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Infrared spectrometric studies of the surface basicity of metal oxides and zeolites using adsorbed probe molecules

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Abstract

Infrared spectra analysis of species formed by acid probe adsorption on divided metal oxides and alkaline zeolites can lead to information on their surface basicity, particularly on the nature and strength of basic sites. Results obtained from carbon monoxide, carbon dioxide, sulfur dioxide, pyrrole, chloroform, acetonitrile, alcohols, thiols, boric acid trimethyl ether, ammonia and pyridine are critically reviewed. It is concluded that no probe can be universally used. Pyrrole in the case of alkaline zeolites, CO_2 for weakly basic metal oxides and for basic OH groups and CO for the characterization of highly basic structural defects on metal oxides activated at high temperature appear quite suitable probes. When other methods are used (TPD, microcalorimetry, volumetry, etc.) IR spectroscopy is a complementary method necessary for the knowledge of the type of sites involved; in particular, data obtained from CO_2 and SO_2 adsorption have to be carefully used since both probes can lead on highly basic metal oxides to polydentate (bulk) species which do not result from their adsorption but from their reaction with the given oxide. Ammonia and pyridine, generally used as probes for the measure of the acidity of catalysts, also adsorb on basic oxides through a dissociative chemisorption.

Keywords: Infrared spectrometry; Surface basicity; Zeolites; Metal oxides

1. Introduction

Acidity and basicity are paired concepts which are very often invoked to explain the catalytic properties of divided metal oxides and zeolites [1]. Extensive investigations have been devoted to solid acid catalysts [2,3] due to their great importance in petroleum chemistry. Studies concerning basic centers, in particular surface oxygens and hydroxyls, are far less advanced.

In view to establish correlations between catalytic activity and surface properties of catalysts, it is important to determine the number, nature, strength and location of the active sites. For that, a great number of physical and chemical methods have been developed. To estimate proton-accepting (basic) properties of the surface, two groups of methods can be used: titration with various reagents such as benzoic acid [4] and spectral techniques [5]. Among them, infrared spectroscopy, particularly for the study of adsorbates, is certainly the most commonly used.

Knözinger [3] defined the criteria for the selection of probe molecules for surface acidity measurements. A classification of such probe molecules was given. The aim of the present review is to examine infrared results relative to acidic probe adsorption on metal oxides and zeolites.

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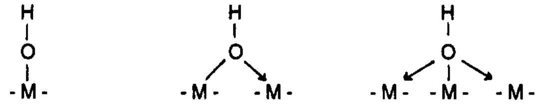
1.1. Carbon monoxide

CO adsorption can be used to characterize both acidic and basic sites of metal oxides.

1.1.1. Hydroxyl groups

It has been shown that the CO molecule was a good probe for the determination of the OH acid strength of metal oxides [6] and molecular sieves [7]: the OH vibration frequency shift caused by the hydrogen bonding of OH with CO can be related to its Brønsted acidity. Zaki and Knözinger [6] reported that the OH groups of MgO and CeO_2 were too basic to be perturbed by CO at 78 K. Among the different OH groups presented by metal oxides like alumina or chromia:



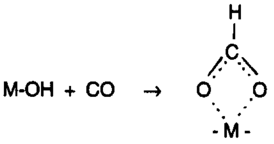
Type I Type II Type III

those of the highest wavenumber, assigned to type I OH groups were almost unaffected by CO adsorption, confirming that these OH groups are basic. In contrast, the doubly and triply bridging OH configurations, type II and III, respectively, did form OH· · ·CO H-bonded surface complexes. These results show that low temperature IR spectroscopy of adsorbed CO permits a distinction of the acido-basic properties of different OH configurations on a given metal oxide: the proton acidity increases with the increase of the coordination number of the OH groups.

These results demonstrate that type I OH groups present a nucleophilic character. This character has been proved in surface organometallic chemistry: the surface hydroxyl groups of alumina, magnesia and zinc oxide can make a nucleophilic attack at the coordinated CO of carbonyl of group VIII metals such as $M_3(CO)_{12}$ [M = Fe, Ru, Os] with the formation of a stable surface hydrido cluster [8]. The nucleophilic character of surface OH groups seems to vary according to the following order [9]:

Mg–OH > Zn–OH > La–OH > Al–OH

The nucleophilic character of some OH groups explains their reactivity towards CO leading to formate species [9]:



It has been recently reported that CO adsorption on a partially reduced CeO_2 sample produced formate species at room temperature [10]. The high frequency OH groups would be involved in the reaction. Several mechanisms have been proposed to explain the formation of formate species [10]. It was found that a deep reduction of CeO_2 facilitated this formation due to the activation of CO: CO would be adsorbed on Ce^{3+} ions or Ce^{4+} ions with oxygen vacancies and then would react specifically with the high frequency OH groups leading to formate species via an unstable intermediate, formyl species [10].

Results obtained in our laboratory confirmed that reduction of ceria favored the formation of formate species from CO interaction [11]. They did not show a direct participation of OH groups to their formation. They rather suggested the participation of hydrogen stored, in equilibrium with the hydroxyls. However, the reduction by H_2 of a metal oxide is not necessary to form formate species at room temperature. It has been shown that CO adsorption on thoria activated under vacuum at 773 K also produced formate species at room temperature [12]. Their formation occurs at higher temperature on other oxides: 373–573 K on MgO or γ-Al_2O_3 [13] or near to 473 K on ZnO [14].

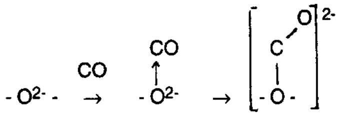
1.1.2. Basic oxygen centers

The coordination of CO to cationic sites via a σ-donor bond generally shifts the ν(CO) frequency, observed at 2143 cm^{-1} in the gas phase, towards higher wavenumbers. From the ν(CO) shift, it is possible to compare the strength of Lewis acid sites on different metal oxides. The following rank has been observed [15]:Al_2O_3 >

$TiO_2 > ZrO_2 > ZnO > ThO_2 \geq CeO_2 \geq La_2O_3$.

However, attention should be paid to low valent transition metal ions having a significant d electron density: back-bonding could occur decreasing the $\nu(CO)$ frequency [16].

CO can also interact with basic O^{2-} sites to lead, at 100 K, to the formation of surface 'carbonite' CO_2^{2-} ions:



$$-O^{2-}- \xrightarrow{CO} -\overset{\overset{CO}{\uparrow}}{O^{2-}}- \rightarrow \left[\begin{matrix} O \\ C \\ | \\ -O- \end{matrix}\right]^{2-}$$

where the CO molecule participates in the role of Lewis acid. Such an interaction has been evidenced on alkaline-earth oxides evacuated at high temperature [17,18]. The carbonite species react with the excess of CO at temperatures higher than 100 K giving rise to more complex species, having a strong absorption in the UV region [19]. Coluccia et al. [18] studied IR spectra of such systems at room temperature and concluded that CO disproportionation occurs, leading to the formation of negatively charged polymeric structures like $(CO)_n^{2-}$ and carbonate ions. The overall process may be described as:

$$xO^{2-} + (n+x/2)CO \rightarrow (CO)_n^{x-} + x/2CO_3^{2-}$$

The IR study of CO chemisorption on MgO [20] had in particular shown that a ketenic-like species was formed. Babaeva et al., adsorbing $^{12}C\,^{16}O$, $^{13}C\,^{16}O$ and $^{12}C^{18}O$ on MgO and CaO, confirmed later the formation of the dioxoketene $O{=}C{=}CO_2^{2-}$ ions [21]. Zecchina et al. [22] proposed that the first species formed (chelated or multidentate CO_2^{2-}) generates $C_3O_4^{2-}$ by addition of two CO molecules at 77 K. Further addition of CO molecules at room temperature leads to oxygen-sensitive $C_{2n}O_{(2n+1)}^{2-}$ species. Long exposure favors disproportionation reactions.

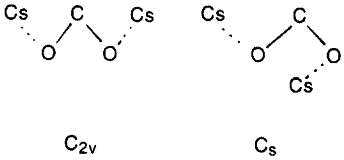
In our laboratory similar results have been observed on lanthana activated at 973 K [23]. Raising the temperature from 100 K to room temperature in the presence of CO led to the following chemical transformations:

$$O^{2-} \xrightarrow{CO} CO_2^{2-} \xrightarrow{CO} C_2O_3^{2-} \xrightarrow{CO,O^{2-}} CO_3^{2-} + (CO)_n^{2-}$$

Measurement of the amount of CO adsorbed on the carbonite form allowed us to conclude that all the surface oxygen ions on lanthana were not basic enough for chemical interaction with CO. The strongest basic sites responsible for CO adsorption may correspond to structural defects like edges or steps where oxygen ions have a lower coordination number [23].

Adsorption of CO at room temperature on ThO_2 activated at 973 K under vacuum also gave rise to a complex absorption in the 1200–1000 cm^{-1} frequency range sensitive to O_2 and H_2O. By analogy with results obtained on alkaline-earth-metal oxides it was assigned to the formation of CO_2^{2-} species, showing the strong basicity of ThO_2 [24]. The appearance, at 243 K, of bands near 2100 cm^{-1} and below 1400 cm^{-1}, was associated with the formation of dioxoketene species.

A recent study has been devoted to CO adsorption at room temperature on ceria reduced by CO at 873 K. Two types of species were found to occur characterized by bands at 1160 and 1300 cm^{-1} (species A), and 771, 1071 and 1270 cm^{-1} (species B) [25]. Both disappeared after adsorption of oxygen. Their nature was deduced by comparing their spectra with those obtained from the interaction of CO_2 with alkali metals [26]. When the alkali metal was caesium, two Cs_2CO_2 isomeric species were evidenced, one with C_{2v}, and the other with C_s symmetry:



C_{2v} C_s

For each of these species two bands described as $\nu_a(OCO)$ and $\nu_s(OCO)$ modes were observed at 1328.7 and 1186.7 cm^{-1} for the C_{2v} structure, and at 1320.0 and 1050.0 cm^{-1} for the C_s geometry. These values correlated nicely with those due to species A and B, respectively. Carbonite species are formed on ceria through a non-redox interaction process of CO with some O^{2-} surface sites. The adsorption sites would be defect sites, easily carbonated on basic oxides under ambient atmosphere, explaining why it is necessary to activate basic oxides at high temperature to decompose carbonate species and thus to liberate defect sites. CO adsorption on ZrO_2 activated at 923 K also gives rise to a complex spectrum in the 2300–900 cm^{-1} range [27] suggesting that carbonite species and derivatives can also form even on ZrO_2, considered as a not very basic oxide.

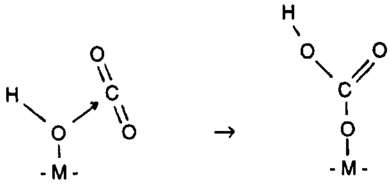
In conclusion, CO adsorption on MgO, CaO, BaO, La_2O_3, ThO_2, CeO_2 and ZrO_2 activated at high temperature shows the presence of highly basic O^{2-} sites. Complex species are formed and it is necessary to accurately assign the spectra before conclusions regarding the structure of these sites can be made. A criterion in favor of the formation of carbonite species is their high sensitivity towards dioxygen.

1.2. Carbon dioxide

1.2.1. Metal oxides

Because carbon dioxide is acidic, it adsorbs specifically on basic sites of metal oxides. A large number of species can be formed:

– *on basic hydroxyl groups*, there is formation of hydrogen carbonate species $HO–CO_2^-$. It is generally considered that, among the different types of OH groups persisting after activation of the metal oxides, type I OH groups, e.g., OH groups coordinated to only one coordinatively unsaturated cation, are mainly involved in the formation of hydrogen carbonate species. Results relative to zirconia clearly demonstrate that point [28]. The following mechanism has been proposed [29]:

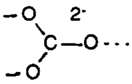


Experiments involving CO_2 adsorption on methanol precovered samples, carried on Al_2O_3 [30], ZrO_2 [28], ThO_2 [31] and CeO_2 [31] also showed that monodentate methoxy species react with CO_2 at room temperature leading to the formation of methyl carbonate species $–O–C(=O)–OCH_3$, confirming the proposed mechanism.

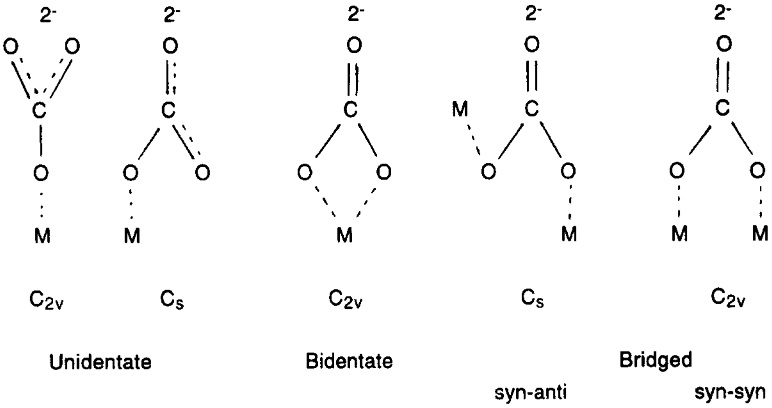
On some oxides, like ThO_2, not only type I OH groups ($\nu(OH) = 3741$ cm^{-1}) but also a part of type II hydroxyls ($\nu(OH) = 3668$ cm^{-1}) interacted with CO_2. The appearance of the 3610 cm^{-1} band [$\nu(OH)$] and that of another characteristic band near 1230 cm^{-1} [$\delta(OH)$] confirmed the formation of $HOCO_2^-$ species [12]. The intensity of the 1230 cm^{-1} band has been taken as a measure of the number of basic OH species. It has been correlated to the conversion of COS in COS hydrolysis, used as a test-reaction specific of OH basicity [32]. On a series of mixed oxides (ZrO_2–Al_2O_3, ZrO_2–TiO_2 and TiO_2–Al_2O_3), it was found [33] that there was a good correlation between COS activity and the intensity of the $\delta(OH)$ vibration of hydrogen carbonate species formed from CO_2 adsorption indicating that both methods can be used to compare the basicity of surface hydroxyl groups. A similar correlation has been observed on Al_2O_3, TiO_2 and ZrO_2 but not on ZnO [34] which adsorbed CO_2 into the form of hydrogen carbonate species but which is completely inactive towards COS hydrolysis. The difference in behavior of ZnO towards COS and CO_2 indicated the competition between the Lewis basic sites O^{2-} and the basic OH^- groups. CO_2 is just acidic enough ($\delta^+{}_C(CO_2) = 0.3$) to interact with the OH groups whereas COS is not ($\delta^+{}_C(COS) = 0.11$).

– *On basic oxygen ions*, different kinds of carbonate species can be formed, depending or not of the participation of neighboring metal ions to the adsorption (see Scheme 1).

Other species, ill-defined, like:



are such that the three oxygen atoms interact with the metal ions *M*. These polydentate species correspond to an incorporation of carbonate ions into the oxide, explaining their designation as bulk carbonates.



Scheme 1.

The free carbonate ion (D_{3h} symmetry) presents three IR active bands:

$\nu_3(E)$, asymmetric $\nu(CO)$ vibration: 1415 cm^{-1}.

$\nu_2(A_2')$, out of plane $\pi(CO_3)$ deformation: 879 cm^{-1}

$\nu_4(E)$, in plane $\delta(CO_3)$ deformation: 680 cm^{-1}

whereas the totally symmetric $\nu(CO)$ vibration, $\nu_1(A_1')$ at 1063 cm^{-1}, is only active in Raman. In the adsorbed state, the symmetry is lowered and the species formed generally present two $\nu(CO)$ bands either side of a wavenumber of 1415 cm^{-1}. Due to the loss of the D_{3h} symmetry, these two bands result from the splitting of the degenerate ν_3 vibration. It has been considered that the $\Delta\nu_3$ splitting characterizes the structure of the species formed: it is about 100, 300 and 400 cm^{-1} for unidentate, bidentate and bridged species, respectively [35]. However, there is some confusion in the literature about such a relation and it has been proposed, for instance, that some bridged carbonate species present a separation in the order of 50–150 cm^{-1} [36]. By comparing X-ray structural and IR spectral data, a strong correlation has been found for a large variety of carbonate complexes between the angular distortion (from D_{3h}) within the carbonate ligand, expressed as $\Delta\alpha$, difference between the largest and the smallest O–C–O angles, and the separation between the two highest energy C–O stretching modes $\Delta\nu_3$ [36]. It was shown that bidentate carbonate species generally have $\Delta\nu_3 > 250$ cm^{-1} and bridged carbonate species have $\Delta\nu_3 < 250$ cm^{-1}; the only unidentate carbonate structurally characterized has $\Delta\nu_3 = 80$ cm^{-1}.

Busca and Lorenzelli [35] reported that considerations about thermal stability have also to be taken into account to determine the structure of the carbonate species. For instance, an unidentate structure should be normally less stable on a surface than the corresponding bidentate structure. If species show a strong resistance to thermal decomposition and a rather low $\Delta\nu_3$ splitting, they can correspond to polydentate structure, not very different from that of bulk species.

Note that the loss of symmetry from D_{3h}, due to CO_2 adsorption, makes the ν_1 band (close to 1050 cm^{-1}) slightly active in infrared. Normal coordinate calculations [37] for unidentate and bidentate CO_3^{2-} ions showed that, in the C_{2v} symmetry, ν_{3h} (high component of the ν_3 vibration), ν_{3l} (low component of the ν_3 vibration) and ν_1 vibrations can be described separating the contribution of surface oxygens (O_s) to oxygen atoms not bound to the surface (O):

	ν_{3h}	ν_{3l}	ν_1
Unidentate	$\nu_a(OCO)$	$\nu_s(OCO)$	$\nu(CO_s)$
Unidentate	$\nu(C{=}O)$	$\nu_a(O_sCO_s)$	$\nu_s(O_sCO_s)$

From these considerations, we have assigned the different bands given by adsorption on ThO_2 [38], ZnO [39] and CeO_2 [11]. In addition to hydrogen carbonate species, essentially polydentate and bidentate species are formed whereas on some ZrO_2 preparations like yttria-stabilized tetragonal ZrO_2, Morterra et al. reported carbonate-like species with a $\Delta \nu_3$ splitting of 20 cm^{-1}, tentatively assigned to monodentate carbonate complexes [40]. On CeO_2 evacuated at 823 K, desorption of species by heating under vacuum at increasing temperature did not modify the wavenumbers of the remaining bands showing that the corresponding adsorption sites were thermally stable. By contrast, on H_2-reduced ceria some changes were observed during the desorption by increasing temperature. They were due to a surface reoxidation and explained by the thermal dismutation of complex carboxylate like species [11]. Therefore CO_2 is not an inert gas and it can reoxidize a surface partly reduced. This oxidizing effect has been confirmed using diffuse reflectance spectroscopy in the UV–Vis. region. Reducing CeO_2 by H_2 at temperature higher than 473 K led to the appearance of a band at 17 000 cm^{-1} [41] characterizing the Ce(III)–Ce(IV) interaction [42]. Its intensity notably increased by reduction at 573 and 673 K. Addition of oxygen at room temperature completely eliminated this band as a result of the Ce(III) reoxidation. In the same manner, it has been shown that CO_2 addition at room temperature also tended to decrease the intensity of the 17 000 cm^{-1} band demonstrating the oxidizing properties of CO_2.

The localization of the carbonate species formed either on the surface (under the form of unidentate, bidentate or bridge species) or in the bulk (polydentate species) is essential for the interpretation of results obtained by other methods like temperature programmed desorption [43] or microcalorimetry [44]: the heat evolved from the CO_2 interaction can result not only from its adsorption on basic surface sites but also from its reaction with the bulk. It has been shown for instance that atmospheric CO_2 not only converted lanthanum oxide into surface carbonates but also into bulk carbonates [45,46]. In agreement, the adsorption of CO_2 on La_2O_3 activated at 1023 K led to the appearance of two bands at 1490 and 1400 cm^{-1} due to the formation of polydentate carbonates. The same bands were observed on La_2O_3 activated at only 823 K [47].

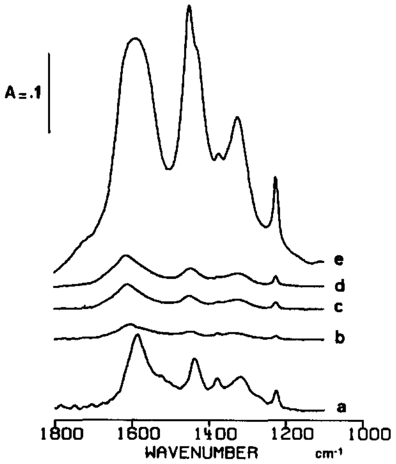


Fig. 1. IR spectra of CO_2 adsorbed on TiO_2–ZrO_2 (P_e = 10 Torr); (a) TiO_2; (b) 77% TiO_2 – 23% ZrO_2; (c) 45% TiO_2 – 55% ZrO_2; (d) 30% TiO_2 – 70% ZrO_2; (e) ZrO_2.

In spite of these disadvantages (possibility of reoxidation and formation of bulk carbonates), CO_2 can be used as probe for the determination of the relative basicity of different metal oxides. For example, we have used it to follow the variation of the basicity of series of mixed oxides TiO_2–ZrO_2 [48] or TiO_2–Al_2O_3 [33] according to their composition. For instance, Fig. 1 shows spectra of species formed in the same conditions on different TiO_2–ZrO_2 samples (all the spectra have been ratioed to the same surface area). It clearly appears that the mixed compounds are much less basic than pure TiO_2 and pure Al_2O_3.

1.2.2. Zeolites

CO_2 adsorption has also been widely studied on alkaline zeolites. A band generally appeared at ca. 2360 cm^{-1}, its intensity being pressure dependent. It was assigned to the asymmetric stretching vibration ν_3 and characterized cation–dipole interactions. The higher the polarization strength of the cation ($Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$) the more pronounced was the shift of its wavenumber towards higher frequencies. This kind of interaction induces a loosing of the CO_2 molecular symmetry, leading to the activation of the stretching ν_1 mode, explaining the appearance of a weak band near 1380 cm^{-1} [49]. CO_2 can also chemisorb on the zeolite oxygens to form carbonate species [49].

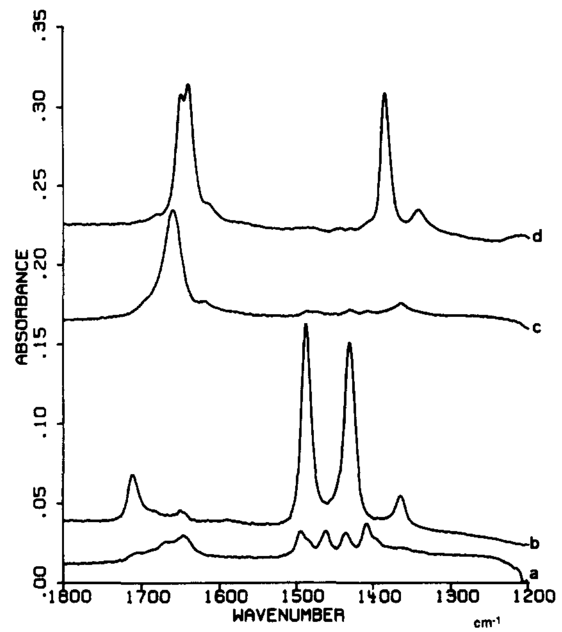
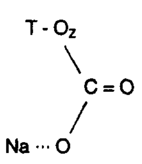
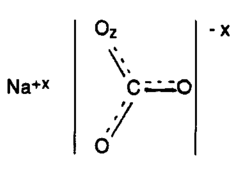


Fig. 2. IR spectra of chemisorbed species formed from CO_2 adsorption on X-type zeolites, (a) LiX; (b) NaX; (c) KX; (d) CsX (32% exchanged).

We have adsorbed CO_2 on a series of X-type zeolites and the bands observed after evacuation at room temperature are reported in Fig. 2. The case of NaX has been particularly studied by Jacobs et al. [50]. The pair of bands at 1711 and 1365 cm^{-1} has been assigned to species I, in which CO_2 would be bicoordinated to both a T atom and a residual cation. It can be converted to species II, characterized by bands at 1488 and 1431 cm^{-1}, which presents a true carbonate structure.



Species I



Species II

As noted by Jacobs et al. [50] this conversion of species I to II did not occur in the case of CsX samples since only a couple of bands at 1644 and 1385 cm^{-1} appeared. On LiX, no CO_2 adsorption into the form of carbonate species was observed.

The formation of carbonate species from CO_2 adsorption proves that alkaline zeolites possess O^{2-} basic sites. They are less abundant in Y than in the corresponding X samples. This could be attributed to the higher Si/Al ratio in the former, leading to a lower average negative charge sitting onto the lattice oxygen atoms. However the amount of carbonate species formed is always very low. Jacobs et al. [50] reported that after outgassing at room temperature, no more than 3 molecules of CO_2 per unit cell remain adsorbed in NaX zeolite, making difficult any correlation with a particular structural site.

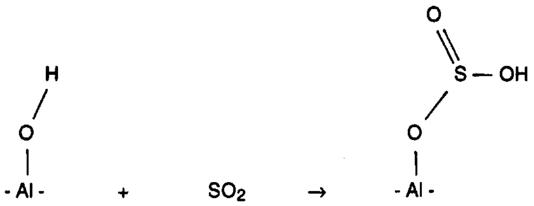
1.3. Sulfur dioxide

1.3.1. Metal oxides

Only a few IR studies have been devoted to SO_2 adsorption on metal oxides [51–53], Al_2O_3 excepted [54–59], since the latter oxide is used as a Claus catalyst.

The results are often contradictory; in particular the interaction of SO_2 with *hydroxyl groups* is still unclear. With acidic OH groups, such as the free silanol groups of silica, the shift of the SiOH band, from 3750 to 3660 cm^{-1}, indicated a weak perturbation by hydrogen bonding, SO_2 playing the role of a Lewis base [53]. On alumina, the nature of SO_2 interaction with surface OH groups is less certain. Chang invoked hydrogen bonding [54], while Karge et al. suggested that SO_2 was adsorbed on basic hydroxyl groups [60]. Gravimetric measurements performed in our laboratory showed that SO_2 was chemisorbed on fully hydroxylated alumina samples [56]. Preadsorption of CO_2 proved evidence that SO_2 interacted with free hydroxyl basic groups: SO_2 preadsorption on alumina prevented that of CO_2, in particular the formation of hydrogen carbonate species, showing there was indeed an interaction between SO_2 and surface OH groups.

Different kinds of species can be formed. On Na/Al_2O_3 activated at 623 K introduction of SO_2 gave rise to the appearance of a broad band in the 3600–3300 cm^{-1} range and to a continuum of absorption [59]. They can be considered as characteristic of ($OH^- \cdot \cdot \cdot SO_2$) interaction as a precursor to a hydrogen sulfite species. The formation of the latter species through the interaction of SO_2 with basic OH groups has been postulated [53,56]:



However, definite vibrational assignments on alumina are hampered by the paucity of data below 1000 cm^{-1}, a region where alumina is not transparent to the IR beam. Use of solids presenting a partial transparency to about 600 cm^{-1}, like sodium doped silica [61], or, even better, sodium doped silicon carbide (prepared by wet impregnation of SiC with NaOH and then calcined in air at 873 K [62]) gave valuable information on the nature of species formed. Chemisorbed SO_2 gave rise to bands at 657 and 560 cm^{-1} (Fig. 3) which were also present in the spectrum of $Na_2S_2O_5$ [63,64] and can therefore be attributed to disulfite species [62]; it could occur from the reaction:

$$O^{2-} + 2SO_2 \rightarrow S_2O_5^{2-}$$

Addition of water is expected to lead to hydrogen sulfite species:

$$S_2O_5^{2-} + H_2O \rightarrow 2H\,SO_3^- \ (\text{or } 2HOSO_2^-)$$

However the band at 635 cm^{-1} formed by water addition seemed too thermally stable to characterize hydrogen sulfite species, and was rather assigned to sulfite ion [65]. From the IR spectrum of $CsHSO_3$ [64], hydrogen sulfite species were expected to give a band near 623 cm^{-1}, not observed from SO_2 addition on the studied catalyst.

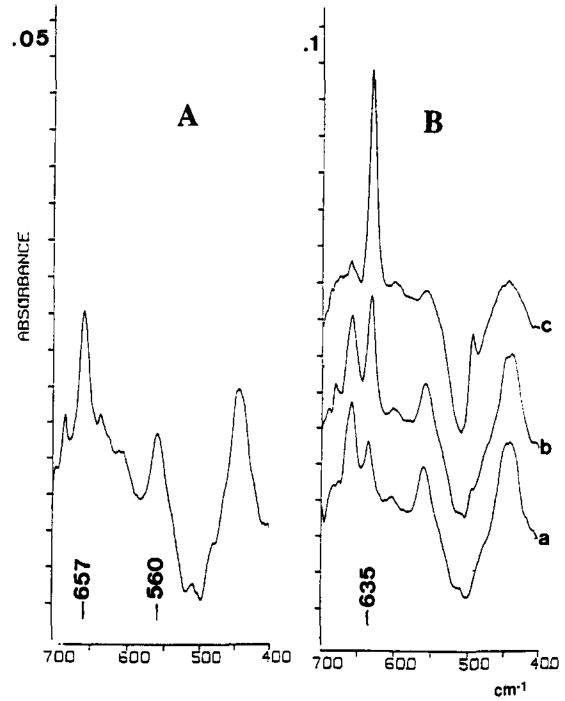


Fig. 3. IR spectra of species formed from, (A) SO_2 adsorption on Na-3%/SiC, (B) after H_2O addition, (a) 55 μmolg^{-1}; (b) 215 μmolg^{-1} (c) 430 μmolg^{-1}.

The structure of the hydrogen sulfite ions cannot be specified. It seems to be HSO_3^- from the observation of a Raman line due to a ν(SH) band in aqueous solution [63] but SO_2OH^- has also been suggested [64].

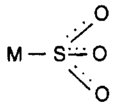
It therefore appears that the interaction between SO_2 and basic OH groups is much more difficult to study by IR spectroscopy than that between CO_2 and OH^-. UV spectroscopy could be a more appropriate technique since Karge et al. [60] showed that hydrogen sulfite and disulfite species on alumina gave absorption bands near 250 nm. However, results obtained by this technique in our laboratory seemed to indicate that this assignment was not unequivocal [66].

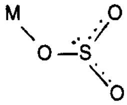
Considering now *aprotic basic sites*, Zotin and Faro [67] succeeded in using SO_2 as a probe molecule to compare the basicity of alumina catalysts doped with Na^+ or SO_4^{2-} ions. They observed that the presence of sodium significantly increased the capacity of alumina for irreversible adsorption of SO_2 at 373 K. In contrast, the presence of sulfate strongly inhibited the irreversible adsorption.

They found a linear correlation between the intrinsic activity of the alumina catalysts in the $H_2S + SO_2$ reaction and their basicity. Saad et al. [59] confirmed the results and showed that doping Al_2O_3 by Na^+ increased the number of sulfite species, SO_3^{2-}, characterized by an IR band near 1070 cm^{-1}.

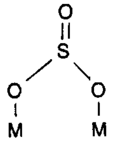
The nature of the species formed is difficult to access. Sulfite species, SO_3^{2-}, are expected to occur. The SO_3^{2-} ion has C_{3v} symmetry and is characterized by a non-degenerate vibration ν_1 at 960 cm^{-1} and a doubly degenerate mode at 1010 cm^{-1}. The latter is split into a doublet in sulfite complex of lower symmetry. Chang [54] considered that when sulfite species were bonded through the sulfur to a surface, the symmetry is preserved and the ν(SO) frequencies increased whereas a bond through the oxygens lowered the symmetry and the frequencies.

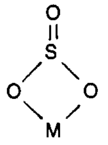
The sulfite ion is pyramidal and it can coordinate to a metal, according to Nakamoto [68], in a form of monodentate, bidentate or bridged. The following structures are probable for a monodentate coordination:



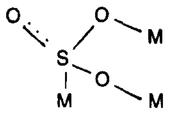


Bidentate sulfites can be chelated or bridged:





Tridentate species can also be considered:



Chang [54] observed for the first time the appearance of two bands at 1050 and 1326 cm^{-1} by introducing SO_2 on activated alumina. They correspond to two different species, called I and II respectively. Species I formed first. Evacuation at 373 K eliminated species II whereas species I partially resisted evacuation until 573 K. Its thermal stability was in favor of the formation of sulfite. The author suggested it was bonded through the sulfur. Some years later, Karge et al. [55] restudied the adsorption of SO_2 on alumina, looking in particular at the nature of the adsorption sites by pre-poisoning them with acid and base probes. They showed that pretreatment by acids (BF_3, HCl, acetic acid) blocked the formation of the 1060 cm^{-1} band, confirming it corresponds to a species formed by SO_2 adsorption on a basic site. Results from our laboratory [66] using ^{18}O exchanged alumina and $S^{18}O_2$ allowed us to exclude the formation of a C_{3v} symmetry Al–SO_3 species. On alumina, Datta et al. [57] distinguished among five types of species, one characterized by bands at 1065 and 1135 cm^{-1} was assigned to sulfite species. Their high vibration frequencies suggest that it is bonded to the surface of alumina via the sulfur atom. Its formation would need both acid and base sites.

Use of CeO_2, MgO and ZrO_2 metal oxides, showing a greater transparency below 1000 cm^{-1}, allowed us to observe a more complete spectrum in this range [69]. It was more complex than expected from alumina results. Different species were present, as shown by the variation of the relative intensity of the different bands between 1050 and 900 cm^{-1} with evacuation temperature. For instance, on ZrO_2, two pairs of bands at 1027 and 923 cm^{-1} and at 998 and 966 cm^{-1} were clearly observed, the former corresponding to a more stable species. On MgO, the bands persisting after evacuation at 573 K were sharp [70] and could characterize the formation of polydentate species since most of the bulk metal sulfites present a very strong IR band near 950–960 cm^{-1} and weaker ones near 1000 and 1210 cm^{-1} [71].

Gravimetric measurements after evacuation at different temperatures, showed that the amount of adsorbed SO_2 was higher on MgO, CeO_2, Na^+–Al_2O_3 and ZrO_2, than on alumina, itself higher than on TiO_2, anatase or rutile. This led to a classification of metal oxides according to the number

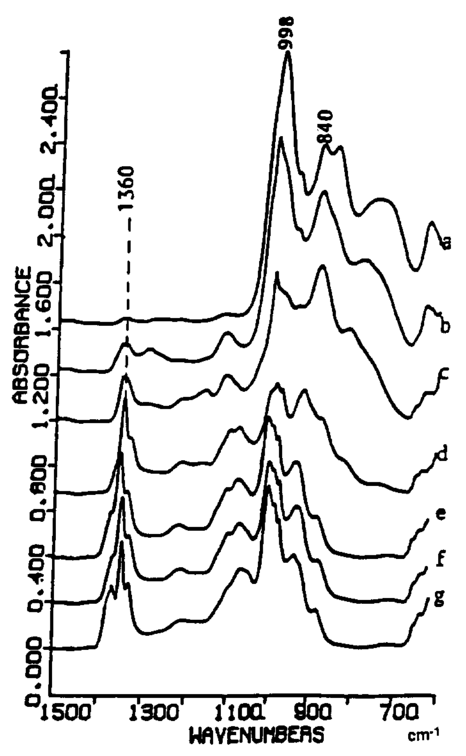
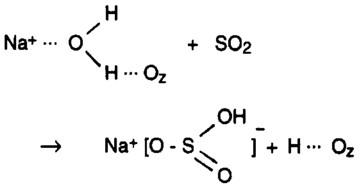


Fig. 4. IR spectra of species formed from SO_2 introduction on CeO_2, activated at 723 K, followed by evacuation at, (a) room temperature; (b) 373 K; (c) 473 K; (d) 573 K; (e) 673 K; (f) 773 K and (g) 873 K.

of sites [69]. However the very high stability of species formed on CeO_2 was found very surprising. The variation of IR spectra versus the evacuation temperature (Fig. 4) showed the appearance at 373 K of weak bands near 1360 cm^{-1}, their intensity increasing with the evacuation temperature. They were due to a partial transformation of sulfite into sulfate species [70], which occurred without oxygen, due to the oxidizing properties of CeO_2. The redox process has been confirmed by UV–Vis. spectroscopy [70]: heating CeO_2 under SO_2 without any oxygen led to the appearance at 473 K of a broad band at 17 000 cm^{-1}, characteristic of the Ce^{III}–Ce^{IV} interaction. The reduction of Ce^{4+} ions into Ce^{3+} explains the concomitant formation of sulfate species, observed by IR spectroscopy.

1.3.2. Zeolites

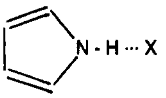
Karge and Ziolek studied SO_2 adsorption on sodium *X*- and *Y*-type zeolites by various spectroscopies including ultraviolet-visible, electron paramagnetic resonance and infrared spectroscopy ([72] and references therein) in order to determine the mechanism of the Claus reaction. They observed by IR spectroscopy a low frequency band (LBF) at 1240 cm^{-1}. The structure of the LBF species remained a matter of debate. Karge et al. first suggested a correlation with SO_2^- radicals observed by EPR. Later, from a combination of UV-vis and IR techniques, they proposed the formation of HSO_3^- species, characterized by a signal at 215 nm. The lack of the zeolite transparency to the IR beam below 1200 cm^{-1} prevents any further characterization of LBF species by IR spectroscopy. HSO_3^- would form via interaction either with basic hydroxyls or chemisorbed water [73]. They proposed the following scheme [74]:



The authors suggested that those LBD species were relevant intermediates in the Claus reaction.

1.4. Pyrrole

Pyrrole is a H-bond donating molecule and can then form H-bonded species:



The ν(NH) frequency shift, followed by IR spectroscopy, is related to the basicity of the *X* group, which can be eventually a surface O^{2-} or OH^- group. The ν(NH) band is situated at 3497 cm^{-1} in the spectrum of pyrrole in solution, at 3410 cm^{-1} for pyrrole in liquid state [75]. This low frequency is assigned to a hydrogen bond between the NH group and the ring of another pyrrole molecule (intermolecular bond).

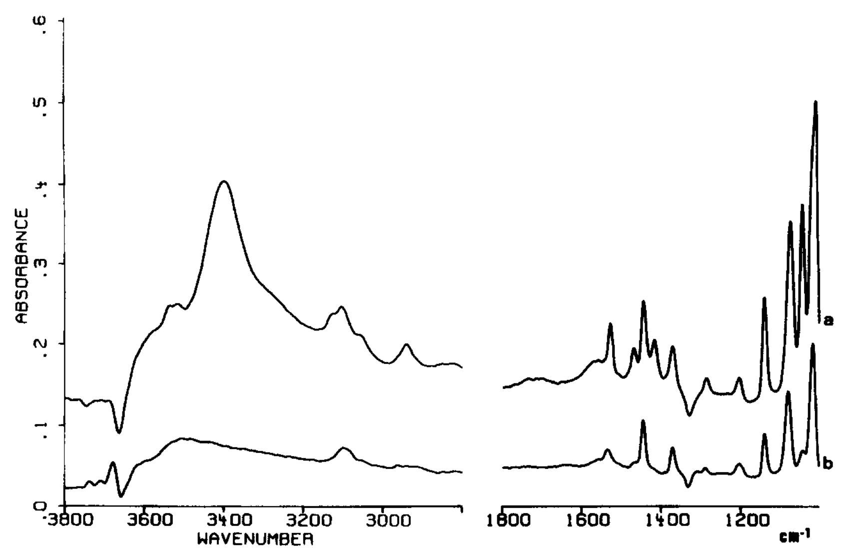
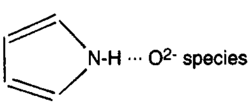


Fig. 5. IR spectra of species formed from pyrrole adsorption on ThO_2, (a) $P_e = 2$ Torr; (b) followed by evacuation at rt.

1.4.1. *Metal oxides*

Scokart and Rouxhet [75] studied the possibility of using pyrrole as a probe to detect basic sites on the surface of metal oxides and to estimate their strength. Adsorption of pyrrole on alumina gave rise to a broad band at 3260 cm^{-1}, whereas it was situated at 3360 and 3340 cm^{-1} on magnesia and thoria, respectively. This suggested that alumina was more basic than MgO and ThO_2, which is a surprising result. On the other hand, they found, as expected, that basic sites present on alumina were removed by fluoride treatment. As for SiO_2–Al_2O_3 samples, basic sites were clearly detected only at high alumina contents which was tentatively attributed to the presence of a demixed alumina phase.

Pyrrole adsorption on thoria has thoroughly been studied by Lamotte in our laboratory [12]. Addition of a large amount of pyrrole ($P_e = 1.85$ Torr) on activated thoria leads to the spectrum reported in Fig. 5a. It presents a sharp band at 3400 cm^{-1} characterizing species close to pyrrole in the liquid state. However, comparison with this spectrum (Table 1) shows the appearance of extra bands in the 1600–900 cm^{-1} frequency range, particularly at 1445, 1373 and 1207 cm^{-1}. These bands persist after evacuation at room temperature (Fig. 5b) contrarily to those due to pyrrole in the liquid phase. After such an evacuation a band at 3320 cm^{-1} is noted but it is quite weak. It can characterize:



It was concluded that species different from the latter were formed. Their spectrum was quite similar to that of potassium pyrrolate [76], showing that some pyrrole molecules dissociatively chemisorb on ThO_2, under the form of pyrrolate species. Addition of small amounts of pyrrole on activated thoria specified that it was the first molecules introduced on the activated oxide which dissociated.

The study has recently been extended to other metal oxides [77]. It was first found that introduction of a small amount of pyrrole on highly dehydroxylated ceria gave rise to $\nu(CH)$ bands at 3100 and 3060 cm^{-1} and to ring stretching vibrations (ν_R) at 1444 and 1367 cm^{-1}. Observation of a $\nu(OH)$ band at 3628 cm^{-1} on H_2-reduced ceria or at 3670 cm^{-1} on unreduced ceria confirmed the dissociative adsorption of pyrrole leading to hydroxyl species and the adsorbed $C_4H_4N^-$ pyrrolate anion. The spectrum obtained on highly dehydroxylated alumina was quite different: it presented a continuum extending from ca. 3650 cm^{-1} over a large frequency range. Such

Table 1
Wavenumber (in cm^{-1}) and assignment of IR bands due to pyrrole in liquid phase and potassium pyrrolate [74]

Pyrrole pure liquid	Attribution	Pyrrolate of K
3400 s	ν(NH)	
3139 m		3090 w
3114 m	ν(CH)	3074 m
3104 m		3051 m
1529 m		
1472 m	Cycle	1453 m
1416 m	vibrations	1442 m
1384 m		1361 m
1230 w	δ(CH)	
		1200 m
1142 m	δ(NH) cycle	1132 w
1075 m		1091 s
1047 s	δ(CH)	1036 m
1015 vs		1015 vs
		882 s
881 vw	cycle	
867 w		
840 vw	γ(CH)	
		813 m
738 vs	γ(CH)	736 vs
649	cycle	672 vs
560	γ(NH)	

vs: very strong; s: strong; m: medium; w: weak; vw: very weak.

a continuum was observed in the IR spectra of pyrrole/potassium methanolate liquid solutions and attributed to easily polarizable hydrogen bonds [78]. The following species has been deduced:

$$C_4H_4N^- \cdots H^+O^{2-}$$

with a hydrogen bond between the so-produced surface hydroxyl and pyrrolate ion species. The difference between ceria and alumina has been explained taking into account the difference of basicity of the two oxides: when O^{2-} is very basic, the hydrogen atom is localized on this sites (CeO_2) giving rise to a free ion pyrrolate and unperturbed OH species. When O^{2-} is less basic (Al_2O_3), an easily polarizable hydrogen bridge links pyrrolate species and the OH group formed. The complexity of the spectrum in the 3300–2000 cm^{-1} range has been explained involving a non-planar ring for the pyrrolate species, as shown by the appearance of a band at 2940 cm^{-1} assigned to a fundamental aliphatic ν(CH) vibration, and a series of bands at lower wavenumbers due to a vibrational coupling between the ν(CH) modes and a ring deformation mode at ca 220 cm^{-1} [77].

1.4.2. Zeolites

Barthomeuf [79] studied pyrrole adsorption on faujasite, *L* zeolites and mordenites with different alkali-metal cations. The $\Delta\nu$(NH) frequency shift was used to monitor the framework basicity and correlated well with the charge on oxide ions as calculated with the Sanderson electronegativity equalization principle. The wavenumber of the ν(NH) vibration mode was observed to decrease when the negative charge on oxide ion increased. The changes in basic properties with the Al/(Al + Si) content were also consistent with the calculated oxygen charge except for mordenite. Huang and Kaliaguine [80] confirmed that the basic strength of cationic zeolites increased in the order $Li < Na < K < Rb$. They specified that basic sites are framework oxygens adjacent to the cations.

In our laboratory, pyrrole adsorption has been investigated on a series of alkali-metal cation *X* zeolites (X = Na, Li, K, Cs 32% exchanged). Spectra after pyrrole evacuation at 373 K are shown in Fig. 6. It clearly appears that the wavenumber of the broad band near 3200 cm^{-1} decreases from Li (3284 cm^{-1}) to Na (3211), K (3187) and Cs (3182 cm^{-1}). In agreement with [80], many bands are noted below 3100 cm^{-1} (near 2945 strong, 2850, 2825, 2705 and 2600 cm^{-1}). They were described as combination bands [79,80] and taken as a distinct indication of the presence of strong basic sites. To our knowledge, no specific assignment of these bands has been proposed.

The observation of a ν(NH) perturbed band between 3300 and 3150 cm^{-1} is in favor of $C_4H_4NH \cdots O$ species [77]. This is confirmed by the wavenumber of ν_R bands near 1533 (B_1-15 mode) and 1425 cm^{-1} (B_1-14 mode) and that of a ν(CH) band at 3138 cm^{-1}, close to those observed in the spectrum of pyrrole in the liquid

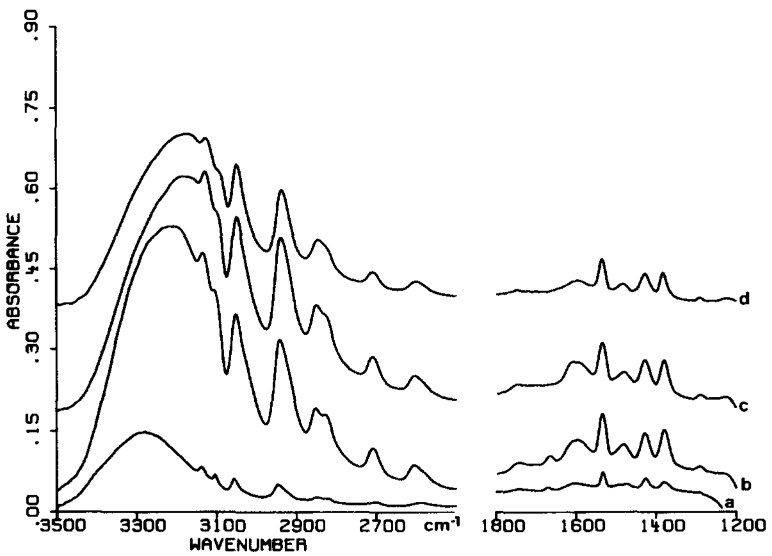
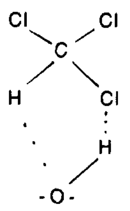


Fig. 6. IR spectra of species formed from pyrrole adsorption on *X*-type zeolites, after evacuation at 373 K on (a) Li*X*; (b) Na*X*; (c) K*X* and (d) Cs*X* (32% exchanged).

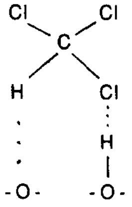
state (Table 1). The appearance of a series of bands in the 3000–2600 cm^{-1} frequency range resembles the features observed on alumina and characterizes $C_4H_4N^- \cdots {}^+HO$ species. It was concluded [77] that pyrrole was bound to basic O centers through a dissymetric hydrogen double well potential. For low basic sites (Li*X*) the deeper potential well is located near the pyrrole ring ($C_4H_4NH \cdots O$ species). When the strength of the basic sites increases, $C_4H_4N^- \cdots {}^+HO$ species becomes relatively more important (K*X* and Cs*X*).

1.5. Chloroform

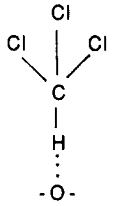
It is a weak acid and it has been used as an IR probe of basic surface sites of metal oxides. Paukshtis et al. studied $CHCl_3$ and $CDCl_3$ adsorption on various oxides [81]. Two types of adsorbed species were detected according or not surface OH groups were perturbed:



or



and



Results have been used to calibrate the strength of surface basic centers on the pKa scale. The strongest (+14) centers were observed on CaO, whereas on MgO and BeO, their strength is 9–10, on Al_2O_3 it is no more than +7. The study has been extended to alumina modified by various cations [82,83].

In 1983, Gordymova and Davidov [84] reported that CCl_4 decomposed in alkali media and deduced that chloroform must also undergo conversions. Therefore, its application as a test for basic surface centers would be rather problematic.

They indeed observed on γ-alumina, besides the $\nu(CH)$ ($CHCl_3$) or $\nu(CD)$ ($CDCl_3$) band at 3025 or 2255 cm^{-1}, extra bands at 1605, 1390 or 1595 and 1365 cm^{-1}, respectively. Their intensity increased with time at room temperature and they persisted under evacuation. They were assigned to formate species. The authors also observed an irreversible modification of surface hydroxyls by chlorine. It was concluded that the oxidizing destruction of chloroform on metal oxides restricted its use to identify basic centers. Such a decomposition has also been observed on TiO_2 anatase, at room temperature [85].

Later, Berteau et al. [83] used $CDCl_3$ as a probe to compare the basicity of modified aluminas. Studying exclusively the $\nu(CD)$ range, they reported that the spectra always presented a main band at 2253 cm^{-1}, assigned to $CDCl_3$ attached to weak basic centers. It was narrow when anions (SO_4^{2-}, PO_4^{3-}, Cl^-, F^-) were incorporated to alumina. It extended toward lower wavenumbers in the case of pure alumina. A second band at 2225 cm^{-1} was clearly evidenced in the case of Mg^{2+} and Na^+/Al_2O_3 samples, demonstrating the presence of stronger basic sites. From intensity measurements, it was deduced that cations increased the number of weak (2253 cm^{-1}) and strong (2225 cm^{-1}) basic centers. A very good agreement was observed between the measurement of total basicity from temperature programmed desorption of CO_2 and FT–IR spectroscopy of adsorbed deuterochloroform. The authors concluded that the latter technique was appropriate for basicity measurements.

In our laboratory, we have adsorbed $CDCl_3$ on various Na^+/Al_2O_3 samples [85]. No clear effect on the $\nu(CD)$ vibration was observed, the amount of Na^+ varying from 0 to 5000 ppm. On all the samples, weak bands due to formate species were formed. It appears that $CDCl_3$ does not seem to be a very sensitive probe. Results obtained on MgO pretreated at different temperatures or doped with Li, Na and Pb confirmed that $CDCl_3$ was a rough probe suitable for testing only an average state of the surface basic centers, but unable to subtle differentiate their basic strength [86].

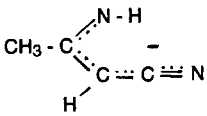
1.6. Acetonitrile

Acetonitrile has been used as a spectroscopic probe to characterize the acidity and basicity of divided metal oxides. Thanks to the nitrogen electron doublet, it can be used as a base or electron donor. The $\nu(C{\equiv}N)$ wavenumber increases when electron donor–acceptor complexes $CH_3CN\cdots A$ are formed, A being a Lewis [87–90] or a Brønsted acid site [91,92]. With strong Brønsted acids, protonation occurs [91] giving rise to a high $\Delta\nu(C{\equiv}N)$ shift (~ 75 cm^{-1}), however still less important than that observed (~ 110 cm^{-1}) when CH_3CN is complexed with carbocations [93].

Hydrogen atoms of CH groups in α of the C≡N bond, as those of the methyl group of acetonitrile, present a proton donor character, in such a way that the formation of the CH_2CN^- carbanion can be observed from the rupture of a C–H bond. When the cation is Na^+ or Li^+, the $\nu(C{\equiv}N)$ of the carbanion has been reported near 2050 cm^{-1} [94]. On a metal oxide, the following reaction occurs:

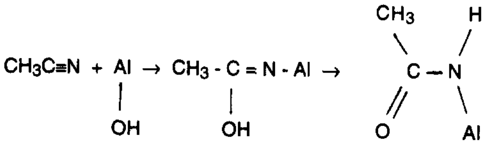
$$O^{2-}(surf) + CH_3CN \rightarrow OH^-(surf) + CH_2CN^-(ads)$$

The reaction involves the acid-base character of the OH/O^{2-} and CH_3CN/CH_2CN^- couples; moreover, it requires the participation of a cationic adsorption sites to stabilize the CH_2CN^- carbanion. The $\nu(C{\equiv}N)$ wavenumber of the carbanion characterizes the cationic site; as an example, on ZnO [95] it is at 2121 cm^{-1}, on MgO, at 2190 cm^{-1} [96]; on ceria [97] it depends on the state of the adsorption site: 2098 (Ce^{4+}) or 2028 cm^{-1} (Ce^{3+}). CH_2CN^- can be solvated by a CH_3CN molecule. The $CH_2CN^-(CH_3CN)$ complex would be the intermediate of the dimerization reaction leading to the following anion:

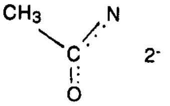


Its characteristic wavenumbers are $\nu(\mathrm{NH}) = 3260\ \mathrm{cm}^{-1}$, $\nu(\mathrm{C{\equiv}N}) = 2110\ \mathrm{cm}^{-1}$ [98]. The formation of these anionic species CH_2CN^- and polyanions can be easily confirmed by comparing results obtained by adsorption of $(CH_3)_3C\text{–}C{\equiv}N$, a compound that cannot lead to a dissociative adsorption; in accordance, by contrast to CH_3CN, $(CH_3)_3C\text{–}C{\equiv}N$ adsorption on ZnO [95] and on CeO_2 [97] does not give rise to any band in the 2000–2200 cm^{-1} frequency range.

Another type of species can result from the acetonitrile interaction with hydroxyls: it is of the acetamide type. Knözinger et al. [99] considered it would result from a nucleophilic attack of a coordinated molecule by a surface OH^- group:

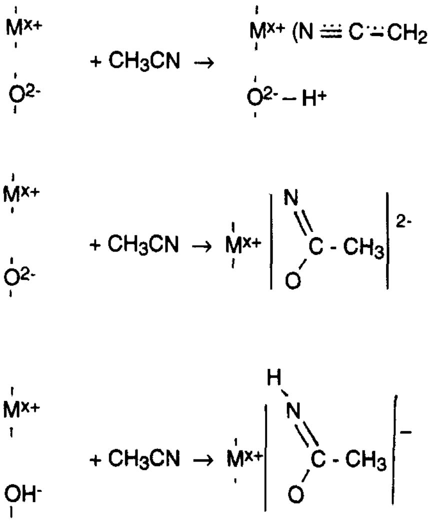


Such a species is characterized by strong bands in the 1700–700 cm^{-1} frequency range and its formation has also been reported on oxides like SnO_2 [100], α-Fe_2O_3 [101], ThO_2 [12], silica-magnesia mixed oxides [102], ZnO [95] and ZrO_2 [103]. Binet et al. [97] studied in detail CH_3CN adsorption on CeO_2. Using deuterated compounds, they concluded that it was rather the dianion of acetamide:



which was formed rather than the monoanion. Its formation is due to the reactivity of surface O^{2-} sites. Due to the complexity of the spectra of acetamide species formed, it is difficult to distinguish the formation of acetamide dianion to that of acetamide monoanion. Only comparison of results obtained from acetonitrile adsorption on the metal oxide and on the same oxide preexchanged by D_2O allows one to make conclusions.

Therefore, on basic sites, adsorption of CH_3CN leads either to the amide or the CH_2CN^- species, following the reactions:



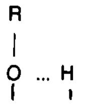
The formation of the $(CH_2CN)^-$ anion evidences the strong basicity of O^{2-} sites. The mechanism of acetamide dianion formation is not clear yet. It can involve O^{2-} basic sites or it may result from the activity of basic hydroxyls leading intermediately to acetamide monoanion $(CH_3CONH)^-$ followed by the rupture of the NH band due to the presence of strong basic sites.

1.7. Alcohols

1.7.1. Metal oxides

We have studied the adsorption of alcohols with different acidities: $(CF_3)_3COH$ (pKa = 5.4), $(CF_3)_2CHOH$ (pKa = 9.3), CF_3CH_2OH (pKa = 12.3) and CH_3OH (pKa = 15.1) on a δ-Al_2O_3 sample activated at 723 K [104]. The amount of species adsorbed increased with the basicity of the alcohol.

Two types of irreversibly adsorbed species (species which are not removed by a relatively short evacuation at room temperature) can be formed: alkoxy species I, resulting from dissociative chemisorption on a very weak Lewis acid site placed near a very strong basic one, and undissociated species II, coordinated on strong Lewis site [105]: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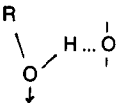

II

A detailed analysis of the IR spectra allowed us to discriminate between the two types of species:

(i) in the 3000–2800 cm^{-1} range, for primary and secondary alcohols, dissociative adsorption generally shifted the $\nu(CH)$ wavenumbers to lower values whereas coordinative adsorption increased the $\nu(CH)$ frequencies [105,106].

(ii) in RCH_2OH and R_2CHOH spectra, the $\delta(OH)$ mode is coupled with the CH_2 and CH bending modes [107,108]. If the alcohols are dissociatively adsorbed, these couplings are suppressed and the spectra of adsorbed species might be similar to those given by the corresponding ROD alcohols.

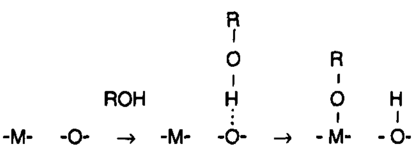
We found that the irreversible adsorption of halogeno-alcohols was dissociative whatever the metal oxide (Al_2O_3 [109], TiO_2 [110] and others [111,112]). In contrast, methanol chemisorption can be at least partly associative, for instance, on Al_2O_3 [113] and TiO_2 [114].

Poisoning experiments with bases such as $(CH_3)_2O$ or $(CH_3)_3CC{\equiv}N$ allowed us to conclude that the number of acidic sites not involved in the irreversible adsorption of alcohols on δ-Al_2O_3 increased with the alcohol acidity [104]:

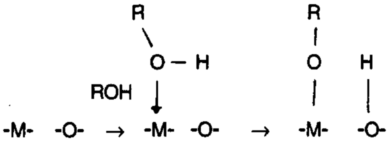
$$(CF_3)_3COH > (CF_3)_2CHOH > CF_3CH_2OH$$
$$> CH_3OH,\ (CH_3)_2CHOH$$

Note that similar co-adsorption experiments using carboxylic acids, such as formic acid, and bases, showed a less specific adsorption on these acids [115] in agreement with De Cheveigne et al. [116].

Acidic alcohol adsorption therefore mainly involves cation-anion couples having a predominant basic character. The following mechanism of dissociation occurs on such sites:



Adsorption of less acidic alcohols like methanol is much less specific since it could also occur on couples having a predominant Lewis acid character:



From these results, we developed a method of characterization of the surface basicity of oxides using adsorption of hexafluoroisopropanol as a probe [111,112]. Gravimetry, volumetric analysis, microcalorimetry and Fourier transform infrared spectroscopy have jointly been used. Unicomponent oxides and mixed oxides have been studied: SiO_2, Al_2O_3, TiO_2 (anatase), Fe_2O_3, MgO, ThO_2, ZnO, $MgAl_2O_4$, $ZnAl_2O_4$, $Zn_{1.5}Al_2O_{4.5}$.

IR spectroscopy first showed that $(CF_3)_2CHOH$ chemisorption was completely dissociative up to near the saturation coverage. In agreement, new surface hydroxyl groups were formed. A particular case was relative to silica: the first species formed, which corresponded to the more strongly adsorbed one, was due to a reaction with surface hydroxyl groups leading to an ether-like species [111] from the following reaction, involving OH groups:

$$\equiv Si-OH + ROH \rightarrow \equiv SiOR + H_2O$$

The irreversibly adsorbed amount at room temperature was generally close to 2.8–3 $\mu mol\,m^{-2}$, the case of SiO_2 (1.3 $\mu mol\,m^{-2}$) excepted.

The adsorption isotherms generally presented a similar shape, typical of a predominant strong irreversible adsorption followed by a narrow range of pressure-dependent adsorption [111]. The calorimetric adsorption isotherms were also similar in shape, except for silica. These features confirmed that the adsorption mechanisms of $(CF_3)_2CHOH$ can be assumed to be the same, whatever the oxide (SiO_2 excepted), allowing us to take the released heat as a measure of the relative strength of the basicity of ionic oxides. Even if small amounts of ether-like species were formed, the heat released must be very low, as on silica, and therefore negligeable.

The differential adsorption heats of $(CF_3)_2CHOH$, reported as a function of the amount adsorbed, were composed of three regions. At the very beginning, a sharp decrease of q_{diff} was observed, due to the adsorption on a few very strong sites, possibly arising from surface defects. In the intermediate region, a plateau or a slight decrease in q_{diff} values was observed, corresponding to the heats released during adsorption on the predominant surface sites. At the end, a further sharp decrease was observed, corresponding to the saturation of the chemisorption sites and to the formation of small amounts of physisorbed or liquid-like species.

From the comparison of the q_{diff} values measured in the intermediate region, it was possible to compare the basic strength of the main exposed sites of different oxides.

The oxides can be classified into three groups:

(i) the strongly basic oxides, whose basicity decreases according to the following order:

$$ThO_2 > ZnO > MgO > Fe_2O_3 \sim TiO_2$$

(ii) the less basic ones, such as alumina. It has been shown that the strength and distribution of surface basic sites on the two stoichiometric spinels $MgAl_2O_4$ and $ZnAl_2O_4$ closely reproduce those of alumina,

(iii) the non-stoichiometric aluminate having an excess of Zn^{2+} ions. This excess induces an increased basicity, still lower than that of ZnO.

Unfortunately due to the particular apparatus used [111], no reliable information on the basicity of the very strong sites has been obtained. This is a limitation of the work, because it is possible that the few sites of very high basicity are those predominantly active in catalysis, although they would also be the first to be poisoned and to become inactive.

1.7.2. *Zeolites*

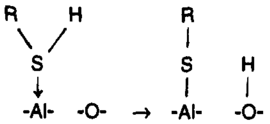
A lot of studies have been devoted to methanol adsorption and transformation over H-zeolites [117] since this transformation is the basis of several industrially important reactions, such as the MTG (methanol-to-gasoline) and the MTO (methanol-to-olefins) processes. On alkali cation exchanged zeolites, methanol interaction seems quite weak [118]. On Na-ZSM-5 and K-ZSM-5 Mirth et al. [119] reported that methanol is coordinatively adsorbed on the cation and formed weakly hydrogen-bonded clusters at high equilibrium pressures. A comparative study of methanol adsorption showed that similar results were obtained on sodium *X* and *Y* zeolites [120]. In particular, spectra did not present any free hydroxyl band before heating which would characterize a dissociative adsorption. It is very difficult to experimentally discern coordinatively adsorbed species to that resulting from hydrogen bonding or Van der Waals interactions. Quantum chemical calculations have shown that the molecules in the free zeolite volumes interacted mainly with oxygen anions from the pore walls [121]. These oxygen anions are easily polarizable and can be considered as soft bases.

1.8. *Thiols*

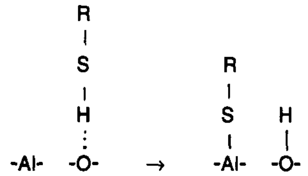
1.8.1. *Metal oxides*

The chemisorption of H_2S and CH_3SH has principally been studied on alumina [122]. Dissociative chemisorption occurs. Poisoning experiments with pyridine showed that thiolate species are formed via two different mechanisms, similar to those reported for alkoxy species from alcohol adsorption [105]. The first step is the adsorption:

- either on a strong Lewis acid site where coordination first occurs; then the S–H bond is broken and the thiolate species is formed:



- or on a strong basic-weak acidic pair site, with the formation of a hydrogen bonded species, followed by the SH dissociation:



On TiO_2 [123] coordinated species have been evidenced.

On Al_2O_3, the origin of two extra bands at 1570 and 1340 cm^{-1} is still unclear. Slager and Amberg [124] assigned them to a Al=O surface mode and to the $\delta(H_2S)$ vibration, respectively. Okamoto et al. [125], and Lavalley et al. [126] showed that they resulted from H_2S and CO_2 coadsorption, CO_2 being either present as traces (impurity) in H_2S [127,128] or as a contaminant on the alumina itself [129]. Okamoto et al. [125] considered the 1570/1340 cm^{-1} bands as being due to unidentate carbonate species, taking into account possible H_2S inductive effects. We preferred to assign them to thiocarbonate or hydrogen thiocarbonate species which allowed us to explain the changes of IR spectra observed when co-adsorbing CH_3SH and CO_2 instead of H_2S and CO_2 [126]. This interaction between CO_2 and H_2S requires therefore the use of very pure H_2S to study its adsorption.

Okamoto et al. [125] reported a systematic investigation of H_2S adsorption on Al_2O_3, modified Al_2O_3 and MoO_3/Al_2O_3. Using temperature-programmed desorption techniques (TPD), coupled with IR and XPS spectroscopies, they found that H_2S chemisorbed on Al_2O_3 in two different modes, associative and dissociative. The latter occurred on coordinatively unsaturated Al^{3+}_{tetr}- strong base pair sites. On a series of Na^+/Al_2O_3 catalysts, they observed, as the sodium amount increased up to 20×10^{13} Na^+ cm^{-2}, an increase of the adsorbed amount of H_2S and a concomitant decrease of the desorption temperature of the dissociated species. Such a decrease is rather surprising since the alumina basicity is expected to increase with the Na^+ amount [130]. We indeed confirmed the TPD results [62] but showed by gravimetric measurements that the amount of H_2S irreversibly chemisorbed at 473 K increased with the Na^+ loading. This apparent discrepancy between the two techniques has been explained considering that a part of the H_2S irreversibly adsorbed did not desorb on Na^+/Al_2O_3 samples: indeed a large amount of residual sulfur was detected after evacuating (desorbing) the Na^+ samples at 573 K [62]. It therefore appears that the TPD of H_2S is not appropriate to study the relative basicity of different oxides. However, this does not mean that H_2S or CH_3SH is not a probe of basicity: anions such as F^- and SO_4^{2-} are known to decrease the basicity of alumina and in accordance, they partially prevent H_2S chemisorption [125].

1.8.2. Zeolites

H_2S adsorption on faujasite type zeolites, such as Na*X* and Na*Y*, depends on their Si/Al ratio [131,132]. On Na*X*, the appearance of a $\nu(OH)$ band was noted at 3650 cm^{-1}. Its absorbance continuously decreased with increasing Si/Al ratio and became zero for Si/Al = 2.5. Concomitantly, a $\nu(SH)$ band was noted at 2560 cm^{-1}. This indicates a dissociative adsorption of H_2S:

$$H_2S + Na^+ \rightarrow H^+ + Na^+(SH)^-$$

Protons, which were generated via dissociation, attacked the zeolite lattice and formed new OH groups. On Na*Y* with a Si/Al ratio of ca. 2.5 or higher, no H_2S dissociation occurred. Karge et al. [132] suggested that Na^+ cations on so-called III sites at the walls of the supercages were involved in this dissociative chemisorption. It was reported that the first H_2S molecules dissociated to S^{2-} and 2 H^+ on strong centers. Subsequent increment of H_2S underwent dissociation to HS^- on weaker centers, whereas an excess of H_2S was adsorbed without dissociation [132]. In our laboratory, we compared CH_3SH adsorption on sodium *X* and *Y* zeolites [120]. Only Na*X* was found to be able to provoke the dissociative adsorption of CH_3SH at room temperature. In addition to the appearance of a new ν(OH) band at 3640 cm^{-1}, the adsorption of the first portion of CH_3SH gave rise to ν(CH) bands at 2950, 2921 and 2857 cm^{-1} very different from those due to physisorbed CH_3SH (3005, 2936, 2845 cm^{-1}). Their low wavenumber is in favor of the formation of $CH_3S^- Na^+$ species.

Ferino et al. [133] reported from temperature-programmed desorption experiments of H_2S from alkali-metal zeolites that the H_2S adsorption mode was governed by the acid-base character of the zeolite. A progressive increase of the zeolite basicity, caused by a high aluminum content (Na*X*) and the presence of increasing amounts of Cs^+ or Rb^+ ions led to the growing establishment of dissociative adsorption.

1.9. Boric acid trimethyl ether

Recently Li et al. [134] showed that $B(OCH_3)_3$ can be used as a novel probe molecule to detect surface Lewis base sites and study their basic strength. $B(OCH_3)_3$ is a typical Lewis acid and a planar molecule. Strong interaction with surface oxygen anions would convert its planar structure into a pyramidal one, leading to the splitting of the degenerate vibration involving the B–O band at 1360 cm^{-1} and the shift towards higher wavenumbers of the ν(C–O) band at 1036 cm^{-1}. From IR results, it was concluded that the Lewis base strength should decrease in the following order:

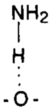
$MgO, CaO > ZrO_2, TiO_2 > SnO_2, Sb_2O_5$

In our opinion, $B(OCH_3)_3$ adsorption is certainly specific to base sites; However the shifts and the splitting of bands due to its coordination to O^{2-} sites do not seem very sensitive to the strength of base sites. Further results are expected before drawing any definite conclusion.

1.10. Ammonia

NH_3 is very often used as a probe to determine the number and nature of acidic surface sites. Different techniques have been used such as, (i) infrared spectroscopy, that well differentiates NH_3 adsorption on Lewis and Brønsted acid sites [135], (ii) microcalorimetry, which allows a simultaneous determination of the strength and energy distribution of the acidic sites [44], (iii) temperature-programmed desorption, which gives information on the strength of the sites [136].

Tsyganenko et al. [135] proposed different types of species for NH_3 adsorption:



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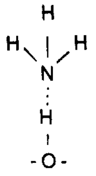

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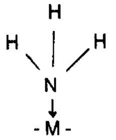
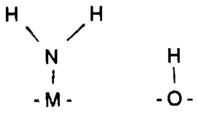


III



IV

The formation of species I (hydrogen bonding to a surface oxygen or the oxygen of a surface hydroxyl groups) and species IV (dissociation to give a NH_2^- and hydroxyl species) involves a basic site or an acid-base site, respectively. Species I were observed on CoO, NiO, CaO and MgO, whereas species IV were noted on CaO, MgO, Al_2O_3 and highly dehydroxylated SiO_2 [135]. They were characterized by a $\delta(NH_2)$ frequency in the region near 1550 cm^{-1}. Observation of NH_2^- species on CaO, SrO, and MgO [137,138] and later on ZnO [139,140] can be due to the presence of strong basic sites. However on Al_2O_3 another interpretation has been proposed [141]: ammonia disproportionation would occur on pairs of acid-base sites on the surface. Therefore it is important to determine the mechanism of NH_2^- species formation before concluding that their formation directly characterizes surface O^{2-} base sites.

1.11. Pyridine

Pyridine (py) is widely used as a probe molecule to determine the surface acidity of metal oxides. It could form coordinated species, py*L*, on Lewis acid sites and pyridinium ions, pyH^+, on protonic sites. The infrared spectra of py*L* and pyH^+ species are clearly distinct, so that the corresponding surface sites can quite easily be distinguished [142]. Physically adsorbed species and H-bonded species can also be formed. Morterra and Cerrato [143] reported that the results depended on the py coverage, the activation temperature of the oxide and the spectral resolution.

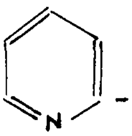
Tizuka and Tanabe [144] showed that, when py was introduced on MgO, CaO and SrO evacuated at high temperature, the color of the oxide surfaces turned to purple instantly while broad unsymmetrical ESR signals were observed. They suggested the formation of bipyridyl anion radicals. Zecchina and Stone studied by UV-vis. diffuse reflectance spectroscopy pyridine adsorption on alkaline earth oxides [145]. They concluded to a dissociative chemisorption of py on O^{2-} ion in low coordination (LC) and LC M^{2+} cation pairs on the surface of the oxide:

$$C_5H_5\underline{N} + \underline{M}^{2+}O^{2-} \rightarrow C_5H_4\underline{N}^{-}\underline{M}^{2+}OH^{-}$$

Coupling of the $C_5H_4\underline{N}^-$ anions then formed bipyridyl anions and other carbanionic derivatives. The ease of formation of the anions increased on passing from MgO to CaO and SrO, in agreement with the increasing basicity of the oxides.

Pyridine dissociative adsorption has been evidenced by Bovet on ZnO [140]. Besides bands at 1605 and 1450 cm^{-1} characterizing pyridine adsorption on Lewis acid sites, a band at 1546 cm^{-1} was well apparent. New OH groups were also noted at 3610 and 3590 cm^{-1}. The latter undoubtly arose from the cleavage of py C–H bonds, since they were observed when introducing C_5H_5N on ZnO previously exchanged by D_2O, whereas a $\nu(OD)$ band at 2650 cm^{-1} was noted when adsorbing C_5D_5N on an unexchanged ZnO sample. Use of different monodeuterated py molecules further evidenced that the cleavage occurred mainly in the ortho position.

The formation of

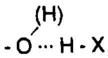


species was therefore postulated [140]. It would explain the occurrence of the 1546 cm^{-1} band. On acidic samples, such a band is considered as characteristic of the formation of pyH^+ species.

These results show that py adsorption is not specific to acidic sites. Dissociative adsorption can occur on basic sites. The purple color, noted on MgO, is not characteristic of this process since the color of the ZnO disk was unchanged after py adsorption. Only a careful assignment of the IR spectra can discriminate between the different adsorption processes which may occur.

2. Conclusion

The basicity strength of a solid surface can be defined as its ability to donate electronic charge to the adsorbed molecule. The best probe molecule would be, for infrared spectroscopy measurements, a H-donating HX molecule able to link to surface base centers like $-O^{2-}-$ or OH^- sites according to a hydrogen bond interaction:



$$\overset{(H)}{-O}\cdots H-X$$

From the ν(H–X) shift, a scale of surface basicity could be drawn.

The molecular probe must interact only with the surface sites to be tested and must not lead to side-reactions which may change the surface properties. Pyrrole and chloroform ($CHCl_3$, $CDCl_3$) are the H-donating probes most often used. As reported in the present review, chloroform does not appear to be a sensitive probe [86]. Moreover it partially decomposes giving rise to formate species, and modifies the surface properties, surface hydroxyls being replaced by chlorine [84]. Pyrrole adsorption on zeolites leads to interesting results [79,80] although spectra are more complicated than generally considered. By contrast, pyrrole adsorption on metal oxides can be dissociative, with formation of pyrrolate species more or less bonded to the resulting hydroxyl group then formed [77]. Spectra are then complex and not easily assignable.

Adsorption of other molecules like alcohols and thiols on basic surfaces is generally dissociative making unsuitable the method based on the hydrogen bond formation. However, good results have been obtained using an acidic alcohol as probe $(CF_3)_2CHOH$ [110,111]. In such a case, infrared spectroscopy is only informative on the nature of species formed. Alkoxy species are evidenced showing that active sites are acid-base pairs. The IR technique has to be coupled with others like gravimetric or volumetric measurements, to determine the amount of species formed, but also microcalorimetry to measure the differential heats of adsorption in order to access to the relative surface basicity. Hexafluoro-2 propanol high acidity makes its adsorption specific to acid-base pair sites of weak acidity but high basicity. Its use has led to reliable results in the case of metal oxides with high surface areas [110,111]. Use of carboxylic acids and phenol is, in our opinion, less convenient since they possess more pronounced basic properties than $(CF_3)_2CHOH$, making their adsorption less specific toward surface acid-base pair sites of high basicity and weak acidity.

Another type of probe usually used for studying the basic centers of the surface of metal oxides and zeolites is carbon dioxide. Analysis of the IR spectra so obtained is very informative about the nature of surface sites involved. In particular hydrogen carbonate species formation is characteristic of the presence of basic hydroxyls, generally of type I. On mixed oxides, it has been found that the intensity of the δ(OH) vibration, near 1225 cm^{-1}, of the hydrogen carbonate species formed from CO_2 adsorption well correlates COS activity, a test-reaction specific to OH basicity [33]. Extension to single metal oxides (ZrO_2, Al_2O_3, TiO_2, ZnO) shows the interest of the method [34]. In particular it appears that ZnO, generally considered as a basic oxide, does not present highly basic hydroxyl groups on its surface.

CO_2 adsorption on O^{2-} base sites leads to the formation of carbonate species. Unidentate species are expected but generally the adsorption occurs on pair sites $\underline{M}^{n+}O^{2-}$, leading to other types of carbonate species like bidentate. It is difficult from IR results alone to draw any conclusion about the relative basicity of different oxides. However, information can be drawn from a series of oxides with low basicity. Fig. 1 well illustrates that point and clearly shows that, despite their higher surface area, mixed oxides such as TiO_2–ZrO_2 present a very weak basicity, much lower than that expected from their composition [33]. On stronger basic oxides, a confusion between unidentate and polydentate carbonate species can arise, since these species present similar wavenumbers. It is then very important to well characterize the species formed since only unidentate ones are specific to surface properties. Infrared spectroscopy alone is not able to determine from CO_2 adsorption the surface basicity of strong basic divided oxides. The heat of CO_2 adsorption is generally considered [44]. However, as discussed by Davidov et al. [86] this approach may be inadequate: the basic properties of surface oxygens are mainly governed by the CO_2–O^{2-} interaction. If bidentate species are formed, and this is generally the case, the heat of CO_2 adsorption will also depend on the energy of CO_2 interaction with M^{n+} cations, which is generally unknown. Low temperature CO_2 adsorption on metal oxides [146] indeed suggests that CO_2 first interacts with cationic sites under the form of a bent side-on adsorbed species, intermediate in the formation of surface carbonate and hydrogencarbonate species [146]. If formation of polydentate carbonate species occurs, this is worse since the heat evolved may correspond to the enthalpy of formation of bulk carbonate. For instance, on CaO, $\Delta H_f = -178$ kJmol^{-1} at 298 K [147], a value very close to that reported by Auroux et al. when adsorbing CO_2 on CaO [44].

Although spectra obtained from CO_2 adsorption on basic surfaces are complex, their assignment is much more simple than those resulting from SO_2 adsorption on the same oxides. Even SO_2 interaction with basic hydroxyls is not well understood yet. As for the structure of sulfite species found on dehydroxylated oxides, it remains unspecified. SO_2 being more acidic than CO_2, its adsorption is less specific [69]. Formation of bulk-like (or polydentate) sulfite species is very likely on basic oxides: it has been reported that the adsorption heat of SO_2 on MgO and Al_2O_3 does not differ significantly from the heat of formation of sulfite phases [148]. Note that CO_2 and SO_2 may not be chemically inert molecules since the former can reoxidize a surface partly reduced whereas the latter can act as a reducing agent.

It is known that the surface of metal oxides presents structural defects like edges and steps where oxygen ions have a lower coordination number. CO adsorption at low temperature seems specific to such sites on highly dehydroxylated basic oxides. The first species formed is carbonite, CO_2^{2-}. Its formation indicates that O^{2-}-sites of low coordination are more basic than surface oxygen ions [23]. Adsorption of probes with pKa higher than 30 on a MgO sample outgassed at 1073 K showed the presence of a very small amount of sites able to dissociate molecules like ammonia, ethylene and benzene. This requires sites of greatest coordinative unsaturation like $Mg^{2+}_{3c}O^{2-}_{3c}$ situated at kinks or corners [149]. Chang and Kokes [150] also reported that toluene dissociated on ZnO. They concluded that the effective 'basicity' of ZnO is comparable to that of the allylic carbanion, but weaker than that of the vinyl carbanion. Use of probes with a so high pKa is therefore very useful to detect such defect sites and seems to have not been very often used yet.

Acetonitrile adsorption on basic metal oxides is complex since it can lead to $(CH_2CN)^-$ anion or acetamide species.

Finally, it appears that probes like pyridine or ammonia, very often used for the determination of the acidity of solids, also adsorb on sites with a high basic character. It is therefore very important, using these two probes to carefully assign the spectra of the species formed before concluding to the acidity or basicity of the analyzed sample.

Acknowledgements

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