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On the role of the calcination step in the preparation of active (superacid) sulfated zirconia catalysts

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In the preparation of active SO_4–ZrO_2 catalysts, several steps involving various chemical and/or physical processes are necessary. In particular it has been reported that, after sulfation of amorphous Zr hydrates, a calcination at $T_{calc} > 773$ K is needed to guarantee the crystallization of ZrO_2 in the tetragonal phase. By the use of a stabilized tetragonal ZrO_2, it is here demonstrated that a calcination at $T_{calc} > 773$ K is indeed necessary for all SO_4–ZrO_2 systems, and that its actual role is the selective elimination of sulfates from highly energetic crystallographic defects. The calcination step at $T_{calc} > 773$ K so creates the conditions for the formation of strong Lewis acid centres, that are necessary in the catalytic process, and the presence of which is here monitored spectroscopically by the reversible adsorption of carbon monoxide.

Keywords: superacid catalysts; sulfated zirconia; surface Lewis acidity; CO adsorption; IR spectra of surface species

1. Introduction

Starting with the early papers by Hino and Arata [1], sulfated zirconia (SZ) has been often described as a solid superacid and, sometimes, as the strongest of the solid superacids ($H_0 \approx -16$ [2]). Still, the superacidity of SZ has been frequently denied (e.g., see ref. [3]), and in some instances SZ has been considered as plain ZrO_2-supported sulfuric acid [4]. This argument is not pertinent to the present note; here it is simply recalled that, in proper circumstances, SZ may exhibit some important catalytic properties that are indeed peculiar of solid superacid systems. For instance, some SZ preparations have been shown to catalyze the isomerization of *n*-alkanes at temperatures as low as ~ 400 K.

Not all SZ preparations present a superacid behaviour or, in other words, SZ is not per se a solid superacid. In fact, in the preparation of an SZ system, some specific physical and/or chemical treatments have been reported in the literature to be necessary in order to give SZ the desired catalytic properties.

Among the physical and/or chemical treatments, the following are most often considered to be strictly necessary:

(i) The *sulfation* step: sulfates loading must be carried out on amorphous ZrO_2 hydrate precursors. If the direct sulfation of crystalline ZrO_2 precursors is used, it has been reported that no appreciable catalytic activity develops.

(ii) The *calcination* step: the still amorphous sulfated ZrO_2 hydrate must be fired (in air, in vacuo, in inert atmosphere) at $T_{calc} > 773$ K, in order to allow the ZrO_2 system to crystallize in the tetragonal form.

(iii) The *activation* step: before the catalytic process, a catalyst that was prepared according to (i) and (ii) must be thermally treated, either in vacuo or in an inert atmosphere, at a temperature T_{act} of the order of ~ 673 K.

The third requirement, i.e., the condition of the activation step, obviously concerns the degree of preliminary dehydration of the catalyst that is needed in order to give the system a good catalytic activity. (Needless to say, if after steps (i) and (ii) the catalyst was not exposed to the atmosphere, but remained either in vacuo or in an inert atmosphere, step (iii) is no longer necessary, as the surface dehydration achieved in step (ii) is maintained.) The requirement of a preliminary dehydration of the SZ catalysts ultimately concerns the still unanswered question whether Lewis or Brønsted acid centres, or perhaps a combination of the two, are responsible for the catalytic activity of SZ systems. The hypothesis of a combined action of Lewis and Brønsted acid sites has been indicated by several authors [5–7] as the most probable explanation for the superacidity of SZ systems. This would be consistent with the observation, to be discussed elsewhere, that neither Lewis nor Brønsted acid sites are,

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in their own categories, particularly strong, and with the observation that the strongest fractions of Lewis acid sites are in any case involved in the catalytic isomerization process [8].

The first statement, concerning the conditions of the sulfation step, turns out to be only partly true. In fact, what has been actually observed so far is that high catalytic activity is exhibited only by crystalline SZ systems with ZrO_2 in the tetragonal form (t-SZ), whereas crystalline monoclinic SZ systems (m-SZ) usually present either null or fairly low catalytic activity [9,10]. But in a recent paper [9] we could show that all kinds of t-SZ systems can be catalytically active, no matter how the tetragonal sulfated ZrO_2 system has been obtained. In particular, if direct sulfation of a phase-stabilized crystalline tetragonal ZrO_2 preparation is carried out, the resulting t-SZ system will be as active as a t-SZ system obtained by the sulfation of an amorphous precursor. In contrast, direct sulfation and calcination of a metastable tetragonal crystalline ZrO_2 precursor (i.e., a non phase-stabilized t-ZrO_2) favours the t- → m-ZrO_2 phase transition and yields m-SZ that is mostly inactive.

As for the second statement, concerning the calcination step, the experimental observation that a calcination at $T_{calc} > 773$ K is needed in order to develop in SZ systems catalytic properties is correct, but the interpretation given so far is incidentally correct only for SZ systems deriving from amorphous precursors. The aim of this note is to show that a calcination step at $T_{calc} > 773$ K is actually needed for *all* SZ systems, and that the necessary change that the calcination step is actually bound to bring about is a real surface chemical process, quite different from a mere (physical) transformation of crystal phases.

2. Experimental

2.1. Materials

Two families of SZ systems have been considered, termed ZS and YZS respectively.

ZS samples. These are standard SZ systems, prepared according to the procedure indicated by the Japanese school as the only procedure leading to superacidity, i.e., by sulfating with either H_2SO_4 or $(NH_4)_2SO_4$ an amorphous Zr hydroxide precursor. All details of the preparation of ZS systems, and their analytical, structural, and morphological characterization, have been reported elsewhere [9]. It is only recalled that, after calcination at $T_{calc} = 673, 823$, and 923 K respectively, the sulfate content of the ZS systems considered in this note is 1.9, 2.6, and 1.5 sulfate groups per nm^2 respectively, and the BET surface area is 230, 188, and 128 $m^2\ g^{-1}$ respectively. The crystal phase of the ZS systems varies, with calcination conditions, from quasi-crystalline tetragonal ($T_{calc} = 673$ K) to crystalline tetragonal ($T_{calc} \geqslant 823$ K).

YZS samples. These are t-SZ systems obtained by sulfating, with either H_2SO_4 or $(NH_4)_2SO_4$, crystalline ZrO_2 stabilized in the tetragonal form by formation of a solid solution with 3 mol% Y_2O_3. Details on the Y_2O_3-stabilized t-ZrO_2 preparation (herewith referred to as YZ, and used as a reference system), and on the sulfation procedures have been reported in a previous note [9]. In particular, the YZS systems dealt with in this contribution were obtained from a single batch containing, before calcination, some 5% sulfates from ammonium sulfate. After calcination at $T_{calc} = 673, 823$, and 923 K respectively, the sulfates content of YZS systems is 4.9, 3.9, and 3.0 sulfate groups per nm^2 respectively, and the BET surface area is virtually constant at 85 $m^2\ g^{-1}$, that is the surface area of the starting YZ system, initially calcined (i.e., before sulfation) at 873 K.

After sulfation and calcination, all samples were cooled to ambient temperature, exposed to the atmosphere, and stored in a closed vessel until they were used for either catalytic or spectroscopic tests.

2.2. Techniques

The calcination step of the SZ systems was carried out at $T_{calc} = 673, 823$, and 923 K in a standard way: the materials deriving from the sulfation process, pre-dried and powdered, were oven calcined in a dry air stream at the desired temperature for 4 h, as reported in a previous note [11]. The use of longer calcination times has been tested, and was observed to have no effect at all on the catalysts physical and/or chemical properties that this note deals with.

Catalytic activity of SZ systems calcined at various T_{calc} temperatures was studied in a quartz flow reactor, under conditions that have been described previously [9]. In particular, the test isomerization reaction of *n*-butane was carried out at 423 K, after a preliminary activation of the catalyst in a dry air flow at $T_{act} = 673$–723 K. Reaction rates are normalized against sulfates content, i.e., are reported as moles of *n*-butane converted per mole SO_4 per unit time.

IR spectra were run at resolution 2 cm^{-1} with a Bruker 113v FTIR spectrometer equipped with MCT detector. SZ samples were prepared in the form of thin-layer depositions spread from aqueous suspensions over a pure Si platelet. The Si platelet was the same for all samples, and the thickness of the samples was kept as constant as possible (~ 5 mg cm^{-2}), in order to allow an acceptable normalization of band intensities against (a virtually constant) sample weight. The samples were placed in quartz vacuum cells suitable for adsorption studies either at ambient temperature or at ~ 77 K, where they underwent vacuum activation treatments, either at the standard temperature $T_{act} = 673$ K or at any other temperature specified in the text. CO adsorption studies were carried out in a strictly in situ configuration

3. Results and discussion

3.1. Catalytic activity as a function of T_{calc}

Fig. 1 compares the *n*-butane isomerization activity at 423 K over ZS (fig. 1a) and YZS specimens (fig. 1b) calcined at different temperatures in the 673–923 K interval. It is quite evident that, for both catalysts, the catalytic activity is virtually null for $T_{calc} = 673$ K, and then becomes higher with increasing calcination temperature. As already mentioned in the experimental section, varying the calcination time does not modify to an appreciable extent the catalytic behaviour of both SZ systems, so that $T_{calc} \approx 773$ K turns out to be a sort of threshold for the development of the catalytic activity in these catalysts.

In the calcination temperature interval explored, the ZS catalysts complete their crystallization in the t-ZrO_2 form (the crystallization process was actually started at ~ 673 K, i.e. much before the onset of a catalytic activity [9]), but no appreciable changes of crystallinity and/or of crystals size and morphology occur in the case of the YZS catalysts [9].

Plots like those of fig. 1a, relative to t-SZ systems deriving from amorphous precursors, are certainly responsible for the current interpretation of the calcination step as the physical process necessary to guarantee crystallization of the SZ system in the tetragonal form. But plots like those of fig. 1b, relative to a phase-stable t-ZrO_2 system, clearly indicate that something else is actually involved in the calcination process, something that concerns *all* SZ catalytic systems, and not only those that still require the completion of the amorphous → crystalline phase transition.

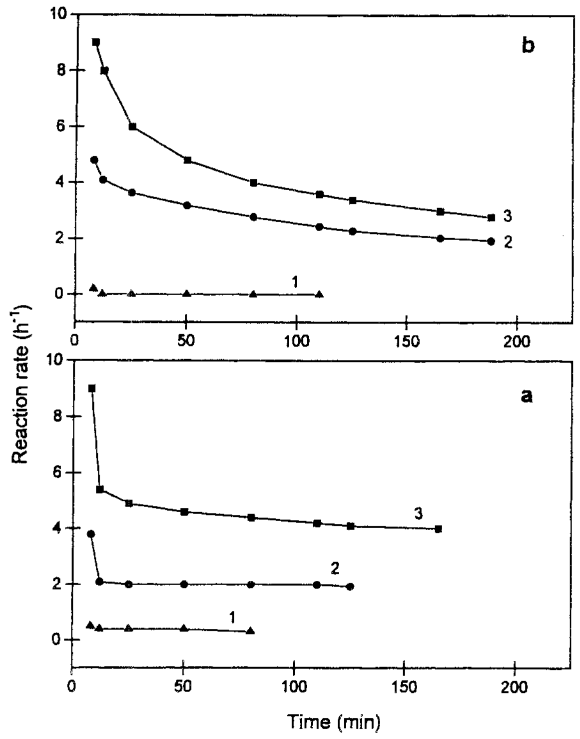


Fig. 1. *n*-butane isomerization activity at 423 K as a function of time on stream for SZ catalysts standard calcined at different temperatures and activated at 723 K in dry air flow. (a) ZS catalysts, calcined at $T_{calc} = 673$ K (curve 1), 823 K (curve 2), and 923 K (curve 3). (b) YZS catalysts, calcined at $T_{calc} = 673$ K (curve 1), 823 K (curve 2), and 923 K (curve 3).

Before the catalytic tests, all catalysts dealt with in fig. 1 were activated at the same temperature (typically 673–723 K, either in vacuo or in a dry air stream), so that the activity differences shown by fig. 1 between samples with $T_{calc} < 773$ K and $T_{calc} > 773$ K cannot be ascribed to different degrees of activation, i.e. to a different degree of surface dehydration. In fact fig. 2, which reports the IR spectra of the OH spectral region for the two catalyst families, shows that within each catalyst family no major differences of surface hydration are exhibited by the samples as a function of the calcination temperature. In particular, it is noted that:

(i) After activation at $T_{act} = 573$ K (curves 1, 2, 3), both catalyst families present two OH bands of rather different intensity. The weaker band is centered at ~ 3760 cm^{-1}, and has been ascribed to terminal OH groups [12], whereas the stronger band is centered at ~ 3650 cm^{-1}, and has been ascribed to tri-bridged OH groups [12]. The assignment of the low ν OH band is not agreed upon by all authors (some think that it is due to bi-bridged OH; e.g., see ref. [6]), and should be thus considered as tentative. But the features of the bridging OH species absorbing at ~ 3650 cm^{-1} will not be discussed here, as their actual nature is not related to the surface features of SZ systems dealt with in this note.

When the activation is carried out at $T_{act} = 673$–723 K, i.e., at the temperatures that have been recognized to be necessary for the activation of the catalysts (see curve 2′), the low ν band due to bridging OH groups declines somewhat, while the high ν band due to terminal OH groups is (almost) completely eliminated. If it is assumed that, in the dehydration process, the cation(s) that carried the OH groups become coordinatively unsaturated (cus) maintaining the crystallographic and coordinative configuration they had in the hydrated system [12], the above observation concerning the evolution of the two types of OH groups during the dehydration at $T_{act} \approx 673$ K may indicate what are the most probable coordinative situations of cus Zr^{4+} centres (Lewis acid sites) present at the surface of active t-SZ catalysts.

(ii) With increasing calcination temperature, the surface OH pattern of ZS samples becomes slightly weaker, especially for what concerns the high frequency terminal OH species. This decline is primarily due to a gradual morphological modification and a gradual decline of surface area of the samples deriving from the amorphous precursor [9]. In contrast, in the case of the model YZS system, that is characterized by constant crystallinity, crystal size, and surface area, the surface OH pattern presents a moderate increase of intensity with increasing

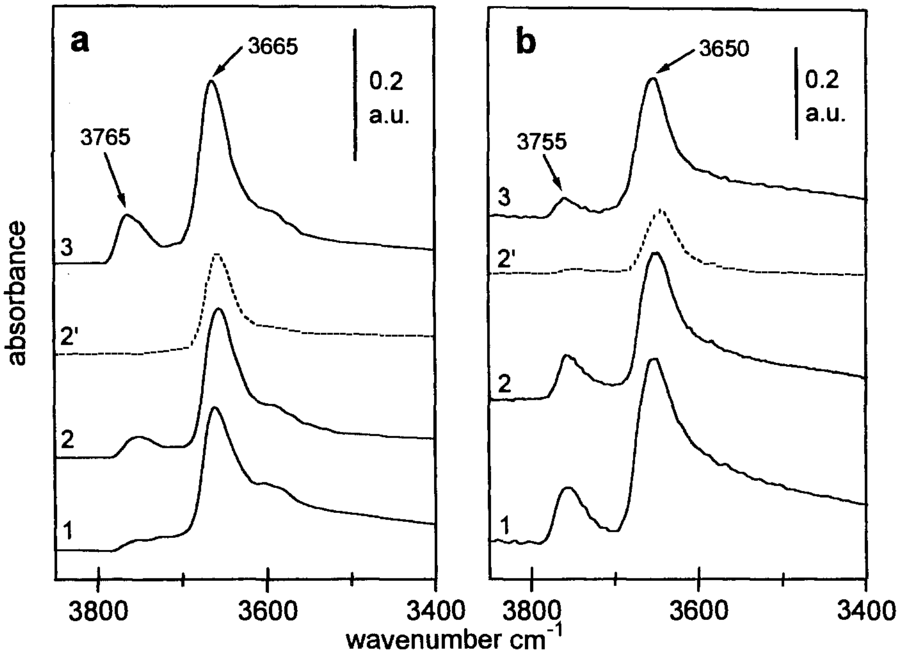


Fig. 2. FTIR spectra (absorbance) of the OH stretching region of YZS catalysts (a) and ZS catalysts (b) calcined at $T_{calc} = 673$ K (curves 1), 823 K (curves 2 and 2′), and 923 K (curves 3). The solid-line spectra correspond to the catalysts vacuum activated at $T_{act} = 573$ K, whereas the broken-line spectra to the catalysts standard activated at $T_{act} = 673$ K.

calcination temperature. This increase is particularly evident in the case of the high frequency terminal OH species.

It is thus deduced that the strong increase of catalytic activity observed with calcination temperature cannot be ascribed to an increase of the surface dehydration degree. Moreover, the moderate increase of OH population with T_{calc} exhibited by the model YZS system suggests that some surface sulfates are probably eliminated during the calcination step at $T_{calc} > 773$ K, so that more surface OH groups are formed; this hypothesis is consistent with sulfate concentration data reported in previous work [9,11] and mentioned in the experimental section.

3.1. *Spectral features of sulfates as a function of T_{calc}*

Fig. 3 reports the spectra of surface sulfates (after a standard vacuum activation at $T_{act} = 673$ K) for YZS samples (fig. 3a) and ZS samples (fig. 3b) calcined at the three temperatures already considered in the previous section. It is quite evident that increasing the calcination temperature of the catalysts brings about a dramatic change in the spectrum of surface sulfates and, thus, in the structure of surface sulfates. The spectral changes are particularly evident in the case of the model YZS system (fig. 3a):

(i) For $T_{calc} < 773$ K, the high frequency band due to $\nu_{S=O}$ vibrations [13] is broad and complex and localized at wavenumber well below 1400 cm^{-1}, whereas the low frequency band due to ν_{S-O} vibrations is also broad and mainly localized at wavenumber well above 1000 cm^{-1}.

(ii) For $T_{calc} \geqslant 773$ K, the spectral components that were dominant in the case of $T_{calc} = 673$ K gradually decline, while new sharp and strong components that were not present before become dominant at ~ 1400 cm^{-1} ($\nu_{S=O}$ vibrations) and 1010 cm^{-1} (ν_{S-O} vibrations).

Fig. 3b shows that the same spectral changes with calcination temperature are also exhibited by surface sulfates of the ZS system, a system that derives from an amorphous precursor and that, during the calcination at $T_{calc} > 773$ K, undergoes a better and better crystallization in the tetragonal form. It is thus deduced that the spectral and structural transformations occurring in surface sulfates during the calcination step are *compatible* with the amorphous → crystalline (tetragonal) phase transition, but are not *caused* by the phase transition, as the same transformations occur in the model YZS system (fig. 3a) whose original crystallinity is not modified by the calcination step [9].

Before other complementary data are acquired and discussed in the next section, we cannot yet postulate what structural differences may exist between sulfates typical of low and high calcination temperatures respectively. Still, considering the spectra in fig. 3, some comments are already possible:

(i) On the basis of our present knowledge of the spectral behaviour of sulfates at the surface of oxides, it can be stated that the sulfate species that become more and more important on catalysts calcined at increasing temperatures possess an increasing covalent character, monitored by the increasing spectral separation between the

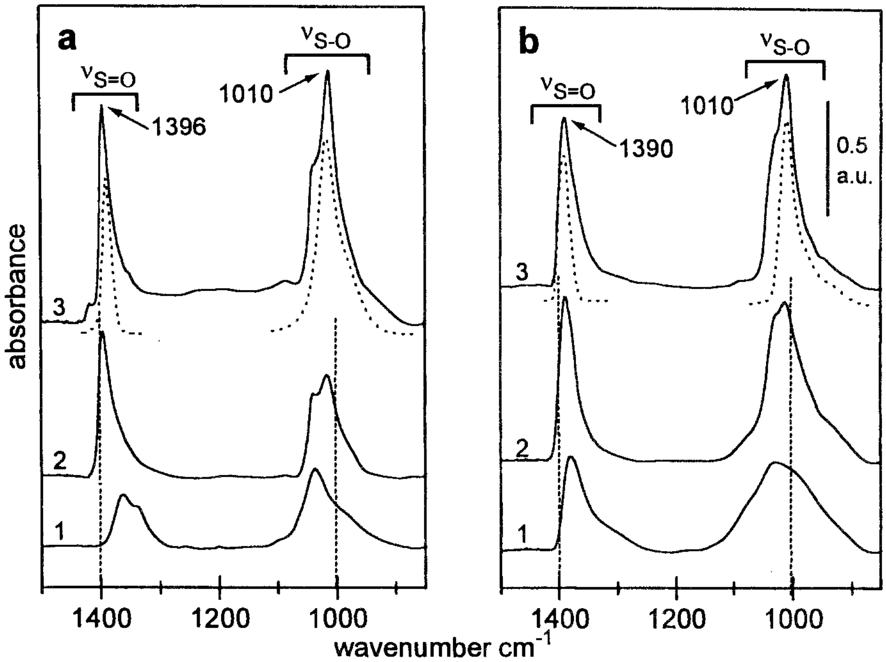


Fig. 3. FTIR spectra (absorbance) of the surface sulfates of YZS catalysts (a) and ZS catalysts (b), calcined at T_{calc} = 673 K (curves 1), 823 K (curves 2), and 923 K (curves 3). The catalysts were standard vacuum activated at T_{act} = 673 K.

high frequency $\nu_{S=O}$ mode(s) and the low frequency ν_{S-O} mode(s) [14]. The degree of covalency of surface sulfates on oxides is known to depend primarily on the degree of surface dehydration [13]; but the data reported in fig. 2 showed that, for any constant activation temperature, there are no major changes of dehydration degree with increasing T_{calc} and, if some change does occur, it is in the direction of an increase of the surface hydroxylation. It is thus deduced that the increase of covalency of sulfates, brought about by high T_{calc}, must be of a structural origin.

(ii) Increasing the calcination temperature produces a strong increase of intensity in the bands of surface sulfates. Considering that an increase of surface sulfates concentration is not possible (especially in the case of the model YZS system, characterized by a constant surface area) and that, if a change of sulfates concentration does occur, it is in the direction of a decrease (monitored by a small increase of the bands of surface hydroxyls), it is deduced that the change (increase) of covalency produces a strong change (increase) of extinction coefficient in the bands of surface sulfates.

This may not be surprising on a spectroscopic ground, as it simply means that the higher is the covalent character of the sulfates, the higher is the change of dipole moment involved in the vibration of the S=O and S–O oscillators [15]. But this certainly indicates that the spectral intensities of sulfate bands cannot be used as such to estimate the surface concentration of sulfates, unless one refers to the changes of intensity of the same spectral species.

3.3. The adsorption of carbon monoxide as a function of T_{calc}

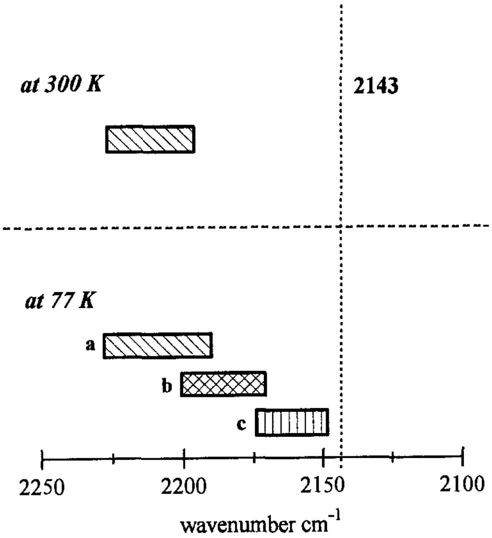
General remarks

When dealing with the surface properties of d^0 metal oxides, the spectroscopic approach to the adsorption of carbon monoxide (CO) is a fairly useful probe. CO adsorbs weakly through a plain (partial) σ-charge release mechanism from the 5σ lone-pair orbital (mainly localized on the C end of the molecule and possessing a slightly antibonding character), yielding C–O stretching bands at wavenumbers higher than that of gaseous CO (2143 cm^{-1}). The upwards frequency shift of the C–O oscillator measures the charge-withdrawing power, i.e., the acidic strength, of the adsorbing site. This is schematically represented in scheme 1.

It should be noted that:

(i) When CO is adsorbed at ambient temperature (~ 300 K), it is known that very low coverages are attained; the upper part of scheme 1 shows that CO uptake yields band(s) at fairly high frequencies. In fact at ~ 300 K CO uptake involves only the strongest surface Lewis acid centres, i.e., surface cationic sites characterized by the highest degree of coordinative unsaturation.

In the case of tetragonal ZrO_2, it was shown in a previous paper [16] that the strongest Lewis acid centres, that correspond to the strongest cus Zr^{4+} sites capable of chemisorbing CO at ~ 300 K, are mainly localized in highly energetic and crystallographically defective situations. The latter can be thought of as steps, corners, kinks, etc., i.e., as the defective situations met in the



Scheme 1. Schematic representation of the spectral ranges for CO adsorption on d^0 metal oxides.

abundant stepped and roundish "side" terminations of the crystallites that high-area non-porous powdery materials are made of. Defective "side" terminations have been shown by (high resolution) transmission electron microscopy to be quite abundant in the case of tetragonal ZrO_2 systems like those dealt with in this work [9,17].

(ii) When adsorbed at temperatures as low as that of boiling liquid nitrogen (77 K), CO yields high coverages and several families of adsorbed species, as shown in the lower part of scheme 1. In particular, in order of decreasing upwards frequency shift of the C–O stretching mode, i.e., of decreasing acid strength, the spectrum may present: band(s) in the spectral range a (2240–2190 cm^{-1}), due to CO adsorbed on strong cus cationic sites (i.e., sites in the defective "side" terminations of the crystallites, and the only sites observable also upon adsorption at $\sim$ 300 K), band(s) in the spectral range b (2200–2170 cm^{-1}), due to CO adsorbed on cus cationic sites located in regular patches of some low-index crystal planes (i.e., sites in the regular "top" terminations of the crystallites), and band(s) in the spectral range c (2175–2145 cm^{-1}), due to CO weakly interacting by H-bonding with some acidic surface OH groups.

CO uptake at $\sim$ 300 K

The spectral effects of adsorbing CO at $\sim$ 300 K on catalysts of the YZS family and of the ZS family, calcined at the usual three T_{calc} temperatures already considered in the previous sections (and then standard activated at $T_{act} = 673$ K), are shown in figs. 4a and 4b respectively.

As usual, the constant crystallinity and the virtually constant surface area of the model system YZS allow a more straightforward interpretation of what happens at the surface of a t-SZ catalyst: after calcination at $T_{calc} < 773$ K (curve 1 of fig. 4a) the adsorptive capacity towards CO at $\sim$ 300 K is virtually null, whereas after calcination at $T_{calc} > 773$ K an adsorptive capacity towards CO develops and keeps gradually increasing, as monitored by the gradually increasing intensity of a CO band centered at $\sim$ 2200 cm^{-1}. A similar behaviour is also exhibited by the ZS system (see fig. 4b), although for $T_{calc} > 773$ K the increasing intensity of the CO band at $\sim$ 2200 cm^{-1} is much less gradual (i.e., much faster) than in the case of YZS, and this in spite of the appreciable

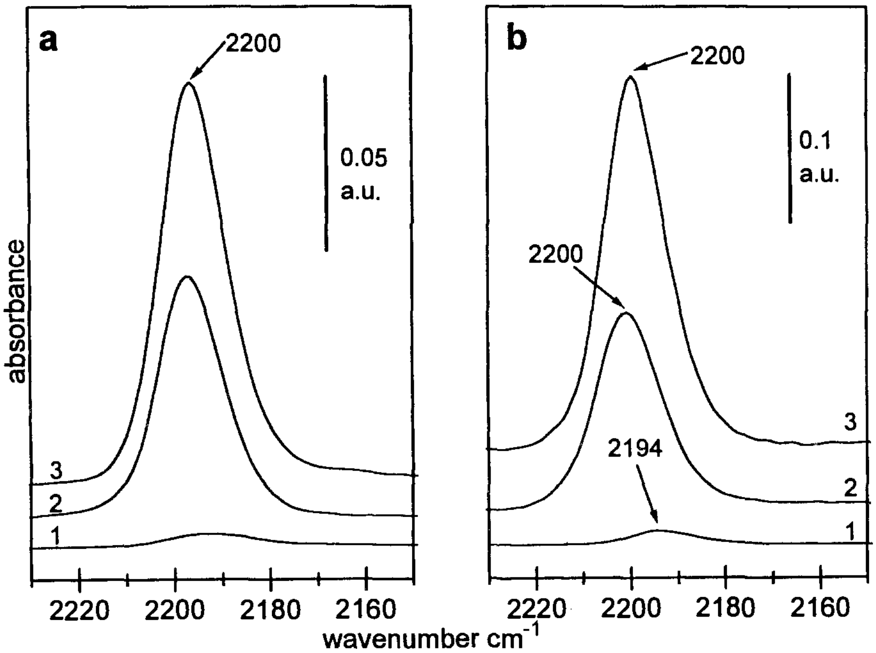


Fig. 4. FTIR spectra (absorbance) of 100 Torr CO adsorbed at ambient temperature onto YZS catalysts (a) and ZS catalysts (b), calcined at $T_{calc} = 673$ K (curves 1), 823 K (curves 2), and 923 K (curves 3). The catalysts were standard activated at $T_{act} = 673$ K.

decline of surface area caused by the calcination step in systems deriving from amorphous precursors.

The meaning of the above observations is:

(i) As long as the calcination of the SZ catalysts is carried out at $T_{calc} < 773$ K, no strong Lewis acid sites (capable of adsorbing CO at ~ 300 K) become available upon vacuum activation, because all the cationic centres located in crystallographically defective situations (and thus capable of creating the strongest cus Zr^{4+} sites) are covered by sulfates. It is recalled that the determinant role played in the catalytic process of *n*-butane isomerization by the strongest family of Lewis acid sites was demonstrated in a previous work [8] by the reversible inhibition of the isomerization reaction caused by CO adsorption.

Surface sulfates occupying the defective "side" terminations of the ZrO_2 crystallites are responsible for (at least part of) the complex $\nu_{S=O}$ band centered well below 1400 cm^{-1} and the complex ν_{S-O} band centered well above 1000 cm^{-1}, as these are the sulfate bands dominating the spectrum of the inactive catalysts calcined at $T_{calc} = 673$ K (see curves 1 of figs. 3a and 3b). These surface sulfates, whose presence inhibits the catalytic activity of t-SZ systems, turn out to be thermally stable at least up to 773 K.

(ii) When the calcination of SZ catalysts is carried out at $T_{calc} > 773$ K, surface sulfates localized on crystallographically defective "side" terminations (i.e., on the highly exposed and energetically rich steps and corners at the edge of the crystallites) are no longer thermally stable, and are selectively eliminated; the best T_{calc} at which their selective thermal elimination occurs depends largely on the preparative history of the material.

The thermal elimination of these sulfates sets free surface cations located in the defective "side" terminations of ZrO_2 crystallites so that, after the calcination step and subsequent exposure to the atmosphere, these cations will become covered (saturated) by a surface hydrated layer. The vacuum or inert atmosphere activation step at $T_{act} \approx 673$ K, that is known to be necessary in order to develop the catalytic activity of a superacid system (obviously, only if the system was exposed to moisture after the preliminary calcination step), will then remove the surface hydrated layer and render cus the Zr^{4+} cations in the "side" terminations. This treatment will so originate the strongest family of Lewis acid sites, responsible for the adsorption of CO at ambient temperature and necessary for the catalytic isomerization process.

It can be thus concluded that, during the preparation of superacid SZ catalysts, the calcination step may *incidentally* coincide with the physical process of crystallization of amorphous ZrO_2 precursors, but its *actual* vital role is a surface chemical process through which highly energetic (i.e., highly uncoordinated) defective terminations of the ZrO_2 crystallites are liberated from sulfates and become available for the formation of strong Lewis acid sites.

Abundant sulfates remain in the SZ systems after the calcination step. Most of these sulfates are localized in the "top" terminations of the crystallites, i.e., in regular patches of low-index crystal planes of tetragonal ZrO_2, and turn out to be responsible for the $\nu_{S=O}$ band at ~ 1400 cm^{-1} and the ν_{S-O} band at ~ 1010 cm^{-1} that dominate the spectrum of SZ systems after calcination at $T_{calc} > 773$ K.

The presence in the IR spectrum of a properly activated SZ system of strong sulfate bands at ~ 1400 and ~ 1010 cm^{-1}, and possibly of *only* these sulfate bands, is the spectral monitor of a catalytically active (superacid) system. Any chemical process (e.g., a reduction with H_2 at $T \geqslant 873$ K [18]) and/or physical process (e.g., a vacuum thermal treatment at $T \geqslant 973$ K [18]) that happens to eliminate the sulfates responsible for the bands at ~ 1400 and ~ 1010 cm^{-1} is bound to induce in the SZ systems an irreversible loss of catalytic activity.

CO uptake at ~ 77 K

The conclusions reached in the previous section still leave an important question to be answered: during the calcination step, do sulfates migrate from the defective "side" terminations to the regular "top" terminations of the crystallites, or sulfates, initially present in both positions, are selectively eliminated from the "side" terminations whereas they remain in the "top" terminations.

Some experimental observations tend to favour the second hypothesis:

– fig. 2a showed that, on increasing the calcination temperature (and at constant activation temperature), there is a moderate increase of surface OH population, that should correspond to a decrease of sulfates population;

– in a recent paper, Srinivasan et al. [19] reported that heating SZ systems above 823 K corresponds to an abundant evolution of sulfur oxides. This datum is confirmed by analytical data on surface sulfates concentration previously reported [11].

In contrast, the spectra in fig. 3 seem to indicate the first hypothesis. In fact, in both $\nu_{S=O}$ and ν_{S-O} spectral regions of surface sulfates, at $T_{calc} > 773$ K we do not observe the selective elimination of one spectral component and the permanence of another one, but rather the transformation of a complex spectral component into another one, not present before. Spectroscopically, this is indicative of a transformation between species rather than of a separation between species.

To solve this problem, and to reach a better understanding of what actually happens on SZ systems during the calcination step, the adsorption of CO at ~ 77 K has been resorted to. In fact, on the basis of the general remarks reported above (and represented in the lower section of scheme 1), CO uptake at ~ 77 K should be able to reveal and differentiate various families of surface Lewis acid sites present on SZ in the various stages of the calcination process.

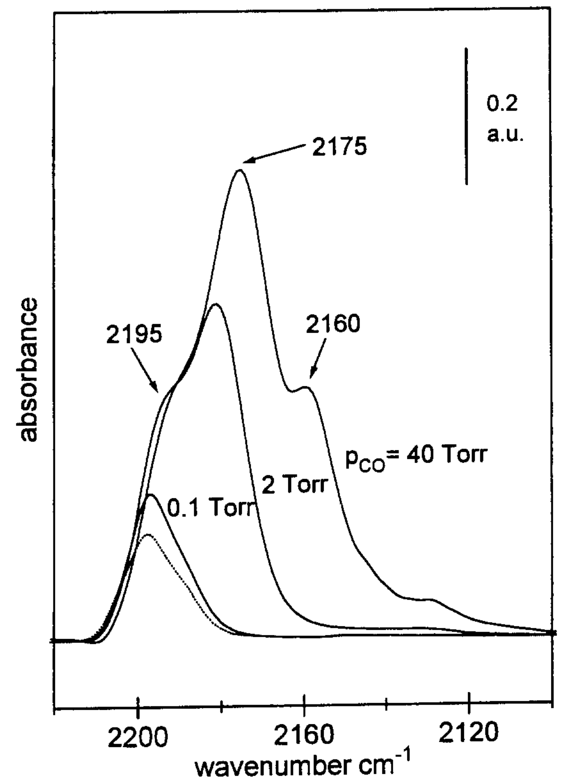


Fig. 5. FTIR spectra (absorbance) of three pressures CO adsorbed at ~ 77 K onto a non-sulfated YZ system (Y-stabilized tetragonal ZrO_2) standard vacuum activated at T_{act} = 673 K. The dotted-line trace corresponds to the band observable upon adsorption of CO at ~ 300 K.

Fig. 5 shows, at three different CO coverages, the spectrum of CO adsorbed at ±77 K onto the reference sample YZ (non-sulfated Y_2O_3-stabilized tetragonal ZrO_2), standard vacuum activated at 673 K. As expected, the spectrum presents three major components: a high frequency band, centered at ~ 2195 cm^{-1}, due to CO/Zr^{4+}_{cus} complexes in defective "side" terminations, a dominating band, centered (at high coverages) at ~ 2175 cm^{-1}, due to CO/Zr^{4+}_{cus} complexes in regular "top" terminations, and a tiny band, present only at high coverages at ~ 2160 cm^{-1}, due to some CO/OH H-bonded complexes. Only the high frequency component is observable also at ~ 300 K, as indicated by the dotted-line spectrum of fig. 5.

Fig. 6 reports the spectra of CO adsorbed at ~ 77 K onto the model system YZS, after standard calcination at the usual three T_{calc} temperatures, and after a standard vacuum activation at 673 K. It is quite evident that, for T_{calc} = 673 K (fig. 6a), CO can only interact by H-bonding with some acidic surface hydroxyls, whereas the two CO components ascribable to adsorption onto surface Lewis acid sites are missing: for low T_{calc} temperatures, sulfates occupy both "side" and "top" terminations of the ZrO_2 crystallites.

For $T_{calc} \geq 823$ K (figs. 6b and 6c), the high frequency CO component starts being formed, confirming that the calcination process has liberated increasing fractions of the highly energetic sites located in "side" terminations. But the CO component at ~ 2175 cm^{-1}, ascribable to CO on sites located in regular "top" terminations, remains totally missing.

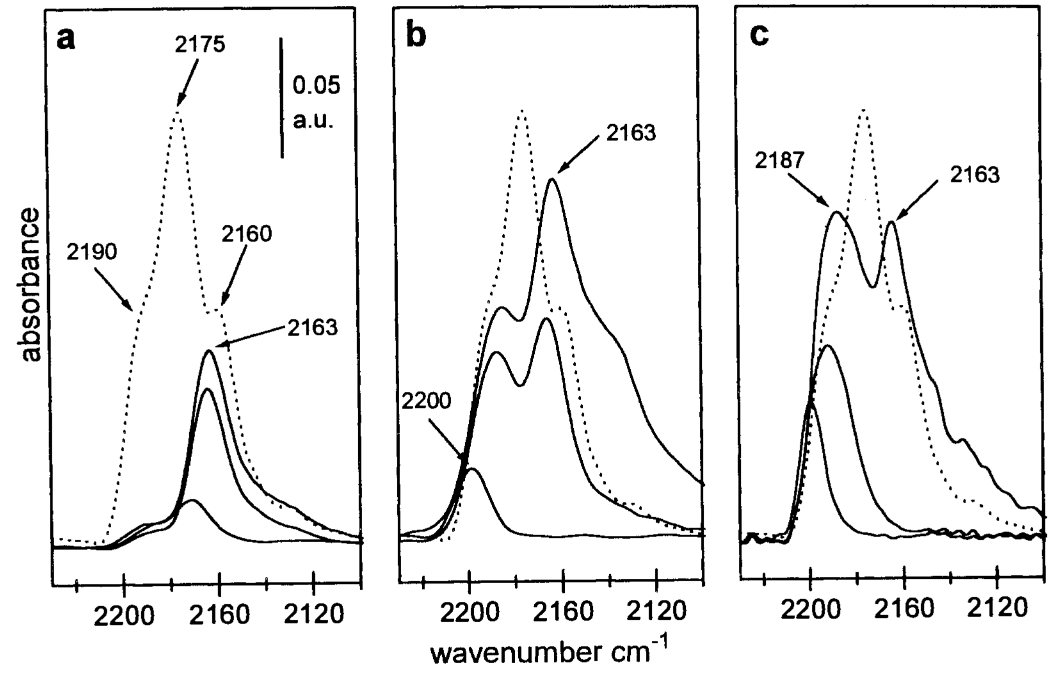


Fig. 6. FTIR spectra (absorbance) of three pressures CO (P_{CO} as for fig. 5) adsorbed at ~ 77 K onto a YZS catalyst calcined at T_{calc} = 673 K (a), 823 K (b), and 923 K (c) and standard vacuum activated at T_{act} = 673 K. Broken-line spectra correspond to the adsorption of the highest CO pressure onto the reference YZ system (as described in fig. 5).

This demonstrates that, of the two hypotheses proposed above, the second one is valid: calcination at $T_{calc} > 773$ K does actually destroy (and does not transfer) the sulfates originally located in the "side" terminations, while abundant sulfates remain in the patches of regular low-index crystal planes. It is so deduced that these sulfates, located in the "top" terminations of the crystallites, do not possess peculiar and constant spectral features, but present spectral features that depend largely on the overall concentration of sulfates and on the surface location of all sulfates:

– when the defective "side" terminations are covered with sulfates, sulfates in the "top" terminations are perturbed and present a lower covalency, so that their $\nu_{S=O}$ and ν_{S-O} modes have relatively low absorption coefficient and fall within the complex and unresolved spectral envelops at $\nu < 1400$ cm^{-1} and $\nu > 1010$ cm^{-1}, respectively (see curves 1 of fig. 3);

– when the defective "side" terminations are rendered free from sulfates and become rich in strong Lewis acid sites (i.e., highly uncoordinated Zr^{4+} centres), sulfates in the "top" terminations reach the maximum covalency, so that their $\nu_{S=O}$ and ν_{S-O} modes become sharp and strong (i.e., acquire high absorption coefficient) and fall at ~ 1400 and ~ 1010 cm^{-1}, respectively (see curves 2 and 3 of fig. 3).

The latter condition is that in which t-SZ systems present their best catalytic properties, and this condition can be reached only if the calcination step has been carried out at $T_{calc} > 773$ K. This requisite of the calcination step is of general validity: in particular, it does not change if the SZ catalytic system has been promoted with the addition of Pt, as it is frequently done in order to improve the catalytic activity (see, for instance, refs. [18,19] and references therein).

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