

CHAPTER III

THEORY

3.1 Acids and bases in Homogeneous phases

3.1.1 Definitions and methodology problems

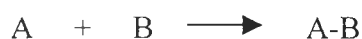
Two acid-base theories are widely utilized today : the Brönsted theory and the Lewis theory. Following the first theory, an acid-base reaction is simply the transfer of a proton from an acid (A₁H) to the base(B)



Acid Acid

Acid strength may be defined as the tendency in giving up a proton and base strength as the tendency to accept a proton : these definitions have only qualitative character. However, by measuring the position of the equilibrium (pK_a) in water solution or in gas phase, the relative strength of acid 2 can be determined quantitatively so conferring to the concepts of acid and base strength a real physical meaning. In this manner it is possible to construct a table in which acids are listed in order of acid strength. The pK_a of the various acids is usually reported with effects are absent, the acidity order can be greatly different.

Following the Lewis theory an acid is any species with a vacant orbital and an acid-base reaction



is a reaction where the unshared pair of the base B forms a (covalent) bond with the vacant orbital of the acid A. In the Brønsted picture the proton itself is the acid since it has a vacant orbital. The Lewis acid-base theory is more general than the Brønsted theory, because it correlates the behaviour of many more processes. The Lewis acid strength concept has been also quantified: however fewer quantitative measurements of acid strength are available compared to that of the Brønsted acids. A simple table of Lewis acidity (for instance corresponding to the pK_a relative to water) is, however, not feasible because Lewis acidity depends upon the nature of base. Another type of common acid-base reaction which can be described in the framework of the Lewis theory is



because covalent bonds are formed through one species contributing a filled and another vacant orbital.

3.1.2 The effect of structure on the strength of acids and bases

After having briefly discussed how the acidity and basicity can be quantified, it is worth to recall main factors affecting the acid and basic strength of molecules.

If we compare the Lewis acid strength of molecules of the form MX_n (M is cation and X is anion), the following empirical rules can be extracted:

1. All other things being equal, the acidity of MX_n decreases with the increase of the M radius (because the attraction between the positive nucleus M and the incoming electron pair is decreasing).

2. All other things remaining equal, the acidity increases with the increase of electronegative character of X.

3. The maximum acidity is found for the compounds where n is minimum.

If we limit ourselves to the Lewis basic strength of oxygen bases OM_2 , the following can be kept in mind:

1. The basicity of O increases with the increase of the electron donating character of M.

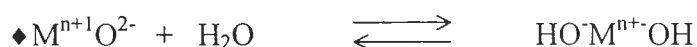
2. When M is a metallic element, the basicity of O increases with the increase of the electropositive character of M (and with the ionic radius as well).

3.1.3 Acid and base at the surface of metal oxides

Oxide catalysts are solid compounds of oxygen and one or more metal or semimetal elements. “True” metal oxides are composed by a metal and oxygen and are consequently characterized by an almost ionic bond. When pure, they are most commonly crystalline materials. The ideal surface of a metal oxide crystal is composed by crystal faces (exposed crystal planes), held together by corner and edges. The coordination of ions at the “ideal” surface is necessarily incomplete with respect to the coordination in bulk. Even more incomplete is the coordination of atoms at corners or edges. Surface reconstruction certainly occurs in order to decrease the energy of the atoms exposed at the surface, but coordinative unsaturation will in part remain. The surface ions can also react with species from the environment, again to

decrease the free energy. However, partly uncoordinated metal cations and oxide anions lie at the surface of metal oxide crystals, even in these conditions. These ions can act as acids and bases, respectively, according to the Lewis definition. So that, Lewis acid sites (coordinatively unsaturated cations) and basic sites (oxide anions) are expected, and actually found, at the surface of ionic metal oxides.

The reversible interaction of water (always present in the environment) with such surfaces is in part dissociative, as shown below:



Where \blacklozenge indicates a coordinative unsaturation responsible for Lewis acidity, so that coordinatively unsaturated cations and anions can in part convert into surface hydroxy-groups. These groups are potentially Brönsted acidic, although they mostly behave as basic $-OH$ groups, because the bond with which they are held to the metal cations is ionic (figure 3.1)

The oxides of semimetals, like silicon, boron, germanium, phosphorus, arsenic, and so on, are also solid active or useful in catalysis. In this case the bond is essentially covalent. These materials can also be crystalline but not unfrequently amorphous. The surface of these materials can be modeled on the basis of the structure of a crystal plane like the surface that is generated when a particle is ideally cut along a plane to form two smaller particles. This would generate again coordinatively unsaturated element and oxygen atoms (or ions). However, the reactivity of these element atoms is so strong that they cannot stay as such in “normal” conditions. The elements of water saturate almost irreversibly the coordinative unsaturations, so that in this case Lewis acidity completely disappears and surface hydroxy-groups are formed, potentially responsible for Brönsted acidity.

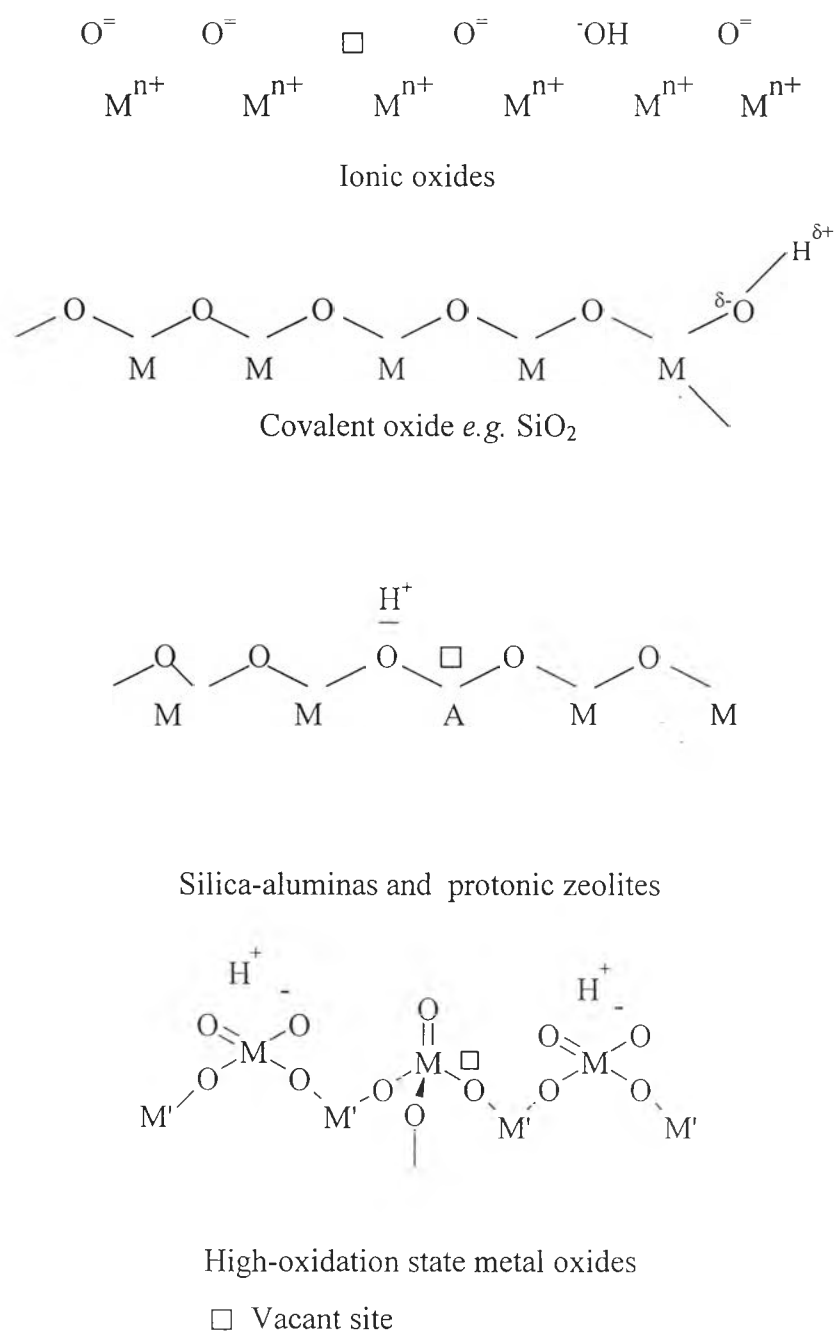


Figure 3.1 Structure of metal oxides

In some cases, by “doping” covalent oxides with elements with lower valency (like Al in amorphous silica or crystalline silicate, giving rise to silica-alumina or ZSM-5 zeolite, respectively) a defect of charge is created, and this causes the formation of strong Brønsted acidity to balance it.

The oxides of metals in a high-oxidation state are also characterized by high covalency of the M-O bond, according to the high Sanderson's electronegativity of their ions. Accordingly, they show weak or no basicity. However, the cations tend to associate with some oxide ions giving rise to metal-oxygen "double-bonds" (vanadyl-, wolframyl-, molybdenyl-cations, etc.) whose coordination is very elastic. In spite of the covalency of metal-oxygen bonds, strong Lewis acidity can appear. The OH's are covalently bonded to the metal and the anion charge resulting from dissociation can be delocalized on terminal "doubly bonded" oxygen. Thus, medium to strong Brønsted acidity appears.

3.2 The basicity measurement of surfaces [Kaßner and Baerns 1996]

3.2.1 Method for characterizing acid-base properties by probe reactions

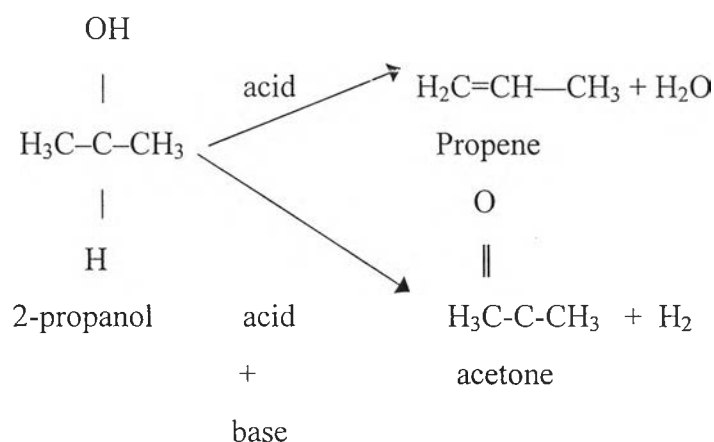
3.2.1.1 Decomposition of 2-Propanol

From the decomposition of 2-propanol to acetone and propene measures of basicity and acidity were derived. The reaction pathways are illustrated in figure 3.2a. Since 2-propanol needs an acid-base pair to be converted to acetone, the acetone-to-propene ratio reflects the basicity, whereas the propene formation rate is solely due to the acidity.

3.2.1.2 Retroaldolization of diacetone alcohol

The retroaldolization of diacetone alcohol (DAA) is mentioned to be solely catalyzed by basic sites. Therefore, this probe reaction was chosen for determining surface basicity independently of acidity. The catalytic activity for the formation of acetone (figure 3.2b) can be used as a direct measure of basicity.

a)



b)

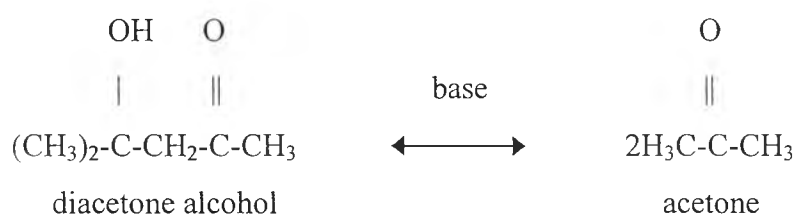


Figure 3.2a) Probe molecule reaction by decomposition of 2-Propanol

b) Probe molecule reaction by retroaldolization of Diacetone alcohol

3.2.1.3 CO₂-TPD/ benzoic acid titration

Quantitative information on the number of basic surface sites and the base strength distribution were obtained by the temperature programmed desorption of CO₂ and the benzoic titration using a series of Hammett indicators in the range $8.2 \leq H_- \leq 26.5$. The base strength H_- is defined in Eq. 3.1. BH represents a neutral acid adsorbed at the catalyst surface and B⁻ is the conjugated base.

$$H_- = pK_{BH} + \log[B^-] / [BH] \quad (3.1)$$

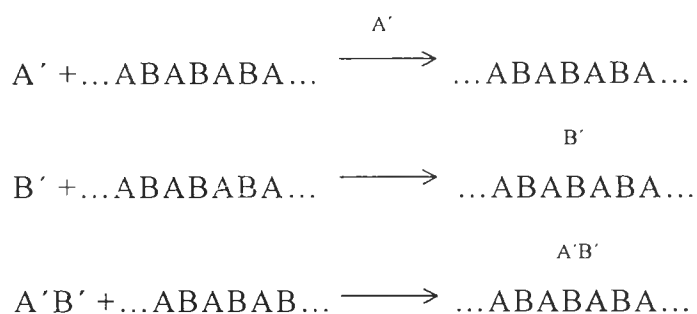
3.2.1.4 Spectroscopic detection of the surface basicity

FTIR spectroscopic experiments were performed in order to reveal the types of adsorption structure of CO₂. A measure of base strength was obtained from the reciprocal value of the difference of the asymmetrical and the symmetrical stretching vibration of the unidentate carbonate which was formed due to CO₂ adsorption.

In some experiments, acidic probe molecules such as CO₂, SO₂ or hexafluoroisopropanol have been used to characterize the surface basicity of some solids.

3.2.1.5 The method of the adsorbed probes molecules

The quantitative concepts of acid-base strength outlined in acid and bases in homogeneous phase are based on the measurement of the equilibrium conditions in acid-base reactions where the reactants are individual molecules immersed in a homogeneous medium. This method requires the measurement of the equilibrium concentration (diluted solutions) or activities (concentrated solutions) of the reactants. It cannot be readily extended to surfaces for two obvious reasons: (i) because of the presence of two phases, (ii) because the acid and basic species constituting the surface array (but the same holds for the AB building units) cannot be treated as separated species. In other words, it is not possible to carry out surface reactions of the Lewis acid-base type.



Involving only single surface sites (A, B, AB) by using probe molecules with predominant basic (B'), acid (A') or dual character (A'B'), respectively, without significantly perturbing all the others (it is worth noticing that this limitation is less important for isolated acid groups embedded in a matrix). In fact any adsorption (coordinative) event at a given site is invariably accompanied not only by the formation of new bonds but also by a modification of the surface relaxation around the adsorption site. In other words the adsorption process modifies the structure of the surface. The extent of this very complex effect (usually named lateral interaction and dying away in a few lattice spacing) depends upon the energy involved in the adsorption event.

While the first obstacle cannot be removed, the second can be partially surmounted if the probing process fulfills the following conditions:

1. The probe molecule must be chosen among those showing minimal interaction energy with the surface (and consequently the smallest perturbative effect of the surface structure).

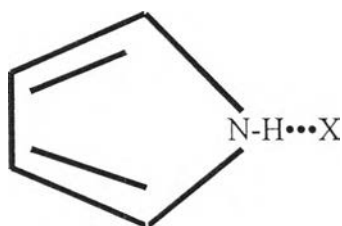
2. The probing process must involve only a minimum fraction of the surface sites ($\theta \rightarrow 0$, θ being the surface coverage: $0 \leq \theta \leq 1$) in order to keep the lateral interactions at the minimum level.

Conditions (1) and (2) must be fulfilled as much as possible if the probing process is intended to give indications on the state of the surface in vacuo, *i.e.* before the perturbation induced by the probing process.

3.2.2 Probe molecules for basicity measurement [Lavalley (1996)]

1) Pyrrole

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



The $\nu(\text{NH})$ 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 $\nu(\text{NH})$ band is situated at 3497 cm^{-1} in the spectrum of pyrrole in solution, at 3410 cm^{-1} for pyrrole in liquid state [Scokart *et al.* (1980)]. This low frequency is assigned to a hydrogen bond between the NH group and the ring of another pyrrole molecule (intermolecular bond).

- Metal Oxides

Scokart *et al.* (1980) 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} . Furthermore, they found that basic sites present on alumina were removed by fluoride treatment. As for $\text{SiO}_2\text{-Al}_2\text{O}_3$ samples, basic sites were clearly detected only at high alumina contents, which was tentatively attributed to the presence of a demixed alumina phase.

IR spectra of pyrrole adsorption on thoria is shown in figure 3.3 . Addition of a large amount of pyrrole on activated thoria leads to the spectrum report in figure 3.3.

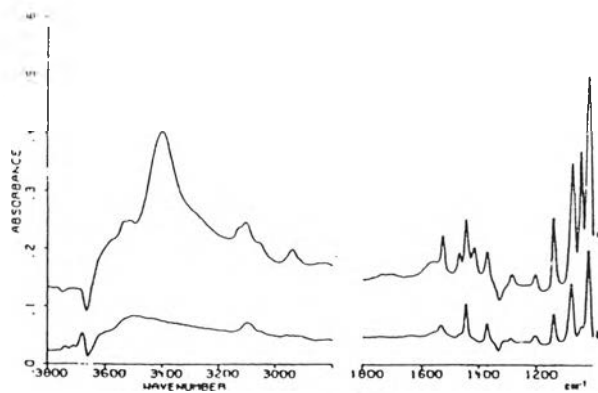
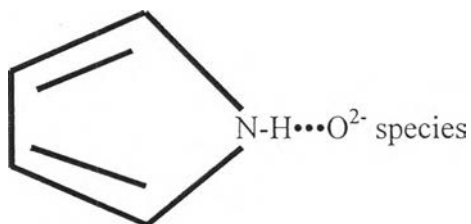


Figure 3.3 IR spectra of pyrrole adsorption on thoria

It presents a sharp band at 3400 cm^{-1} characterizing species close to pyrrole in the liquid state. However, comparison with this spectrum (Table 3.1) shows the appearance of extra bands in the $1600 - 900\text{ cm}^{-1}$ frequency range, particularly at 1445 , 1373 and 1207 cm^{-1} . These bands persist after evacuation at room temperature (figure 3.3b) 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 adsorbed specie of pyrrole as shown below:



It was concluded that species different from the latter were formed. Their spectrum was quite similar to that of potassium pyrrolate, 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 been extended to other metal oxides. It was first found that introduction of a small amount of pyrrole on highly dehydroxylated ceria gave rise to $\nu(\text{CH})$ bands at 3100 and 3060 cm^{-1} and to ring stretching vibrations (ν_{R}) at 1444 and 1367 cm^{-1} . Observation of a $\nu(\text{OH})$ 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 $\text{C}_4\text{H}_4\text{N}^-$ pyrrolate anion. The spectrum obtained on highly dehydroxylated alumina was quite different: it presented a continuum extending from 3650 cm^{-1} over a large frequency range. Such a continuum was observed in the IR spectra of pyrrole/potassium methanolate liquid solutions and attributed to easily polarizable hydrogen bonds. The following species has been deduced:



with a hydrogen bond between the 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 $\nu(\text{CH})$ vibration, and a series of bands at lower wavenumbers due to a vibrational coupling between the $\nu(\text{CH})$ modes and a ring deformation mode at 220 cm^{-1} .

Table 3.1 Wavenumber (cm^{-1}) and assignment of IR bands due to pyrrole in liquid phase and potassium pyrrolate

Pyrrole pure liquid	Attribution	Pyrrolate of K
3400s	$\nu(\text{NH})$	
3139m		3090w
3114m	$\nu(\text{CH})$	3074m
3104m		3051m
1529m		
1472m		1453m
1416m	vibration	1442m
1384m		1361m
1230w	$\delta(\text{CH})$	
		1200m
1142m	$\delta(\text{NH})$	1132w
1075m		1091s
1047s	$\delta(\text{CH})$	1036m
1015vs		1015vs

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

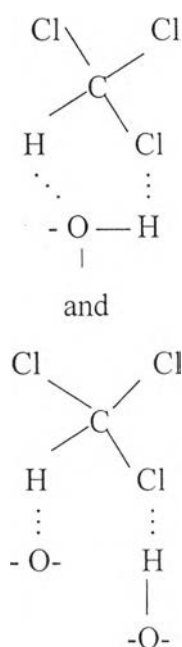
- Zeolites

Pyrrole adsorption on faujasite, L zeolites and mordenites with different alkali-metal cations were detected. The $\Delta\nu(\text{NH})$ frequency shift was used to monitor the framework basicity of these samples and correlated well with the charge on oxide ions as calculated with the sanderson electronegativity equalization principle. The wavenumber of the $\nu(\text{NH})$ 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 (1992) confirmed that the basic strength of cationic zeolites increased in the order of $\text{Li} < \text{Na} < \text{K} < \text{Rb}$. They specified that basic sites are framework oxygens adjacent to the cations.

2) Chloroform

Chloroform is a weak acid and it has been used as IR probe of basic surface sites of metal oxides. CHCl_3 and CDCl_3 adsorption on various oxides is studied. It is found that two types of adsorbed species were detected according or not surface OH groups were perturbed:



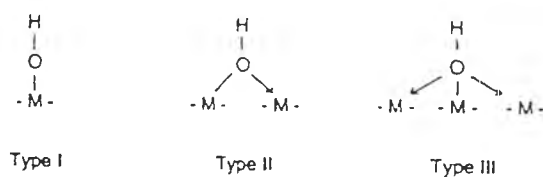
Furthermore, CCl_4 can be decomposed in alkali media and deduced that chloroform must also undergo conversions. Therefore, its application as a test for basic surface centers would be rather problematic. They indeed observed on γ -alumina, besides the $\nu(\text{CH})(\text{CHCl}_3)$ or $\nu(\text{CD})(\text{CDCl}_3)$ 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. These

bands 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 decomposition has also been observed on TiO₂ anatase, at room temperature.

3) Carbon dioxide

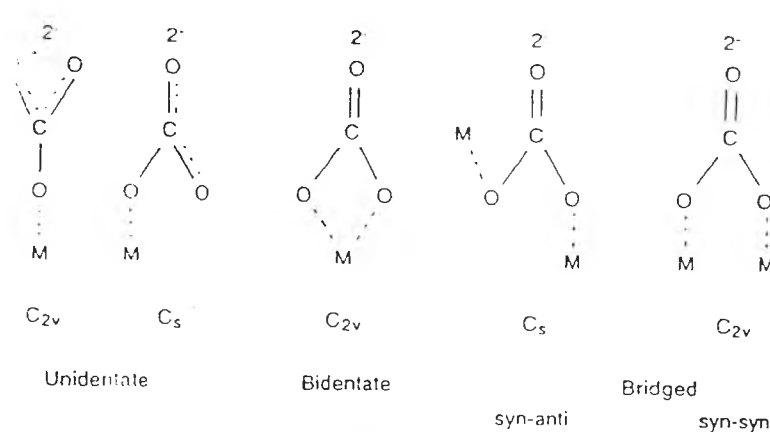
- Metal Oxide

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

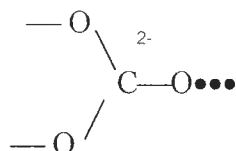


On basic hydroxyl groups, there is formation of hydrogen carbonate species HO-CO₂⁻. It is generally considered that, among the different types of OH groups persisting after activation of the metal oxides, type I OH groups, e.g., OH groups coordinated to only one coordinatively unsaturated cation, are mainly involved in the formation of hydrogen carbonate species.

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 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.

- Zeolites

CO₂ adsorption has also been widely studied on alkaline zeolites. A band generally appeared at 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 induces a loosening of the CO₂ molecular symmetry, leading to the activation of the stretching ν_1 mode, explaining the appearance of a weak band near 1380 cm⁻¹. CO₂ can also chemisorb on the zeolite oxygens to form carbonate species.