which no variation of surface area has occurred yet ($T_{out} = 870$ K); (iii) a sample fully dehydroxylated and sintered to an appreciable extent ($T_{out} = 1070$ K).

Experimental Section

Materials. ZrO_2 was prepared by hydrolysis with pure water of zirconium isopropylate and calcination of the precipitated hydroxide at 720 K, as previously described,¹⁰ following the procedure proposed by Bensitel et al.^{5,6} The crystallinity of the sample (95% monoclinic) was confirmed by X-ray diffraction. The presence of some 1.6% of HfO_2 is unavoidable,⁶ and the sample can be considered very pure. In particular, none of the spectral features observed in the CO stretching region can be ascribed to the presence of Hf ions.¹³

Before adsorption measurements, the sample was treated in vacuo for 2 h at the activation temperatures adopted (670, 870, and 1070 K). It was then contacted at the same temperature with some 50 Torr of O_2 for 30 min (in order to burn off contaminants and to ensure stoichiometry), further outgassed for 30 min, and eventually cooled, in vacuo, to room temperature.

After each thermal pretreatment, the BET surface area of the samples was measured by nitrogen adsorption at 77 K in the BET region employing a Carlo Erba Sorptomatic apparatus.

N_2 and CO specpure (Matheson) were employed. Water was distilled several times in vacuo and rendered gas-free by several "freeze-pump-thaw" cycles.

Methods. Infrared spectra were run at room temperature at a resolution of 4 cm^{-1} on a FTIR spectrometer Bruker 113v. Band integrations and band simulations were carried out by using a Pascal program by Bruker (Simband), through which deconvolutions are carried out by fixing only the number of components (two in the present case) and the maximum acceptable standard deviation, whereas all other parameters, including the percent of Gaussian character of each component, can be allowed to float freely. More details on the method and examples of the band fitting achieved are given in ref 10.

The heats of adsorption were measured on a standard Tian-Calvet microcalorimeter (Setaram, France) connected to a volumetric apparatus, which enabled the simultaneous determination of adsorbed amounts (Δn_a), heat released (ΔQ^{int}), and equilibrium pressure (p) for small increments of the adsorptive, following a technique extensively described elsewhere.¹⁴ The detection threshold of the microcalorimeter, constantly kept at 303 K, was 50 μJ per impulsion; in the present work, the value of the measured heat released upon adsorption of a single dose ranged between 0.10 and 1.0 J. The pressure was measured by means of a transducer gauge (Baratron MKS, 0–100 Torr), which enabled accurate measurements up to 80 Torr.

Samples were used in the form of self-supporting pellets ($\approx 30\text{ mg cm}^{-2}$) for IR measurements and as a loose powder for the microcalorimetric ones.

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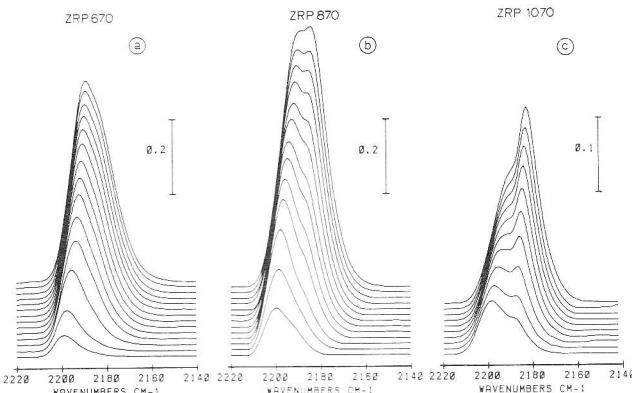


Figure 1. Infrared spectra (absorbance units vs cm^{-1}) of CO adsorbed at room temperature on ZRP670 (a), ZRP870 (b), and ZRP1070 (c). Decreasing CO pressures were used from 150 Torr (top curves) to ≈ 2 Torr (bottom curves).

Nomenclature. The samples are indicated following the pretreatment temperature: *partially dehydroxylated*, ZRP670; *fully dehydroxylated*, ZRP870; *sintered and dehydroxylated*, ZRP1070.

Results

Adsorption of Carbon Monoxide on Variously Activated Samples. The room temperature adsorption of CO on ZrO_2 treated in the conditions here adopted produces absorptions in the 2250 – 2150-cm^{-1} spectral range and is fully reversible.

Figure 1 reports the IR spectra of CO adsorbed at decreasing equilibrium pressure (150 to ≈ 2 Torr; 1 Torr = 133.3 Pa) on ZRP670, ZRP870, and ZRP1070, respectively.

The figure indicates that, at any activation temperature, two CO bands are formed, hereafter referred to as $(CO)_H$ (higher frequency) and $(CO)_L$ (lower frequency). The two ν_{CO} bands are severely overlapped ($\Delta\nu_{max} \approx 10\text{ cm}^{-1}$, whereas $\Delta\nu_{1/2} \approx 10$ – 17 cm^{-1}), and their spectral position varies with CO coverage ($\Delta\nu \approx 4$ – 6 cm^{-1} in the 0–150-Torr range).¹⁵ The two CO frequencies also vary with the pretreatment temperature ($\Delta\nu_{max} \approx 3$ – 4 cm^{-1}), as shown in the three resolved spectra ($p_{CO} = 60$ Torr) in Figure 2. Larger shifts are observed if lower activation temperatures, i.e., lower dehydration stages, are considered (e.g., see the dotted curves in Figure 6b).

The volumetric isotherms ($n_a = \sum n_a$ vs p) (top curves in Figure 3) indicate that the overall activity toward CO varies, as expected, with the extent of surface dehydroxylation and that the shape of the isotherm is modified by the sintering process.

In order to evaluate the individual contributions of the two species to the overall CO uptake, the volumetric isotherms have been decomposed by using the integral molar extinction coefficients (ϵ) of two CO adspecies. By comparison of the "optical" isotherms of CO on ZRP670 (integrated absorbance vs p) with the corresponding volumetric ones (adsorbed amounts vs p), the following ϵ values have been obtained for the high-frequency $(CO)_H$ species and the low-frequency $(CO)_L$ species, respectively:

$$\epsilon_H = (3.9 \pm 0.4) \times 10^6 \text{ cm mol}^{-1}$$

$$\epsilon_L = (2.9 \pm 0.3) \times 10^6 \text{ cm mol}^{-1}$$

These values have been calculated with the assumption that no appreciable variations would occur with cov-

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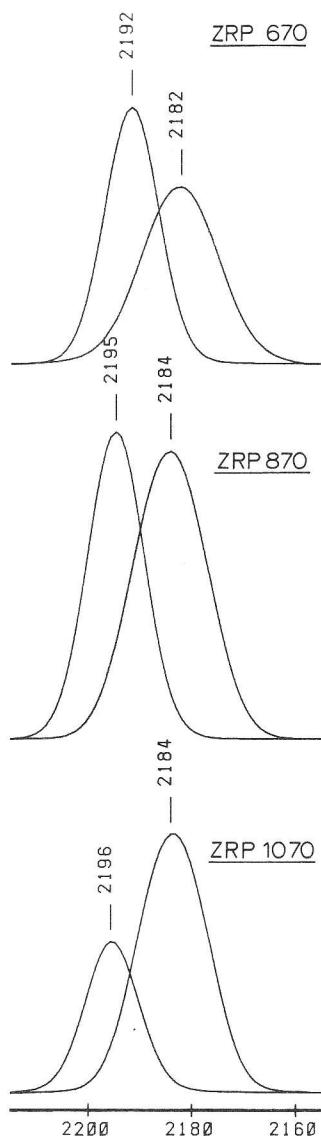


Figure 2. Resolved IR spectra of 60 Torr CO adsorbed at room temperature on ZRP670, ZRP870, and ZRP1070.

erage, in spite of the fact that the frequencies do decrease somewhat upon increasing CO coverage, as reported above. The extinction coefficients calculated for ZRP670 were also used to resolve the adsorption isotherms of ZRP870 and ZRP1070, in that they were assumed not to vary with sample activation temperature, although the ν_{CO} frequencies do vary somewhat with increasing activation temperature. In fact, any variation of the extinction coefficients, which necessarily occurs with the variation of the frequency, falls well within the limits of uncertainty with which the extinction coefficients of adsorbed species can be obtained on heterogeneous systems,¹⁶ like the one under study.

Figure 3 reports the total and the individual volumetric isotherms of the CO species adsorbed on ZRP670, ZRP870, and ZRP1070 in parts a, b, and c, respectively. The dashed range of the curves corresponds to the values obtained by the optical isotherms using ϵ_H and ϵ_L . In all cases, we observe that the overall activity of the $(CO)_H$ species is far lower than that of the $(CO)_L$ one and that $(CO)_H$ saturates at much lower equilibrium pressures. At very low pressure, the higher frequency spe-

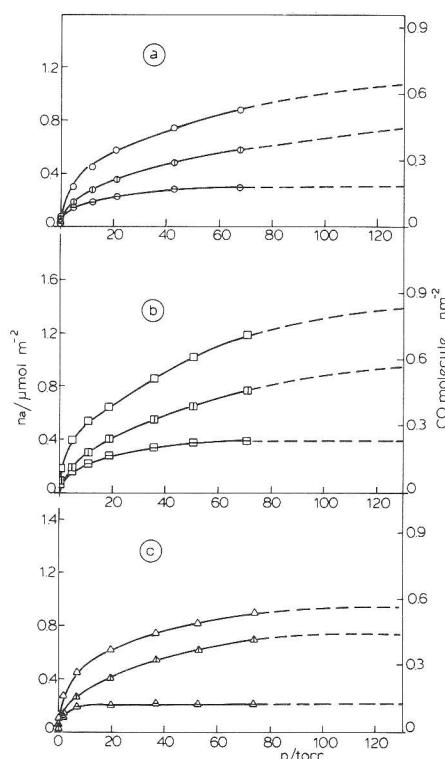


Figure 3. Adsorption isotherms of CO at room temperature on ZrO_2 . Section a: \circ , total isotherm; \square , $(CO)_L$ species; \triangle , $(CO)_H$ species; on ZRP670. Section b: \square , total isotherm; \blacksquare , $(CO)_L$ species; \square , $(CO)_H$ species; on ZRP870. Section c: \triangle , total isotherm; Δ , $(CO)_L$ species; \blacktriangle , $(CO)_H$ species, on ZRP1070. Dashed range of the curves: the values are extrapolated on the basis of the "optical" isotherms by using the two molar extinction coefficients (ϵ_H and ϵ_L).

cies prevails: beyond $p_e \approx 5$ Torr (≈ 2.5 Torr for ZRP1070), CO is mainly adsorbed in the low-frequency form.

The $(CO)_H$ species saturates at $p_{CO} \approx 70$ Torr on ZRP670 and ZRP870 and at $p_{CO} \approx 20$ Torr on ZRP1070: its monolayer capacity may be thus determined quite accurately in the three cases. It turns out to be 0.18, 0.24, and 0.12 $(CO)_H$ molecules nm^{-2} for ZRP670, ZRP870, and ZRP1070, respectively.

The monolayer capacity of the $(CO)_L$ species can be only roughly estimated, as at the maximum equilibrium pressure reached the adsorption process is not yet accomplished. By graphic extrapolation, we could assume its saturation to be some 30% higher than the value found at $p = 130$ Torr, i.e., ≈ 0.50 , ≈ 0.80 , and ≈ 0.80 $(CO)_L$ molecules nm^{-2} for ZRP670, ZRP870, and ZRP1070, respectively.

The variation of the sample surface area, of the total and individual CO monolayer capacities, and of the molar heat of adsorption (Q^{int}/n_a) at $p_{CO} \approx 60$ Torr is reported in Figure 4a-c as a function of the pretreatment temperature. The figure shows the following: (i) The surface area (section a of Figure 4) remains nearly constant ($90-80\text{ m}^2\text{ g}^{-1}$) to activation at temperatures up to 870 K but decreases markedly at higher temperatures ($\approx 36\text{ m}^2\text{ g}^{-1}$ for ZRP1070), indicating the onset of a sintering process. (ii) The total acidity per unit area (section b) reaches its maximum on ZRP870 ($1.04\text{ CO molecule nm}^{-2}$). Activation at a higher temperature (1070 K) almost exclusively affects the sites for $(CO)_H$, as the uptake of CO in the low-frequency form is virtually the same on ZRP870 and ZRP1070. (iii) The molar heat of adsorption Q^{int}/n_a measured at $p_{CO} = 60$ Torr and thus including the contribution of both CO species (section c) exhibits a max-

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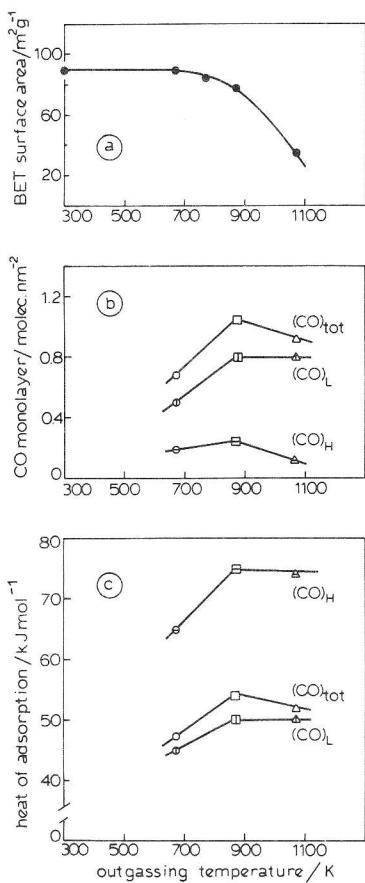


Figure 4. (Section a) Specific surface area as a function of outgassing temperature. (Section b) CO room temperature monolayer capacities as a function of outgassing temperature: O, ZRP670; □, ZRP870; Δ, ZRP1070. (Section c) Molar heat of adsorption of CO adsorbed at room temperature on (O) ZRP670, (□) ZRP870, and (Δ) ZRP1070. ⊕, □, Δ and ⊖, □, Δ: heats of adsorption of $(CO)_L$ and $(CO)_H$ species on ZRP670, ZRP870, and ZRP1070, respectively.

imum value (54 kJ mol^{-1}) after a thermal treatment at $T \approx 870 \text{ K}$ and then declines slightly. The heat values corresponding to the individual contributions of $(CO)_H$ and $(CO)_L$ also increase with outgassing temperature, although to a different extent. Activation at 1070 K only affects the relative number of active sites (section b) but not their individual interaction energies.

A detailed description of the dependence on coverage of the energy of interaction of CO with the zirconia surface is given by the stepwise evolution of the heat of adsorption with coverage. Figure 5a–c reports the partial molar heat of adsorption ($\Delta Q/\Delta n_a \text{ kJ mol}^{-1}$) for each adsorbed dose vs total uptake ($n_a \mu\text{mol m}^{-2}$), whereas sections a', b', and c' report the evolution of the differential heat of adsorption ($\delta Q/\delta n_a = q^{\text{diff}}$) as a function of equilibrium pressure. Due to the simultaneous adsorption of CO on both types of acidic centers (see Figure 1), the measured heat is a mean value averaged on the contribution of both species. The evaluation of the heat of interaction corresponding to the single adsorbed forms $(CO)_H$ and $(CO)_L$ is thus made as follows: (i) The extrapolation to zero coverage of the heat of adsorption yields an estimate of the energy of interaction of CO with the most energetic sites (high-frequency species). This can be made under the assumption that these sites are filled first (see IR spectrum and decomposed isotherms at very low coverages, Figure 3a–c, where $(CO)_H$ definitely prevails). Thus the estimated values for $(CO)_H$ are $65, 73$, and $70 \pm 2 \text{ kJ mol}^{-1}$ for ZRP670, ZRP870, and ZRP1070, respectively.

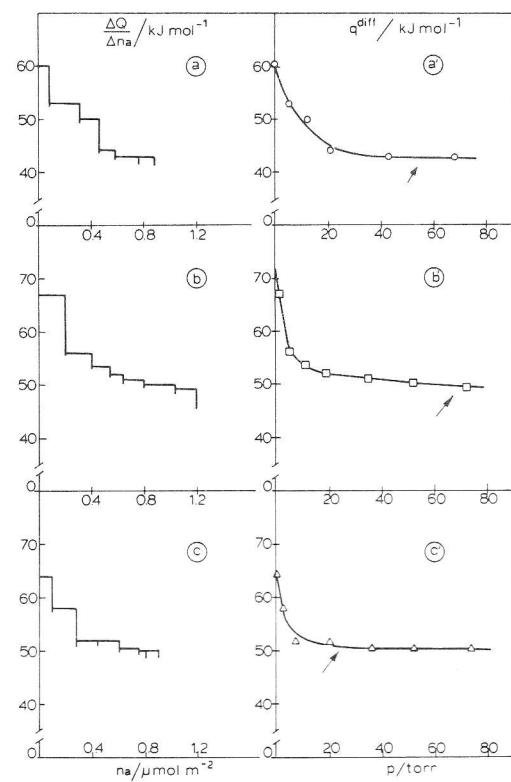


Figure 5. Partial molar heat of adsorption of CO at room temperature on ZRP670 (a), ZRP870 (b), and ZRP1070 (c) as a function of adsorbed amount. Differential heat of adsorption of CO at room temperature on ZRP670 (a'), ZRP870 (b'), and ZRP1070 (c') as a function of equilibrium pressure.

(ii) In Figure 5a'–c', the energy of interaction of the sole $(CO)_L$ species can be evaluated by taking the heat values corresponding to the pressure (arrows in the figure) at which the $(CO)_H$ species has been already saturated. The heat values for $(CO)_L$ are $44 \pm 2 \text{ kJ mol}^{-1}$ for ZRP670 and $50 \pm 2 \text{ kJ mol}^{-1}$ for ZRP870 and ZRP1070.

Adsorption of Water and Its Effect on CO Uptake. The relationship between Lewis acidity and surface rehydration has been checked by adsorbing CO on the ZRP670 sample during the stepwise reconstruction of the surface-hydrated layer via adsorption of H_2O_{vap} at room temperature. This is a reasonable procedure, in that CO adsorption at room temperature is completely reversible, as shown above, whereas the first stages of the rehydration of ZrO_2 were found to be completely irreversible, as monitored by the absence of a detectable H_2O pressure and of any endothermic process upon evacuation.

Parallel infrared and volumetric-calorimetric measurements have been performed as follows: ZRP670 was exposed at room temperature to successive small doses of water up to the complete elimination of activity toward CO. The differential heat of adsorption of the H_2O doses was observed to decrease from 250 to 150 kJ mol^{-1} .

After each irreversible adsorption of water, the same dose of CO ($\approx 8 \mu\text{mol m}^{-2}$) was admitted on the sample, in order to check the residual Lewis acidity on the water-modified surface, and then completely removed by evacuation at the end of the adsorption.

Figure 6a shows the spectral changes produced on ZRP670 by its gradual rehydration, both in the OH stretching region (3900 – 2500 cm^{-1}) and in the coordinated undissociated H_2O region (1800 – 1400 cm^{-1}). Besides the residual OH groups of the still partially hydroxylated surface, whose absorption bands are initially located at 3775 cm^{-1} ($(OH)_H$ species) and 3668 cm^{-1} ($(OH)_L$ species), other

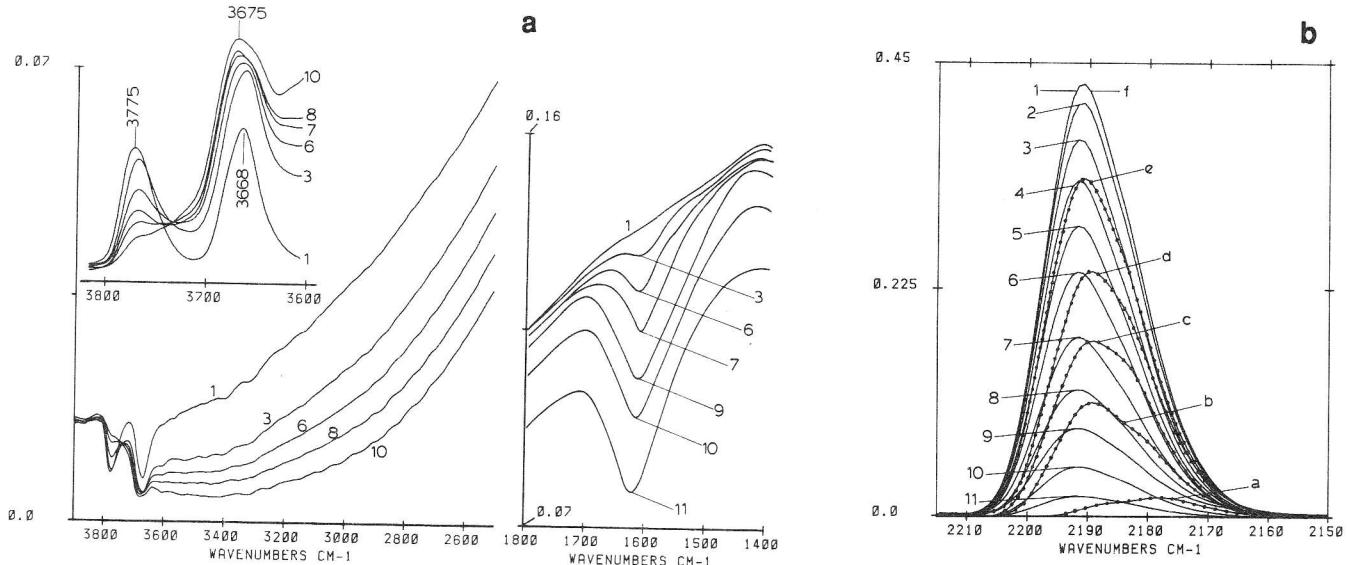


Figure 6. Section a: IR spectral changes (transmittance units vs cm^{-1}) produced in the ν_{OH} and δ_{OH} region of ZRP670 during the early stages of the stepwise rehydration at room temperature corresponding to the suppression of the adsorptive activity toward CO. The inset (absorbance units vs cm^{-1}) shows on an expanded scale the free OH region. The numbers on the curves indicate successive H_2O doses and correspond to some of the CO bands in Figure 6b. Section b: IR spectra (absorbance units vs cm^{-1}) due to 30 Torr of CO adsorbed on an unsintered ZrO_2 sample in various dehydration (dotted lines) and rehydration (solid lines) stages. Dehydration (K): a, 410; b, 510; c, 570; d, 600; e, 640; f, 670. Rehydration: 1 (\equiv f), CO uptake on ZRP670; 2-11, CO uptake after the contact with doses of H_2O (equilibrium $p(\text{H}_2\text{O}) = 0$).

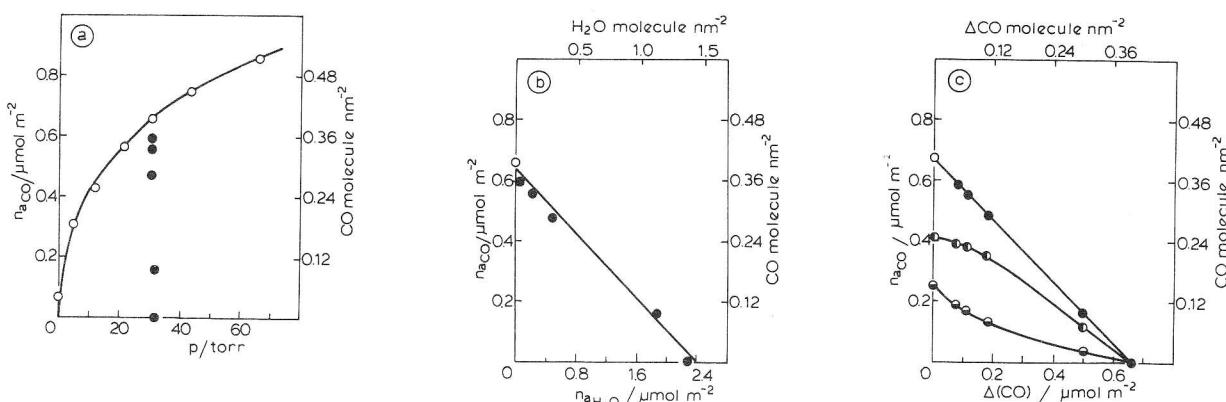


Figure 7. Section a: adsorption isotherm of CO at room temperature on ZRP670 (\circ). Full points (\bullet): amount of CO adsorbed on the progressively rehydrated ZRP670. Section b: amount of CO adsorbed on the progressively rehydrated ZRP670 as a function of the amount of preadsorbed H_2O . Section c: amount of CO adsorbed on the progressively rehydrated ZRP670 as a function of the progressively decreased amount of CO adsorbed: \bullet , total; \circ , $(\text{CO})_L$; \ominus , $(\text{CO})_H$.

absorption bands are observed, located at 3675 cm^{-1} (sharp) and at $3600-2800 \text{ cm}^{-1}$ (broad, ill defined), due to newly formed OH groups, as well as at $\approx 1620 \text{ cm}^{-1}$, due to the coordinated molecular H_2O .

As expected, with the proceeding rehydration the activity toward CO decreases progressively, as shown in the CO stretching region by spectra 1-11 of Figure 6b.

Figure 7a compares the amount of CO adsorbed on the sample, when progressively rehydrated, with the adsorption isotherm of CO on the bare surface (see Figure 3a). Note that the same initial dose of CO, put in contact with the ZRP670 surface, leads to a progressively higher equilibrium pressure, as a consequence of a lowered CO uptake brought about by the chemisorption of H_2O . A complete suppression of the activity toward CO was observed after the adsorption of $2.4 \mu\text{mol m}^{-2}$ of H_2O .

The amounts of CO adsorbed per unit surface area on the progressively rehydrated sample are reported in Figure 7b as a function of the number of preadsorbed water molecules. The dependence of the overall activity toward CO on the extent of rehydration exhibits a surprising linearity. The decomposition of the overall function into

the individual $(\text{CO})_H$ and $(\text{CO})_L$ contributions (Figure 7c), carried out again through the use of the molar extinction coefficients, indicates a somewhat different trend in the suppression of the two types of sites, the strongest ones ($\text{CO})_H$ being preferentially suppressed in the first stages of rehydration.

The molar heat of adsorption of CO, measured during the progressive rehydration of ZRP670, was found to remain nearly constant around 52 kJ mol^{-1} , i.e., at the same heat value observed at the same pressure on the bare ZRP670 sample.

On the spectroscopic ground, we find a constant spectral position for both $(\text{CO})_H$ and $(\text{CO})_L$ at every stage of the rehydration process, as shown in Figure 6b. This is in contrast with the trend exhibited by the spectral position of both $(\text{CO})_H$ and $(\text{CO})_L$ in the various stages of the dehydration pattern, reported as dotted curves in Figure 6b, and requires some discussion.

Discussion

Development of Acidity. The adsorption of carbon monoxide at room temperature reveals that at the sur-

face of pure monoclinic zirconia two families of acidic sites (Zr^{4+}_{cus}) are present and exhibit different relative population, acidic strength, and stability as a function of activation temperature. Coupling IR spectroscopic and volumetric-calorimetric data allowed us to describe, from a quantitative and energetic point of view, the two CO adspecies, whose qualitative features have been described in some detail in previous contributions.^{9,10}

The joint use of microcalorimetric and/or thermogravimetric and IR spectroscopic techniques in the characterization of a surface has already given good results with other systems^{12,17,18} and has been used also by other authors.^{19,20}

The effect of the activation temperature on the development of surface acidity (in particular, the dependence of the two adspecies on the extent of surface dehydroxylation) and on the sintering process is quite evident.

Surface acidity appears after activation at $T \geq 400$ K, and the number of acidic sites of both kind increases with the extent of surface dehydroxylation. The monolayer capacity of the fully dehydroxylated sample (ZRP870) is 1.04 CO molecule nm⁻², corresponding to some 13–17% of the cationic centers, which, assuming a close-packed oxygen lattice, should be exposed as a consequence of the complete dehydroxylation of the surface.

Zr^{4+}_{cus} centers responsible for the $(CO)_L$ species are by far the most abundant sites on both partially (ZRP670) and fully (ZRP870) dehydroxylated samples: they account for ≈73% and 77% of the total CO amount on ZRP670 and ZRP870, respectively. On a partly sintered and fully dehydrated material (ZRP1070), they become even more predominant, accounting for some 87% of the total CO uptake.

The two CO adspecies, characterized by different ν_{CO} frequencies, also have different heats of adsorption, which directly measure the energy of the acid–base interaction at the cus cationic centers. The heat of adsorption turns out to be lower for the low-frequency species than for the high-frequency one, as expected. The data fit, in fact, a correlation between the spectroscopic features (ν_{CO} frequency shift in respect of the gas, molar extinction coefficient) and the adsorption enthalpy of σ -coordinated CO observed with a series of non-d metal cations in oxides^{12,16} and in zeolites.¹⁷

The heat of adsorption for $(CO)_L$ is ≈45 kJ mol⁻¹ on the partially hydroxylated sample and ≈50 kJ mol⁻¹ on the completely dehydroxylated one; correspondingly, the ν_{CO} frequency shifts upward of ≈3 cm⁻¹. For $(CO)_H$ species, the heat of adsorption varies from ≈65 to 73 kJ mol⁻¹, whereas the relevant ν_{CO} frequency shifts ≈3 cm⁻¹.

Differences in the polarizing power of the two cationic centers reflect a different coordinative unsaturation of the relevant Zr^{4+} cations. The unsaturated cations are created by thermal elimination of OH groups: two different free OH species have been observed at the surface of zirconia, giving rise to absorption bands at 3775 and 3668 cm⁻¹. These species have been assigned by Tsyganenko et al.²¹ to terminal and bridged surface OH groups, respectively. A direct correlation between the elimina-

tion of the two different kinds of OH groups and the development of the two families of acidic sites is not possible on the basis of the present data, because of the parallel elimination of the two OH species during the thermal dehydration of the surface.¹⁰ From the present data, it is only possible to suggest that the family of more abundant, less energetic $(CO)_L$ sites is likely to belong to flat (low-index) faces, whereas the family of the relatively few and more energetic $(CO)_H$ sites might be ascribed to less regular and less probable configurations: they could be exposed on rougher (high-index) planes, where the coordinative unsaturation can be expected to be higher, and/or at defective sites, like edges, kinks, and corners of the particles. Any more detailed assignment can be only done on the basis of data relative to more severely sintered material as well as on the basis of information arising from microstructural investigation. Both types of studies are presently being carried out.

On passing from ZRP670 to ZRP870, there is an increase of adsorption energy and of CO stretching frequency, which in the case of pure σ -coordination indicates an increased acidic strength of the relevant sites. As in the 670–870 K temperature interval, the elimination of the last fraction of the surface hydrated layer is accomplished, and the change of acidic strength observed must be ascribed to a modified polarity of the surface, brought about by the elimination of the residual surface hydroxyl groups. No further modification of the polarity of the surface has been revealed, in fact, on the sample activated at 1070 K, whose ν_{CO} stretching frequency and heat of adsorption for both $(CO)_H$ and $(CO)_L$ species are virtually the same found on the sample activated at 870 K. It is thus deduced that the modification of the surface brought about by the incipient sintering process does not affect the nature (i.e., the acidic strength) of the sites but only their number.

In fact, when sintering begins, at $T \geq 900$ K, the room temperature activity toward CO declines. On the sintered, fully dehydroxylated ZRP1070, the lowering of acidity was shown to be due to a lowered population of the sole $(CO)_H$ species (Figure 4b): as suggested above, the Zr^{4+}_{cus} sites responsible for the more energetic $(CO)_H$ species can be expected to involve mainly less probable crystallographic planes and/or highly defective coordinative configurations, which would be first destroyed during the sintering process.

Suppression of Surface Acidity. The stepwise surface rehydration of a partially dehydroxylated ZrO_2 (ZRP670) causes the gradual lowering and eventually the suppression of Lewis acidity.

The surface rehydration upon contact with H_2O vapor occurs fast and irreversibly, indicating that the affinity of the ZrO_2 surface toward water is quite high, as expected of an oxide of high ionic character. The heat of the ZrO_2/H_2O interaction, varying in the early stages of the rehydration from 250 and 150 kJ mol⁻¹, is quite typical, in its highest values, of a dissociative chemisorption of water on oxides.²²

The IR spectra, however, indicate that, besides a dissociative chemisorption of water, yielding a progressive reconstruction of the hydroxylated layer, the rehydration process also involves from the very beginning some σ -coordination of undissociated water molecules, irreversibly held at room temperature. This latter species, which is completely eliminated upon evacuation at 400 K, was observed to involve only cationic centers that are too weak

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to be active toward CO,¹⁰ opposite to the case of the homologous TiO₂.¹²

During the rehydration process, the residual OH groups of the still partially hydroxylated ZRP670, initially free from H-bonding, become involved in H-bonding with the newly formed OH groups and with the coordinated undissociated H₂O molecules. This latter species in particular, whose δ_{HOH} scissors mode is located at gradually higher frequencies, as expected for H-bonding, is responsible for a weak perturbation of the high-frequency OH groups, both the ones initially present at the surface and the newly formed ones, which now absorb at 3675 cm⁻¹. In fact, an evacuation (not shown in the figure) at ≈ 400 K, i.e., at the temperature required to get rid of coordinated H₂O molecules, eliminates the peak at 3675 cm⁻¹ and yields the high-frequency OH band at 3775 cm⁻¹.

Parallel to the restoration of the surface hydrated layer, the activity toward CO declines, as expected, but some peculiar features of this process need to be discussed.

(i) The dependence of the decline of CO adsorptivity on the amount of preadsorbed H₂O is unexpectedly linear. From the slope of the straight line in Figure 7b, it is possible to evaluate that four H₂O molecules must be held irreversibly, either dissociatively or coordinatively, to eliminate one acidic site.

(ii) The spectral position of the two CO adspecies, as well as the relevant heat of interaction, is *unaffected* by the degree of surface hydration, as opposed to what happens during the dehydration process. The adsorption of CO, which is indeed sensitive to the polarity effects related to the degree of surface hydration, so reveals a rather different situation at the surface during the dehydration and the rehydration process. An appreciable effect on the polarity of the surface turns out to be produced by the OH groups, mainly free and thus acting as isolated dipoles, which are abundant at the surface of ZrO₂ at any stage of dehydration.¹⁰ This effect is absent, at least as far as CO can reveal, when H-bonded OH groups are formed, as during the gradual rehydration at room temperature (spectra in Figure 6a). This result indicates, in particular, that the rehydration process is far from being the plain reverse of the dehydration one. In fact, due to the high affinity (sticking probability) of the H₂O/ZrO₂ system and to the nonmobility of the hydrated layer at room temperature, during the rehydration process smaller and smaller surface portions of virtually constant energetic features toward CO remain exposed. During dehydration, accomplished in a rather broad temperature range, the energetic features of the exposed surface vary with continuity.

(iii) Some selectivity was observed spectroscopically in the suppression of the two acidic centers, as the elimination of the (CO)_H sites is somewhat favored at the beginning of the rehydration process. Still, the suppression process is accomplished for the two species at the same time. For this reason, and for the quite close acidity of the two individual species, no selectivity could be observed from an energetic point of view: the molar heat of adsorption, comprehensive of the two individual contributions, remains constant over the whole rehydration process, irrespective of the varied population of the two species, as dose per dose, the heat variations expected from the different abundance of the two adspecies do not exceed the sensitivity of the calorimetric measurement.

Conclusions

The surface dehydroxylation of pure monoclinic zirconia creates coordinatively unsaturated Zr⁴⁺ ions, among which there are two different families which act as Lewis acceptor centers for carbon monoxide at room temperature. The strength and the relative and absolute populations of these sites depend upon the amount of surface hydroxyls present at the surface. Upon incipient sintering, only one species is markedly affected, which has been assigned to Zr⁴⁺_{cus} located at "defective" sites, which are usually smoothed up during the sintering process. The other sites, which are the most abundant and are unaffected by sintering up to ≈ 1100 K, are assigned to cus Zr⁴⁺ cations located on the crystal face(s) most favorably exposed.

Upon rehydration at room temperature, the Lewis acidity is progressively suppressed, and the rehydration pattern is by no means the reverse of the thermal dehydration one. Surface hydroxyls originated by the dissociation of H₂O are H-bonded to one another; as a consequence, both the heat of adsorption of CO and the ν_{CO} stretching frequency, sensitive to the population of free OH groups, turn out to be insensitive to the progressive rehydration. On a quantitative ground, the suppression of surface acidity by water is very effective and occurs via a mechanism involving a 4:1 linear relationship between adsorbed water and suppressed Lewis sites.

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