



IR study of CS₂ adsorption on metal oxides: relation with their surface oxygen basicity and mobility

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Abstract

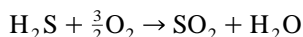
Adsorption of CS₂ on a series of metal oxides (Al₂O₃, ZrO₂, ZnO and CeO₂) activated at 723 or 973 K was studied at room temperature by FT-IR spectroscopy. In addition to hydrogen thiocarbonate and carbonate species, a new species, characterized by bands in the 1200–1000 cm⁻¹ range, was evidenced. Its amount increased by increasing activation temperature of metal oxides. Co-adsorption experiments of CS₂ with either CO₂ or pyridine showed that its adsorption sites are mainly those giving rise to bidentate carbonates from CO₂. Experiments on ZrO₂ prechanged by H₂¹⁸O confirmed CS₂ adsorption on basic O²⁻ sites. Xanthate (COS₂)²⁻ species formation was proposed. Results were compared with metal oxide basicity and a nice agreement was observed. However, on ceria, carbonates formation easily occurred from CS₂ adsorption, even at room temperature, suggesting that CS₂ can probe both surface basicity, through the intensity of bands due to xanthate species, and surface oxygen mobility, involved in the surface transformation of xanthate into carbonate species. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: CS₂ adsorption; FT-IR spectroscopy; Metal oxides; Surface oxygen basicity and mobility; Xanthate

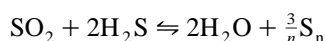
1. Introduction

The Claus process is still the most commonly used technique to remove sulfur from natural gas or contained in industrial and combustion plant streams. It involves two steps [1]:

- First, one-third of the initial H₂S is burned in a combustion chamber at 1200–1500 K

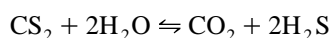
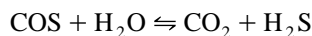


- In the second step, the following reaction occurs, catalyzed by metal oxides, like alumina or titania



The best sulfur recovery efficiency of Claus plants is 98%.

Tail gas generally contains COS and CS₂; their percentage can reach up to 50% of its sulfur total amount. Their elimination generally occurs by hydrolysis, catalyzed by metal oxides in the Claus converters:



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Several publications [2–4] have demonstrated that the hydrolysis of COS proceeds via a hydrogen thiocarbonate intermediate, as shown by infrared spectroscopy. Tested on different metal oxides, it was observed that the COS hydrolysis activity, expressed per unit area, decreased in the following order: $\text{ZrO}_2 > \text{Al}_2\text{O}_3 > \text{TiO}_2 \gg \text{ZnO}$, in nice agreement, ZnO excepted, with the amount of CO_2 adsorbed in the form of hydrogen carbonate species measured by IR spectroscopy [5].

This suggests that COS hydrolysis could be used as a test reaction of metal oxide hydroxyl basicity.

CS_2 is kinetically much more difficult to convert than COS [6]; this low activity is a severe problem since the amount of CS_2 in the tail gas is the same as that of COS. Huisman et al. [6] recently reported that the reaction occurs on Al_2O_3 via hydrogen thiocarbonate species in the 400–700 K range, whereas, on TiO_2 , the mechanism is more sensitive to the reaction temperature. Using realistic industrial Claus conditions, Laperdrix et al. [7] explained why TiO_2 was more effective than Al_2O_3 in CS_2 hydrolysis: TiO_2 is more resistant to deactivation by SO_2 and by sulfates than Al_2O_3 due, in particular, to a difference of sulfate reducibility by H_2S . As for activity, the same order was found for CS_2 hydrolysis [8] as that obtained for COS hydrolysis: $\text{ZrO}_2 > \text{CeO}_2 > \text{TiO}_2 > \text{Al}_2\text{O}_3 \gg \text{ZnO}$, showing that CS_2 hydrolysis can probe the relative basicity of type I (monodentate) hydroxyl groups of metal oxides.

To our knowledge, no paper has reported yet on CS_2 interaction with coordinatively unsaturated oxygen on the surface of metal oxides. This is the aim of the present study. For that, CS_2 has been adsorbed on dehydroxylated Al_2O_3 , ZrO_2 , ZnO and CeO_2 . The results are discussed to determine if CS_2 can probe the basicity of O^{2-} surface sites of metal oxides. Let us remind that basicity is a property difficult to characterize by IR spectroscopy, due to the lack of a universal probe [9].

2. Experimental

$\gamma\text{-Al}_2\text{O}_3$ [B.E.T. surface area $180\text{ m}^2\text{ g}^{-1}$], ZrO_2 ($80\text{ m}^2\text{ g}^{-1}$) and CeO_2 ($170\text{ m}^2\text{ g}^{-1}$) were kindly supplied by Rhodia. ZnO ($12\text{ m}^2\text{ g}^{-1}$) was KADOX-15. The IR spectra were recorded with a Nicolet 710

FT-IR spectrometer (resolution: 4 cm^{-1}). The samples were pressed into discs (10 mg cm^{-2} , except ZnO 50 mg cm^{-2}) and activated in vacuum at 723 K (or 973 K) for 2 h, followed by O_2 treatment ($P_{\text{equilibrium}} = 120\text{ Torr}$) at 723 K for 30 min, then by another evacuation for 1 h at 723 K (973 K). CS_2 ($350\ \mu\text{mol g}^{-1}$) or CO_2 ($P_e = 5\text{ Torr}$) were introduced at room temperature (r.t.). All the spectra were registered at r.t. CS_2 is from Aldrich (99.9% ACS reagent).

3. Results

3.1. Different species formed

3.1.1. Catalysts activated at 723 K

3.1.1.1. $\nu(\text{OH})$ range. The spectrum of alumina activated at 723 K presents, in the $4000\text{--}3500\text{ cm}^{-1}$ range, $\nu(\text{OH})$ bands at 3788 (shoulder), 3769, 3729 and 3672 cm^{-1} assigned to hydroxyl groups of type I_B , I_A , II and III, respectively [10]. A broad shoulder is also noted near 3595 cm^{-1} due to hydrogen bonded OH groups (Fig. 1A(a)). CS_2 introduction at r.t. does not apparently perturb the OH groups after a short contact time. After 15 min, type I OH groups characterized by the 3769 cm^{-1} band, the most basic, becomes slightly affected.

The spectrum of ZrO_2 (Fig. 1B(a)) mainly shows two strong bands at 3770 and 3663 cm^{-1} assigned to terminal and bridged hydroxyl groups, respectively [11]. As soon as CS_2 is introduced at r. t., the intensity of the species at 3770 cm^{-1} strongly decreases whereas a new band appears near 3610 cm^{-1} (Fig. 1B(b)).

The spectrum of ZnO , in the $\nu(\text{OH})$ range, is more complex (Fig. 1C(a)). According to Tsyganenko and Filimonov [12], the strongest bands at 3669 and 3619 cm^{-1} are due to type II and type III OH groups, respectively. That at 3695 cm^{-1} could characterize type I OH whereas bands at 3640 , 3580 and 3445 cm^{-1} are considered as due to hydrogen bonded OH groups. CS_2 adsorption decreases the intensity of all the bands, that at 3640 cm^{-1} excepted, and slightly perturbs the wavenumber of type II and type III OH groups, shifting them to 3660 and 3612 cm^{-1} , respectively (Fig. 1C(b)).

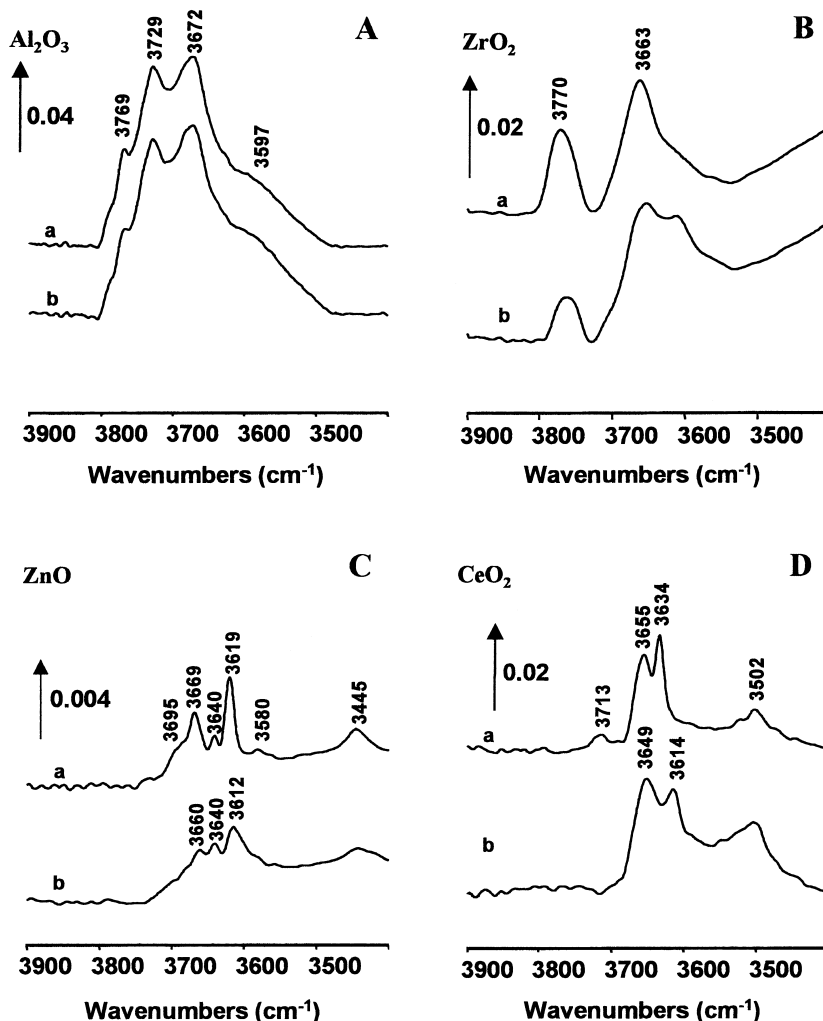


Fig. 1. Effect of CS₂ adsorption at r.t. on $\nu(\text{OH})$ bands of metal oxides activated at 723 K. (A) Al₂O₃; (B) ZrO₂; (C) ZnO; (D) CeO₂. Spectra of samples activated at 723 K (a), followed by introduction of 350 $\mu\text{mol g}^{-1}$ of CS₂ at r.t. (b).

The spectrum of CeO₂ (Fig. 1D(a)) mainly presents two $\nu(\text{OH})$ bands at 3655 and 3634 cm^{-1} , assigned to type II OH groups [13]. Two weaker bands at 3713 and 3502 cm^{-1} are also noted, due to type I and to a non-well crystallized phase, respectively [13]. CS₂ adsorption provokes the disappearance of the 3713 cm^{-1} band, whereas those due to type II OH groups shift to 3649 and 3614 cm^{-1} (Fig. 1D(b)).

It is important to note that all the perturbations reported above persist after CS₂ evacuation at r. t. and therefore, result from irreversible features.

3.1.2. Range below 2000 cm^{-1}

CS₂ introduction on Al₂O₃ activated at 723 K leads to a sharp band at 1515 cm^{-1} characteristic of CS₂ physisorbed species, as evidenced by its disappearance by evacuation at r.t. (Fig. 2A). Two weak bands are also noted at 1345 and 1166 cm^{-1} . The first one has already been observed when adsorbing COS on alumina and assigned to hydrogen thiocarbonate species [4]. It should be accompanied by another one expected near 1570 cm^{-1} , hardly detectable due to its very weak intensity. As for that at 1166 cm^{-1} , it reveals the formation of a new species,

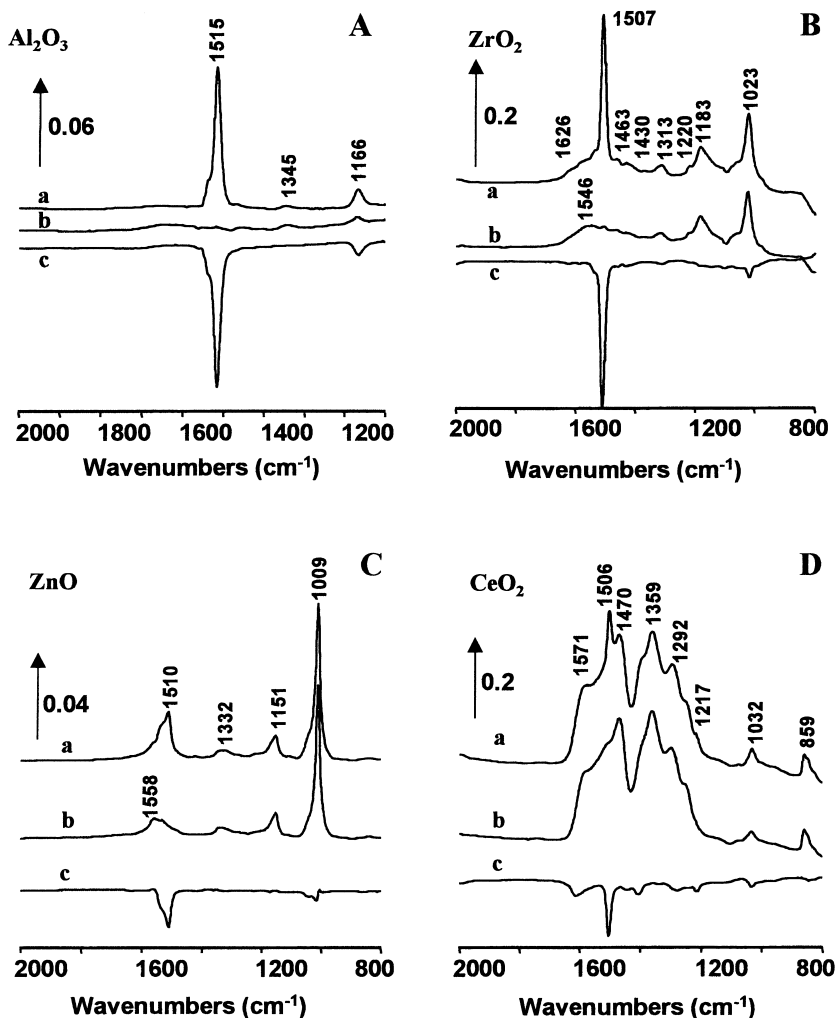


Fig. 2. Spectra of species formed from CS_2 adsorption at r.t. on metal oxides activated at 723 K (2000–800 cm^{-1} range). (A) Al_2O_3 ; (B) ZrO_2 ; (C) ZnO ; (D) CeO_2 (a) After introduction of $350 \mu\text{mol g}^{-1}$ of CS_2 . (b) After evacuation at r.t. (c) Subtracted spectrum: spectrum (b) – spectrum (a).

called X. It tends to disappear by evacuation at r. t. After evacuation at 373 K, no band persists in the 2000–1000 cm^{-1} range. Introduction of a large excess of O_2 on the sample so treated, followed by heating at 723 K for 4 h, provokes the appearance of a band at 1372 cm^{-1} , characterizing the formation of sulfate species [14]. This evidences that sulfur species remained on alumina after CS_2 evacuation at 373 K, without any characteristic band in the 2000–1000 cm^{-1} range.

Many bands appear when introducing CS_2 on ZrO_2 at r.t. (Fig. 2B). They are all due to irreversibly

adsorbed species, that at 1507 cm^{-1} , corresponding to physisorbed CS_2 , excepted. Bands at 1313 and 1546 cm^{-1} characterize hydrogen thiocarbonate species formation [5]. Those at 1626, 1430 and 1220 cm^{-1} are due to hydrogen carbonate species [15], as confirmed below by CO_2 adsorption. A weak one at 1463 cm^{-1} could be due to carbonate species. Those at 1183, 1080 (shoulder) and 1023 cm^{-1} correspond to another species, called X.

On ZnO , CS_2 adsorption (Fig. 2C) leads to the formation of (i) CS_2 physisorbed species (band at 1510 cm^{-1}), (ii) hydrogen thiocarbonate species

(bands at 1558 and 1332 cm^{-1}), (iii) species X, characterized by bands at 1151, 1045 and 1009 cm^{-1} .

A very complex spectrum arises from CS_2 adsorption on CeO_2 (Fig. 2D). The sharp band at 1506 cm^{-1} , which disappears by evacuation at r.t., is due to CS_2 physisorbed species. That at 1360 cm^{-1} characterizes the formation of hydrogen thiocarbonate species [8]. The others are due to bidentate carbonate (1571, 1292, 859 cm^{-1}), hydrogen carbonate (1217, 1397 cm^{-1}) and polydentate or bulk carbonate species (1470 cm^{-1}) as shown from the study of CO_2 adsorption on CeO_2 [16], also invoked below. The extra band at 1032 cm^{-1} characterizes X species.

3.1.3. Catalysts activated at 973 K

The same experiments have been performed on the metal oxides activated at 973 K, in order to specify the role played by the residual OH groups, whose amount is quite weak after activation at such a temperature. Bands similar to those reported above on metal oxides activated at 723 K are observed. However, the intensity of those due to X species is stronger, indicating that the formation of these species does not imply residual hydroxyl groups.

3.2. Adsorption sites

In order to specify the nature of surface sites implied in CS_2 adsorption, co-adsorption experiments have been performed using either CO_2 or pyridine. These probe molecules are often used to characterize surface basic and acid sites, respectively.

3.2.1. CO_2 co-adsorption

Results obtained from CO_2 adsorption on metal oxides activated at 723 K and precovered by CS_2 followed by evacuation at r.t., have been compared to those obtained from CO_2 adsorption on the corresponding pure oxides. Subtracted spectra allow one to determine which CO_2 adsorbed species are poisoned by CS_2 preadsorption.

In agreement with literature [17], CO_2 ($P_e = 5$ Torr) introduction on alumina leads to hydrogen carbonate species characterized by bands at 1648, 1477 (type B_2), 1450 (type B_1) and 1233 cm^{-1} (Fig. 3A(a)). Moreover, broad bands are observed between

1900 and 1700 cm^{-1} and assigned to CO_2 perturbed species [18]. The spectrum obtained from CO_2 adsorption on Al_2O_3 pretreated by CS_2 at r.t. is not very different (Fig. 3A(b)). However, the subtracted spectrum (Fig. 3A(c)) evidences a partial poisoning of the B_2 hydrogen carbonate species (bands at 1648, 1477 and 1233 cm^{-1}), whose formation involves OH groups characterized by the 3770 cm^{-1} band [17].

Two main types of species are formed by CO_2 adsorption on ZrO_2 (Fig. 3B): (i) hydrogen carbonate species giving rise to bands at 1618, 1447 and 1224 cm^{-1} and (ii) bidentate carbonate species (bands at 1562, 1315 and 1061 cm^{-1}), as reported in literature [15]. Fig. 3B evidences that CS_2 preadsorption tends to preferentially poison the latter.

It has been reported that CO_2 adsorption on ZnO [19] gives rise to bidentate carbonate (bands at 1615, 1584, 1345, 999 and 842 cm^{-1}), hydrogen carbonate (1634, 1430 and 1229 cm^{-1}) and carboxylate species (1549 cm^{-1}). CS_2 preadsorption completely prevents CO_2 adsorption as shown by Fig. 3C(b).

On CeO_2 , different types of species are formed from CO_2 adsorption [16]: (i) bidentate carbonate (1574, 1291, 1015 and 856 cm^{-1}), (ii) hydrogen carbonate (1590, 1403, 1217 and 1045 cm^{-1}) and (iii) polydentate or bulk carbonate species (1468 cm^{-1}). Fig. 3D(c) shows that CS_2 preadsorption mainly prevents the formation of bidentate carbonate species.

3.2.2. Pyridine co-adsorption

Fig. 4a reports the spectrum of CS_2 species adsorbed on ZrO_2 activated at 973 K. Mainly species X are observed. Pyridine adsorption on ZrO_2 activated at 973 K evidences, in agreement with literature [15], the formation of coordinated species characterized by ν_{8a} and ν_{19b} bands at 1606 and 1444 cm^{-1} , respectively, revealing the presence of surface Lewis sites of medium acidity (Fig. 4b). Pyridine introduction on the ZrO_2 sample precovered by CS_2 leads almost to the same bands (Fig. 4c), as confirmed by the subtracted spectrum (Fig. 4d). It is worth noticing that pyridine adsorption shifts the bands due to species X from 1184 and 1023 to 1195 and 1018 cm^{-1} . Similar results are obtained when introducing CS_2 on ZrO_2 on which pyridine has been preadsorbed.

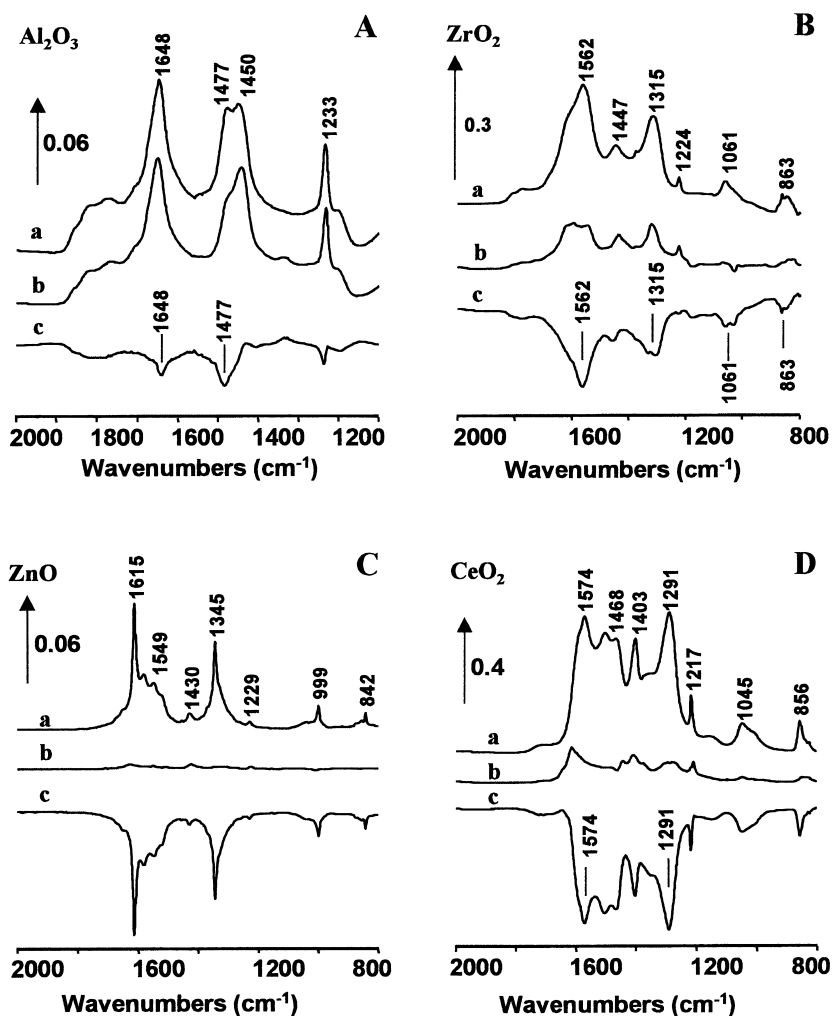


Fig. 3. Spectra of species formed from CO_2 introduction ($P_c = 5$ Torr) at r.t. on metal oxides activated at 723 K (2000–800 cm^{-1} range). (a) On the pure metal oxide. (b) After CS_2 adsorption (introduction of $350 \mu\text{mol g}^{-1}$ of CS_2 followed by evacuation at r.t.). (c) Subtracted spectrum: spectrum (b) – spectrum (a).

3.3. Nature and thermal stability of species X

For this study, ZrO_2 activated at 973 K has been chosen as adsorbent since CS_2 adsorption on it mainly leads to species X, as shown in Fig. 4a.

Fig. 5 allows one to compare the spectrum of CS_2 adsorbed at r.t. on ZrO_2 either treated or not by H_2^{18}O at 973 K and then evacuated at the same temperature. The $^{16}\text{O} \rightarrow ^{18}\text{O}$ exchange slightly shifts the 1080 and 1020 bands to 1075 and 1018 cm^{-1} .

That at 1184 cm^{-1} is more affected since it is observed at 1162 cm^{-1} on the oxygen exchanged ZrO_2 sample. This evidences that O^{2-} surface sites participate to X species formation.

In another experiment (Fig. 6), CS_2 has been first introduced at r.t. on ZrO_2 activated at 973 K and then evacuated at r.t. (Fig. 6a) and 373 K (Fig. 6b). It clearly appears that heating provokes the disappearance of X species as shown by the decrease of 1183 and 1023 cm^{-1} band intensity, whereas bands at

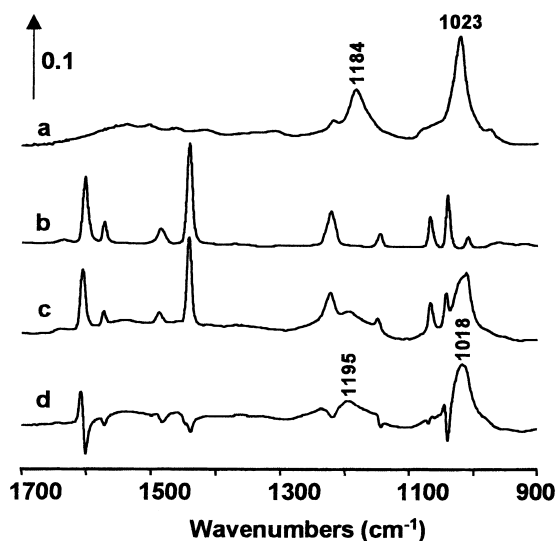


Fig. 4. Effect of pyridine on bands due to species formed from CS_2 adsorption at r.t. on ZrO_2 activated at 973 K. (a) Spectrum of CS_2 species formed on the pure metal oxide. (b) Spectrum of pyridine species formed on the pure metal oxide. (c) Spectrum of pyridine species formed after CS_2 preadsorption. (d) Subtracted spectrum: spectrum (c) – spectrum (b).

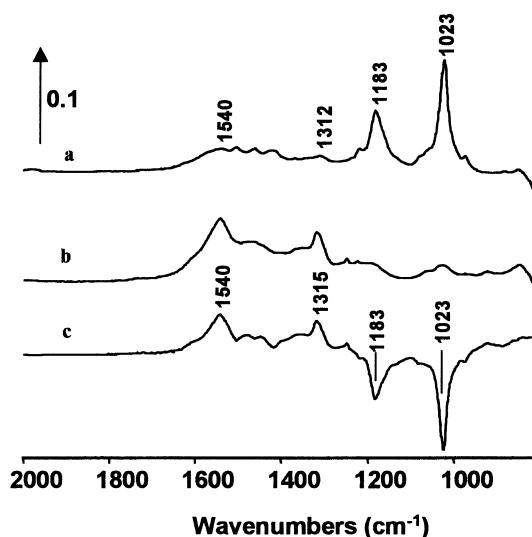


Fig. 6. Spectra of species formed from CS_2 adsorption on ZrO_2 activated at 973 K. (a) After CS_2 evacuation at r.t. (b) After evacuation at 373 K. (c) Subtracted spectrum: spectrum (b) – spectrum (a).

1540 and 1315 cm^{-1} appear, due to hydrogen thiocarbonate or thiocarbonate species.

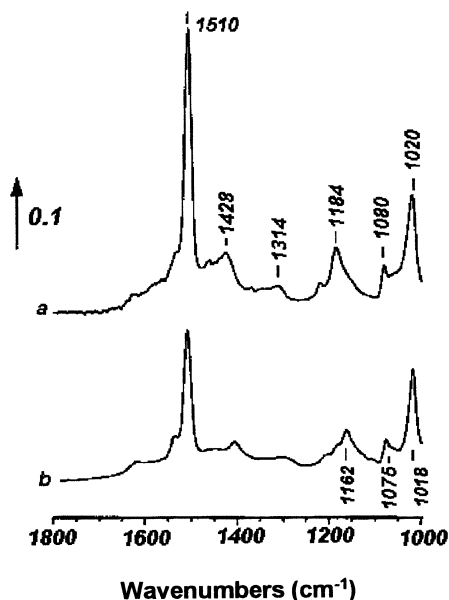


Fig. 5. Spectra of species formed from CS_2 adsorption at r.t. on zirconia activated at 973 K. (a) Zr^{16}O_2 . (b) Zr^{18}O_2 (zirconia pretreated by H_2^{18}O at 973 K and then evacuated at 973 K).

4. Discussion

Fig. 1 clearly shows that CS_2 introduction at r.t. modifies the $\nu(\text{OH})$ bands of activated metal oxides, those of alumina excepted. This is not due to hydrogen bonded species formation since evacuation at r.t. removes molecularly adsorbed CS_2 (band near 1510 cm^{-1}) without modifying the perturbed $\nu(\text{OH})$ bands (Fig. 2). We previously reported [7] that CS_2 addition on alumina activated at 523 K led, after a long contact time at r.t., to hydrogen thiocarbonate and hydrogen carbonate species, at the expense of the highest wavenumber $\nu(\text{OH})$ groups (band at 3767 cm^{-1}). This was explained by CS_2 hydrolysis leading to COS, adsorbed as hydrogen thiocarbonate species. This species plays the role of an intermediate in COS hydrolysis. CO_2 is adsorbed as hydrogen carbonate species [4].

In the present study, alumina is activated at higher temperature. The lower amount of residual hydroxyl groups persisting at 723 K well explains why CS_2

hydrolysis hardly occurs (Figs. 1A and 2A). On the other metal oxides used, more basic (principally on ZrO_2 and CeO_2), the strong decrease of the type I $\nu(\text{OH})$ band intensity (Fig. 1B and D) evidences that CS_2 transformation occurs, even at r.t., as shown by the appearance of bands due to hydrogen thiocarbonate and hydrogen carbonate species (Fig. 2) and in nice agreement with reactivity results [8].

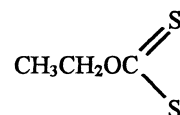
Another hypothesis to explain the changes of $\nu(\text{OH})$ bands after CS_2 introduction is the partial sulfidation of the surface of metal oxides, as shown in the case of alumina, by the reoxidation experiment at high temperature, transforming residual sulfur species into sulfates.

Fig. 2 clearly evidences the formation of another type of species, called X, from CS_2 adsorption on all the metal oxides used. It is characterized by bands reported in Table 1.

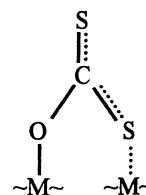
Since the intensity of these bands is higher when the metal oxides are activated at high temperature, we deduce that species X does not result from CS_2 interaction with residual OH groups. Co-adsorption experiments with CO_2 strongly suggests that its adsorption site is the same as that giving rise to bidentate carbonate species with CO_2 . Implication of surface O^{2-} sites is confirmed by the experiments (Fig. 6) comparing results obtained on ZrO_2 and ZrO_2 exchanged by H_2^{18}O . Moreover, X species formation is not prevented by pyridine co-adsorption. Pyridine preadsorption only slightly shifts the wavenumber of bands characteristic of species X (Fig. 4), as already observed in the case of pyridine- CO_2 co-adsorption and explained involving an increased basicity in surface oxygens [20].

We propose that X species are dithiocarbonate species, $(\text{CS}_2\text{O})^{2-}$, also called xanthate. Little et al. [21] reported in 1961 that the spectra of copper and zinc ethyl or butyl xanthates show well-defined bands at 1200 and 1120 cm^{-1} , assigned to vibrations of the

C–O–C linkage, while an intense band at 1060 cm^{-1} was assigned to the C=S stretching mode. Studying compounds like ethyl xanthate interacting with copper, Brienne et al. [22] reported the formation of copper xanthate, characterized by bands at 1193, 1189, 1122, 1034 and 1009 cm^{-1} , e.g. in the same frequency range as those presently observed. The following structure was considered:



On ZrO_2 activated at 973 K (Fig. 6), oxygen exchange experiments allow one to assign the 1185 cm^{-1} band to the $\nu(\text{C–O})$ vibration, the two others, at 1080 and 1022 cm^{-1} , being rather due to $\nu(\text{C–S})$ vibrations, supposing a structure like:



We can remark that $(\text{COS}_2)^{2-}$ species with a higher symmetry (C_{2v}), present quite different bands [23], since the C–O stretch and the antisymmetric C–S stretch have been identified at 1506 and 606 cm^{-1} , respectively.

It therefore, appears that CS_2 interacts with basic O^{2-} sites. Co-adsorption experiments with CO_2 specify that these O^{2-} sites are partially (ZrO_2 , Fig. 3B) or totally (ZnO , Fig. 3C) those of $\text{O}^{2-}\text{M}^{x+}$ pair sites giving rise to bidentate carbonates with CO_2 .

Using different probe molecules like carbon dioxide, sulfur dioxide or hexafluoroisopropanol, the following classification of metal oxides according to the number of basic sites has been established [24]:



As for ZnO , its basicity can be considered as close as that of MgO [25–27], itself being slightly lower than that of CeO_2 [27]. The intensity of bands due to

Table 1
Wavenumbers of bands characterizing species X

Metal oxide	ν (cm^{-1})
Al_2O_3	1166
ZrO_2	1183, 1080 (sh), 1023
ZnO	1151, 1045 (sh), 1009
CeO_2	1032

xanthate species on Al_2O_3 , ZrO_2 and ZnO (Fig. 2) is in agreement with the relative basicity of these three metal oxides since it is quite weak on alumina. Moreover, the stability of xanthate species towards evacuation at r.t. (Fig. 2) is also low in the case of alumina, indicating a weaker interaction.

The results on CeO_2 are not so clear since the bands due to xanthate species are weak (Fig. 2D), in spite of the great basicity of ceria. Moreover, bands due to carbonate species are quite strong, even on CeO_2 activated at 973 K. This clearly shows they do not arise from CO_2 adsorption resulting from CS_2 hydrolysis. It is well known that the oxygen mobility on the surface of ceria is quite high [27]. We therefore suggest that, on this metal oxide, the xanthate $(\text{OCS}_2)^{2-}$ species first formed from CS_2 adsorption can easily give rise to monothiocarbonate species $(\text{O}_2\text{CS})^{2-}$, themselves leading to $(\text{CO}_3)^{2-}$ species, even at r.t. In such a case, this transformation would account for the surface oxygen mobility since it involves an $\text{O} \leftrightarrow \text{S}$ replacement in the xanthate species first formed. Recently Martin and Duprez [27] reported on a series of metal oxides that the oxygen mobility can be paralleled with the surface concentration of basic sites measured by CO_2 chemisorption. However, the basicity of CeO_2 could not alone explain the exceptional mobility on this oxide, due to a large part to the presence of oxygen vacancies [27]. One can wonder if CS_2 would not be a very suitable probe to distinguish the surface basicity through the amount of xanthate species formed and the oxygen mobility, through the easiness to transform xanthate into carbonate species. For instance, on zirconia (Fig. 6), xanthate species are stable at r.t. Heating at 373 K under evacuation, transforms them into (hydrogen) monothiocarbonate species showing in such a case, by contrast to ceria, that heating is necessary to involve this transformation. Moreover, the oxygen mobility of zirconia is not sufficient enough to lead to carbonate species under the conditions used here.

5. Conclusion

In previous studies we have shown that COS hydrolysis [5] and CS_2 hydrolysis [8] could be used as test-reactions for metal oxide hydroxyl basicity.

The present paper reports that the IR study of species formed by CS_2 adsorption on highly dehydroxylated metal oxide surfaces reveals its specific interaction with basic O^{2-} sites leading to xanthate species. Moreover, the transformation of xanthate into carbonate species at low temperature could account for the surface oxygen mobility. These two properties are very important in surface chemistry and difficult to characterize by probe adsorption. CS_2 seems a suitable probe. However, these preliminary results have to be confirmed by extending the study to metal oxides with a high basicity, like calcium oxide, or with a high oxygen mobility, like ceria-zirconia mixed oxides. Moreover, on a given metal oxide, it would be important to determine which coordinatively unsaturated O^{2-} sites, situated on regular surface planes or on defects like corners or edges, interact with CS_2 . In our opinion CS_2 seems to be more specific than CO_2 and so it could lead to informative complementary results on the surface properties of metal oxides.

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