Combined FTIR, reactivity and quantum chemistry investigation of COS hydrolysis at metal oxide surfaces used to compare hydroxyl group basicity

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Received 15 March 1995; accepted 8 March 1996

Three distinct approaches were used in the present work to investigate COS hydrolysis at metal oxide surfaces: (i) in situ FTIR spectroscopy, to provide information on the type of reaction intermediate species formed; (ii) reactivity measurements; (iii) quantum chemical calculations using ab initio Slater type orbital wavefunctions (STOP package) for COS and the semi-empirical GEOMOS-GREEN package, to give transition state structures and activation energy barrier heights. These three methods were found to be in excellent agreement. In particular, it is confirmed by FTIR and quantum chemical calculations that the COS hydrolysis mechanisms on Al_2O_3, TiO_2 and ZrO_2 are all of the type already published for the Al_2O_3 type I surface hydroxyl case. The relative activity hierarchy of these catalysts towards COS hydrolysis per unit area is: $ZrO_2 \gg Al_2O_3 > TiO_2$. This agrees with the amount of CO_2 adsorbed in the form of hydrogen carbonate species measured by FTIR spectroscopy and the calculated barrier heights, more product-like C–O distance in the transition state and carbonyl charge. ZnO was investigated by FTIR spectroscopy and using GEOMOS. Both approaches indicate the formation of the monothiocarbonate adduct instead of hydrogen thiocarbonate species which explains the complete inactivity of ZnO for COS hydrolysis.

Keywords: oxide; hydroxide; basicity; FTIR; hydrolysis; reactivity

1. Introduction

Carbon oxysulfide is a polluting by-product of the Claus reaction which is industrially used to transform H_2S into sulphur. Eliminating COS from the gaseous effluent improves the Claus process and protects the environment. For that purpose COS hydrolysis is generally used [1]:

$$COS + H_2O \rightarrow CO_2 + H_2S\,,$$

H_2S being treated in the Claus converters.

In a recent work [2], we studied this reaction on alumina evidencing the interaction between COS and basic surface hydroxyls which leads to the hydrogen thiocarbonate reaction intermediate. Much work has been carried out on alumina or modified alumina which shows the activity is related to catalyst basicity [3]. However, little fundamental work has been devoted to this reaction on other metal oxide surfaces except TiO_2 and ZrO_2 [4,5].

The present work aims at comparing the reaction using Al_2O_3, ZrO_2, TiO_2 and ZnO which have different acid–base catalytic properties. The active sites and COS adsorbates are determined. The relative activities of these oxides towards COS hydrolysis are then compared to the basicities of the hydroxyl groups obtained from the number of hydrogen carbonate species resulting from CO_2 adsorption.

2. Methods

2.1. Catalysts

ZrO_2 (70 $m^2\ g^{-1}$) is prepared by room temperature hydrolysis of a zirconium *n*-propylate solution [6]. γ-Al_2O_3 (215 $m^2\ g^{-1}$) and TiO_2 (124 $m^2\ g^{-1}$) were provided by Rhône-Poulenc. The ZnO is Kadox-15 (12 $m^2\ g^{-1}$).

2.2. Reactivity

The analyses were carried out on 0.02 g samples compacted into 0.5–1mm diameter pellets. The reaction was carried out at 373 K and atmospheric pressure, after activating the catalyst in a helium flux (100 $cm^3\ min^{-1}$). The reaction mixture comprises 1% COS, 2.3% H_2O and 96.7% helium. The contact time (*W/F*) is 2.3×10^{-3} kg h mol^{-1}. Product analysis has been carried out by GLC with a Porapak Q column.

2.3. Infrared spectroscopy

The IR study was carried out with a Nicolet MX-1 FTIR spectrometer (resolution 2 cm^{-1}). The samples were pressed into discs (10 mg cm^{-2}, except ZnO 50 mg cm^{-2}) and activated in vacuum at 523 K. Isotope exchange ($^{16}O \rightarrow {}^{18}O$) of the ZnO surface was made by introducing $^{18}O_2$ at 550°C and evacuating at this temperature. The operation was repeated three times.

2.4. Quantum chemistry

Quantum chemical calculations were carried out for Slater type orbitals using the Green matrix method implemented at both levels of calculation in the ab initio (STOP 94-Green) and semi-empirical (GEOMOS) packages [7,8]. The present study checks the adsorbate geometries using STOP 94 and provides a complete reaction path study by running GEOMOS with a full geometry optimisation and stepwise increments of the reaction coordinate.

These calculations focus on reaction intermediate and transition state structures and potential energy barrier heights. Run times represent 2–8 h on IBM RISC RS 6000 machines (340 and 355) for a full reaction pathway.

3. Results

3.1. Reactivity

The oxide activity expressed as conversion percentage is presented in table 1. The results show Al_2O_3 to be slightly more active than ZrO_2, whereas TiO_2 is substantially less so and ZnO completely inactive towards this reaction. When the activities are expressed per unit area, the value for ZrO_2 is highest, whereas alumina is substantially lowered towards the TiO_2 value. The reaction was studied as a function of time, no deactivation was noted and the regime is reached rapidly (after 30 min reaction).

3.2. IR spectroscopy

3.2.1. COS adsorption

COS adsorption on alumina has been already reported [2]. The IR spectrum of ZrO_2 activated at 523 K presents two bands in the 3900–3300 cm^{-1} region at 3774 and 3672 cm^{-1} corresponding to the hydroxyl group vibrations (ν(OH)). Introduction of 350 μmol g^{-1} COS (fig. 1A) leads to a marked decrease in the 3774 cm^{-1} band intensity. In the 1800–1000 cm^{-1} region (fig. 1B), bands implying formation of two types of species are detected [9]:

– Hydrogen carbonate species. These are characterised by bands situated at 1222 cm^{-1} (δ(OH)), 1440 cm^{-1} ($\nu_s(CO_2)$) and 1617 cm^{-1} ($\nu_a(CO_2)$).

– Hydrogen thiocarbonate species. These species give rise to bands situated at 1320 cm^{-1} ($\nu_s(CO_2)$) and 1550 cm^{-1} ($\nu_a(CO_2)$).

Fig. 2A presents the IR spectrum of TiO_2 activated at 523 K. The hydroxyl groups give rise to ν(OH) bands at 3720, 3672 and 3640 cm^{-1}. COS introduction shows the involvement of the high wavenumber bands at 3720 and 3672 cm^{-1}. The concomitant formation of hydrogen carbonate species is characterised by bands at 1580 and 1460 cm^{-1} (fig. 2B). The hydrogen thiocarbonate species leading to bands at 1511 and 1312 cm^{-1} are observed.

Zinc oxide activated at 523 K presents different ν(OH) vibrations characterised by bands at 3668, 3642, 3619, 3574 and 3445 cm^{-1}. COS introduction on this sample (fig. 3A) provokes a slight decrease in band intensity in two cases (3668 and 3619 cm^{-1}), whereas below 1600 cm^{-1} (fig. 3B) three bands are observed at 1551, 1508 and 1128 cm^{-1}, all intense. The same three bands appear when COS is adsorbed on this surface after it has been strongly dehydroxylated by activation at 823 K (fig. 4a).

COS was adsorbed on ZnO exchanged by $^{18}O_2$ at 823 K. The results obtained (fig. 4b) show a shift in the band observed at 1128 cm^{-1} to 1118 cm^{-1} after $^{16}O \rightarrow {}^{18}O$ substitution. Conversely, the two bands at 1551 and 1508 cm^{-1} are hardly changed. After some time (fig. 4e), the 1118 cm^{-1} band slips back to its original position (1127 cm^{-1}). A shoulder at 1498 cm^{-1} also clearly appears whereas the 1551 cm^{-1} band remains unaffected.

3.2.2. CO_2 adsorption

CO_2 adsorption on metal oxides has been studied previously by several groups [10]. In this section, attention is focused especially on the formation of hydrogen carbonate species. Their number indicates the relative basicity of surface hydroxyl groups on the oxides. It is measured from the area of the δ(OH) band due to $HOCO_2^-$ species in the 1210–1230 cm^{-1} range from CO_2 adsorption. The results expressed per unit surface area are presented in table 2. This species is formed by CO_2 interaction with the most basic hydroxyl groups (except in the case of ZnO) [11]. This quantitative measurement counts the number of hydrogen carbonate species, which follows the order $ZrO_2 > ZnO > Al_2O_3 > TiO_2$.

3.2.3. Quantum chemistry results

The information from structural calculations with full geometry optimisation confirms that the reaction mechanism on the three oxides studied for their activity in this reaction (ZrO_2, Al_2O_3 and TiO_2) is always similar to that previously published for COS hydrolysis on alumina [2].

The most basic hydroxyl groups of type I are shown to be involved in the initial nucleophilic attack of COS.

Table 1
Catalytic activities of different metal oxides

Catalyst	Surface area ($m^2 g^{-1}$)	Conv. (%)	Conv. ($\% m^{-2}$)
ZrO_2	70	23	0.33
Al_2O_3	215	26	0.12
TiO_2	124	9	0.07
ZnO	12	0	0

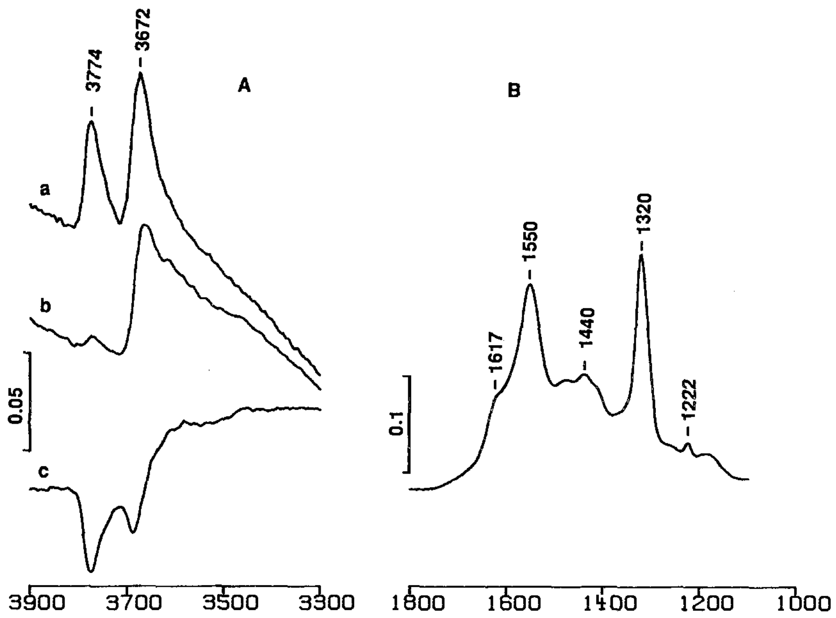
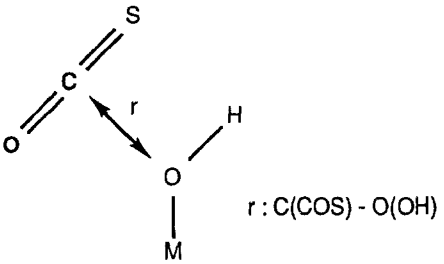


Fig. 1. IR spectra resulting from COS adsorption at room temperature on ZrO_2 activated at 523 K. (A) ν (OH) bands (a) before and (b) after introduction of 350 μmol g^{-1} of COS (contact time: 1 h); (c) difference of spectra (b) – (a). (B) bands due to COS adsorption.

The rate limiting step is shown to be the hydrolysis step involving a water molecule via a cyclic (nearly hexagonal) transition state in which the water molecule valence angle has widened from 104.5° to values close to 119° for the three active oxides.

Activation barrier heights calculated for both type I hydroxyl nucleophilic attack of COS and hydrolysis by water imply the same order of activity as observed by the experimental procedure described above ($ZrO_2 \gg Al_2O_3 > TiO_2$).

Table 3 shows the calculated barriers heights and the corresponding COS carbon to OH oxygen distance (r):



This distance indicates that the lower the transition state energy, the more product-like its structure [12].

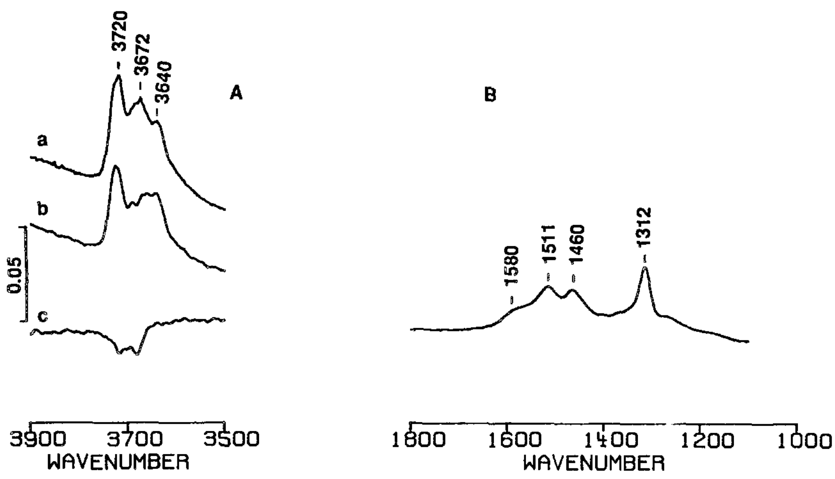


Fig. 2. IR spectra resulting from COS adsorption at room temperature on TiO_2 activated at 523 K. See fig. 1, for further details.

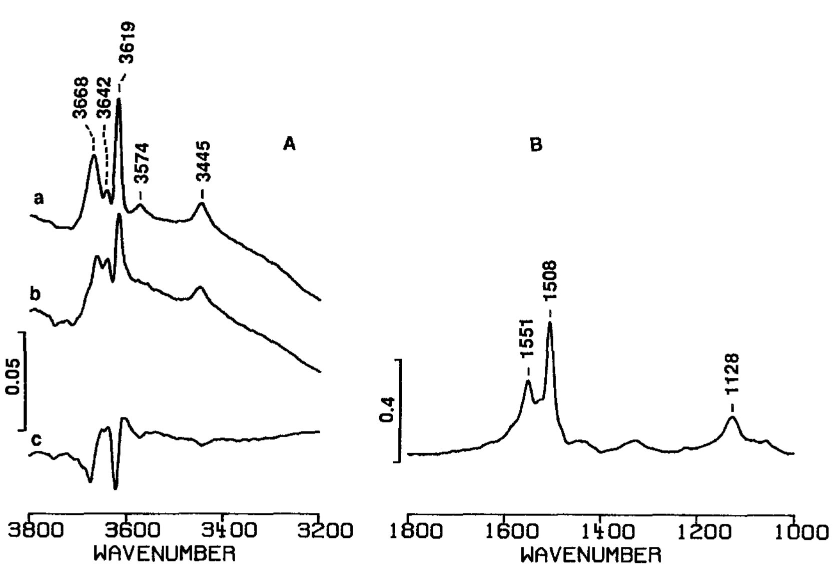


Fig. 3. IR spectra resulting from COS adsorption at room temperature on ZnO activated at 523 K. See fig. 1 for further details.

Calculated (Mulliken) charges on the COS carbon also follow the order of activity measured experimentally and expressed per unit area in table 1.

This excellent agreement prompted a full investigation of the ZnO case. Calculations indicate a very weak physisorption interaction between COS and type I OH on ZnO dominated by dispersion (essentially repulsive) interactions. The COS molecule was found to form a more stable adduct across a surface Zn–O bond.

Calculations also showed that CO_2 interacts with the type I hydroxyl groups of all four oxides to form nearly symmetric hydrogen carbonate species, albeit weakly interacting in the case of ZnO, where type II and type III hydroxyls proved inert unless they opened first to type I groups.

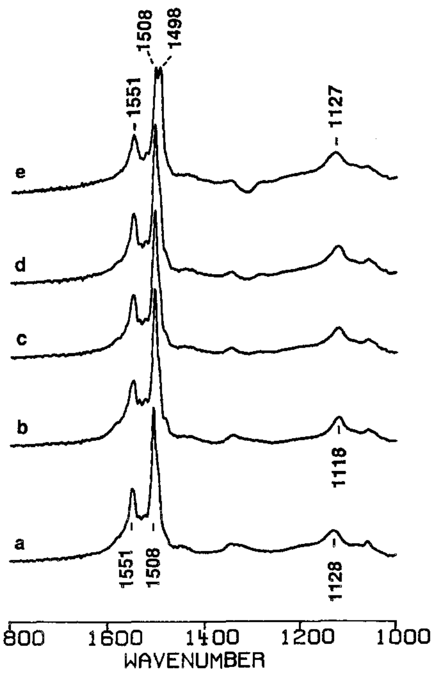


Fig. 4. IR spectra resulting from COS adsorption (350 μmol g^{-1}) at room temperature: (a) on ZnO activated at 823 K (contact time: 2 min); (b) on ZnO exchanged by $^{18}O_2$ at 823 K, after a contact time of 2 min; (c) 30 min; (d) 1 h; (e) 2 h.

3.2.4. Discussion

The surface hydroxyls of ZrO_2 are of the following two types, monodentate (type I) and bidentate (type II) [13]. The corresponding bands are at 3774 and 3672 cm^{-1}, respectively (fig. 1). COS interaction with the basic hydroxyls (mostly type I) results in a reaction yielding hydrogen thiocarbonate species formed as an intermediate of the COS hydrolysis reaction as observed on alumina [2].

In the case of TiO_2, hydroxyl groups give rise to bands at 3720, 3672, 3640 cm^{-1} (fig. 2). The first band corresponds to monodentate species, the two latter are assigned to two types of bridged hydroxyl group corresponding to different lengths of the Ti–O bond [11]; COS adsorption leads to a slight perturbation of the 3720 and 3672 cm^{-1} bands. This interaction is less pronounced than for alumina and zirconia. Under these conditions, the concomitant formation of hydrogen thiocarbonate and hydrogen carbonate species is detected.

The IR spectrum of ZnO activated at 523 K (fig. 3) presents two intense peaks at 3667 and 3620 cm^{-1} ascribed to type II and type III hydroxyls, respectively,

Table 2
Relative number of $HOCO_2^-$ species formed from CO_2 adsorption (P_e = 10 Torr) on different metal oxides activated at 523 K

	Catalyst			
	ZrO_2	Al_2O_3	TiO_2	ZnO
$I\,\delta(OH)$[a] (au cm^{-1} m^{-2})	1.8	0.34	0.15	0.85

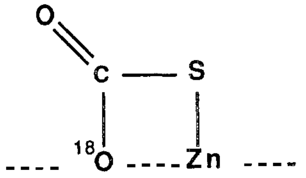
[a] Area of the δ(OH) band of the $HOCO_2^-$ species.

Table 3
Calculated activation energy (barrier heights), distance along the reaction coordinate and partial charges governing hydrolysis

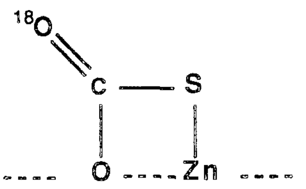
	Metal		
	Al	Ti	Zr
attack by OH (type I) of metal oxide substrate [a]			
activation energy (kcal/mol)	29.4	42.3	17.8
distance C(COS)–O(OH) r (Å)	2.08	2.11	2.01
hydrolysis by H_2O			
partial charge $M^{\delta+}(OH)$	0.31	0.39	0.28
partial charge $C^{\delta+}O$	0.07	0.03	0.09
activation energy (kcal/mol)	37.1	54.1	28.0
distance C(CO)–O(OH) r (Å)	2.83	2.81	2.87

[a] ZnO: no significant interaction of this type by calculation.

by Tsyganenko et al. [11]. These authors consider that 3641 and 3448 cm^{-1} peaks correspond to OH groups interacting by hydrogen bonds. COS adsorption on this sample slightly perturbs the type II and type III hydroxyls without leading to formation of hydrogen thiocarbonate species as opposed to the observations regarding Al_2O_3, ZrO_2 and TiO_2. A different species is observed however, characterised by bands at 1551, 1508 and 1128 cm^{-1} (fig. 3). The same species form on very dehydroxylated ZnO and prove sensitive to the $^{16}O \rightarrow {}^{18}O$ isotope exchange. Apparently, surface O^{2-} sites are involved (fig. 4a). The isotope shift (10 cm^{-1}) from 1128 to 1118 cm^{-1} (fig. 4b) thus observed is slight (10 cm^{-1}) compared with that expected (30 cm^{-1}) for a ν(CO) vibration. We suggest the involvement of Zn^{2+} O^{2-} pairs, the COS being adsorbed on basic O^{2-} sites. The postulated species on ZnO preexchanged by $^{18}O_2$ is



Assuming only one type of species forms at the surface, a valid interpretation of the two bands at 1551 and 1508 cm^{-1} would be a Fermi resonance between the ν(C=O) and the first ν(C–S) harmonic. The monothiocarbonate ion CO_2S^{2-} presents fundamental peaks at 1445, 1202 and 603 cm^{-1} [14]. A time dependent modification could occur by desorption and re-adsorption leading to the following species:



This explains the 1498 cm^{-1} band (fig. 4e). The very slight isotope effect is again explained by assuming the Fermi resonance coupling.

In the case of very hydroxylated ZnO, CO_2S^{2-} species are absent as are hydrogen thiocarbonate species. Results obtained on alumina [2] show the latter to predominate for samples activated at low temperature, e.g. on a very hydroxylated surface. These results indicate the low basicity of ZnO surface hydroxyl sites.

CO_2 is another probe molecule able to provide information on the basicity of OH groups on metal oxides [15]. Work on ZrO_2 and TiO_2 [6], Al_2O_3 [16] and ZnO [17] shows hydrogen carbonate formation by CO_2 adsorption. Table 2 presents the relative numbers of the former. These species are formed with the type I surface hydroxyls with the exception of ZnO. Both CO_2 and COS probes interact similarly with basic surface hydroxyls. A good correlation was obtained between oxide activity and the number of hydrogen carbonate species (fig. 5), except for the case of ZnO. The difference in behaviour of ZnO towards COS and CO_2 indicates the competition between the Lewis basic sites O^{2-} shown above and the basic OH groups. CO_2 is just acid enough ($\delta_C^+(CO_2) = 0.3$) to interact with the OH groups whereas COS is not ($\delta_C^+(COS) = 0.11$).

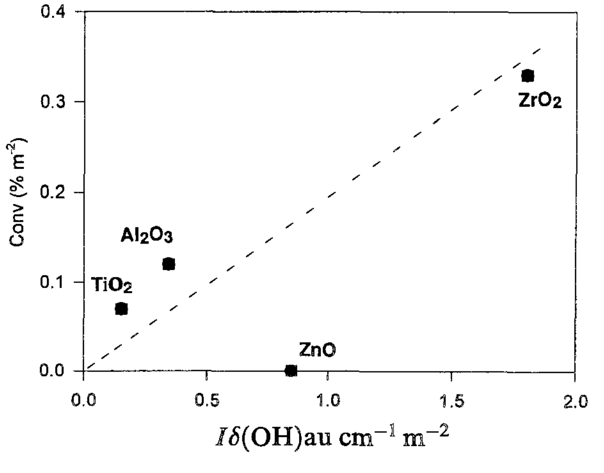


Fig. 5. Variation of COS conversion with the area I of the band δ(OH) (at 1220 cm^{-1}) of $HOCO_2^-$ species formed from CO_2 adsorption on different metal oxides.

Quantum chemical calculations have confirmed that the most likely adsorption reaction pathways lead to species corresponding to those invoked to explain IR spectroscopy data. The CO_2S^{2-} species on ZnO is a typical example of a case where the structures calculated with GEOMOS correspond to the species already discussed from an experimental standpoint. The barrier heights calculated as described above confirm the reactivity measurements and it is significant that the localised (partial positive) charges on the carbonyl carbon of adsorbed COS are also in this same order.

ZnO is known to be a very basic oxide [18]. This study shows that surface hydroxyls are only very slightly basic. Therefore, there is no direct relation between the surface O^{2-} site and the OH^- groups. This is not so surprising if we consider water dissociation on Zn^{2+} O^{2-} sites. The proton associated to the O^{2-} ions is only slightly basic or even acidic considering the multidentate geometry of this oxygen. The OH^- group bound to the Zn^{2+} ion could be monodentate. The correspondent Zn–O(H) bond is much less ionic than the surface Zn^{2+} O^{2-} bonds. Moreover, in the case of ZnO the full d shell of the d^{10} configuration leads to an even less basic OH group than in the case of oxides like TiO_2 or ZrO_2 with an incomplete d shell.

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