

CHAPTER III

THEORY

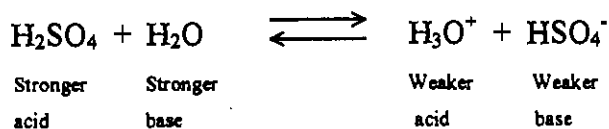
Several chemical reactions used heterogeneous catalysts, particularly, metal oxide catalysts. It has long been known that the surface of metal oxide catalysts contains hydroxyl group and O^{2-} anion, the greater activity has been attributed to the acid site and basic site. To well understand the nature of acidity and basicity on surface of catalysts, one needs some background of acid-base properties. In this chapter, some acid-base properties are briefly described which will help in understanding the nature and measurement of acid-base on surface of catalyst.

3.1 Fundamentals of acid-base properties [Morrison and Boyd 1992, Gates 1992, Zecchina *et al.* 1998, and Busca 1998]

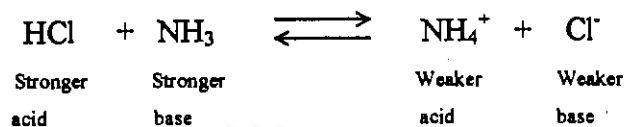
The terms of acid and base have been defined in a number of ways, each definition corresponding to a particular way of looking at the properties of acidity and basicity. It is useful to look at acids and bases from two of these viewpoints.

3.1.1 The Lowry-Brönsted definition

An acid is a substance that gives up a proton. A base is a substance that accepts a proton. When sulfuric acid dissolves in water, the acid H_2SO_4 gives up a proton (hydrogen nucleus) to the base H_2O to form the new acid H_3O^+ and the new base HSO_4^- .



When hydrogen chloride reacts with ammonia, the acid HCl gives up a proton to the base NH₃ to form the new acid NH₄⁺ and the new Cl⁻.

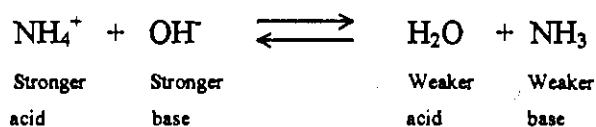


According to the Lewis-Brønsted definition, the strength of an acid depends upon its tendency to give up a proton, and the strength of a base depends upon its tendency to accept a proton. Sulfuric acid and hydrogen chloride are strong acids since they tend to give up a proton very readily; conversely, bisulfate ion, HSO₄⁻, and chloride ion must necessarily be weak bases since they have little tendency to hold on to protons. In each of the reactions just described, the equilibrium favors the formation of the weaker acid and the weaker base.

If aqueous H₂SO₄ is mixed with aqueous NaOH, the acid H₃O⁺ (hydronium ion) gives up a proton to the base OH⁻ to form the new acid H₂O and the new base H₂O.



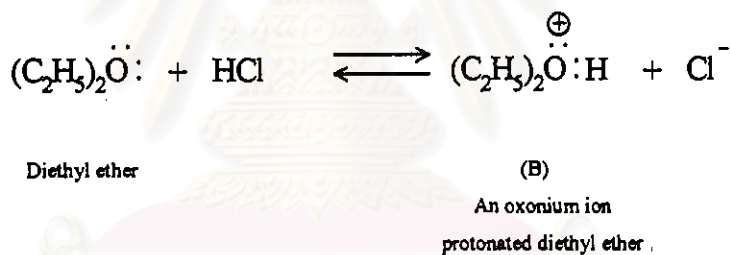
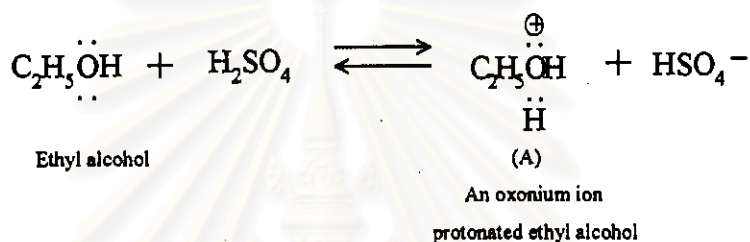
When aqueous NH₄Cl is mixed with aqueous NaOH, the acid NH₄⁺ (ammonium ion) gives up a proton to the base OH⁻ to form the new acid H₂O and the new base NH₃. In each case the strong base, hydroxide ion, has accepted a proton to form the weak acid H₂O. If these acids in the order shown are arranged. It must necessarily arrange the corresponding (conjugate) bases in the opposite order.



Acid strength $\text{H}_2\text{SO}_4, \text{HCl} > \text{H}_3\text{O}^+ > \text{NH}_4^+ > \text{H}_2\text{O}$

Base strength $\text{HSO}_4^-, \text{Cl}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{OH}^-$

Like water, many organic compounds that contain oxygen can act as bases and accept protons; ethyl alcohol and diethyl ether, for example, form the oxonium ions A and B. For convenience, it shall often refer to a structure like A as a protonated alcohol and a structure like B as a protonated ether.

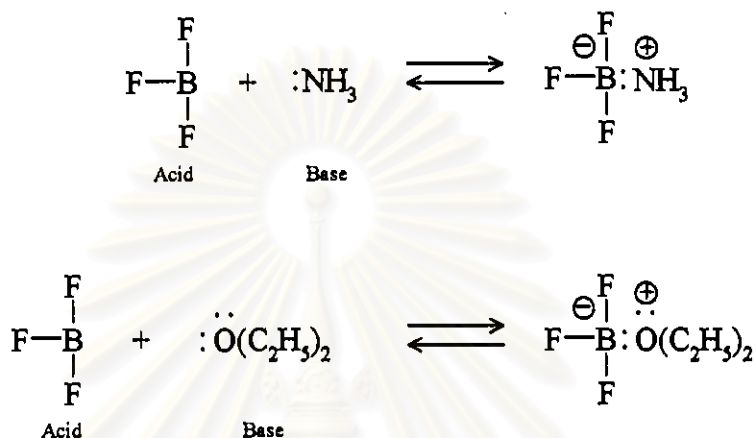


3.1.2 The Lewis definition

Unlike the previous definition, the acid-base definition of Lewis does not require a proton transfer to classify a substance to be acid or base. According to this definition, an acid is a substance that can take up an electron pair to form a covalent bond. A base is a substance that can furnish an electron pair to form a covalent bond. Thus an acid is an electron-pair acceptor and a base is an electron-pair donor. This is the most fundamental of the acid-base concepts, and the most general; it includes all the other concepts.

A proton is an acid because it is deficient in electrons, and needs an electron pair to complete its valence shell. Hydroxide ion, ammonia, and water are bases

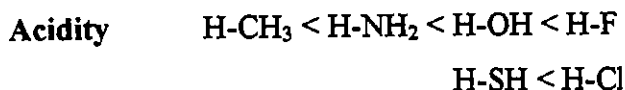
because they contain electron pairs available for sharing. In boron trifluoride, BF_3 , an electron pair in to complete its octet. Boron trifluoride is an acid and combines with such bases as ammonia or diethyl ether.



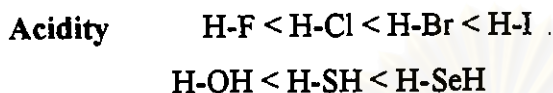
Boron in these formulas are written as a formal negative charge because it has one more electron—half-interest in the pair shared with nitrogen or oxygen—than is balanced by the nuclear charge; correspondingly, nitrogen or oxygen is shown with a formal positive charge.

Aluminum chloride, AlCl_3 , is an acid, and for the same reason. In stannic chloride, SnCl_4 , tin has a complete octet, but can accept additional pairs of electrons (*e.g.* in SnCl_6^{2-}) and hence it is an acid, too.

To be acidic in the Lowry-Brønsted sense, a molecule must, of course, contain hydrogen. The degree of acidity is determined largely by the kind of atom that holds the hydrogen and, in particular, by that atom's ability to accommodate the electron pair left behind by the departing hydrogen ion. This ability to accommodate the electron pair seems to depend upon several factors, including (a) the atom's electronegativity, and (b) its size. Thus, within a given row of the Periodic Table, acidity increases as electronegativity increases:



And within a given family, acidity increases as the size increases:



Among organic compounds, they can expect appreciable Lowry-Brønsted acidity from those containing O-H, N-H, and S-H groups.

To be acidic in the Lewis sense, a molecule must be electron-deficient; in particular, we would look for an atom bearing only a sextet of electrons.

To be basic in either the Lowry-Brønsted or the Lewis sense, a molecule must have an electron pair available for sharing. The availability of these unshared electrons is determined largely by the hold them: its electronegativity, its size, and its charge. The operation of these factors here is necessarily opposite to what we observed for acidity; the better an atom accommodates the electron pair, the less available is for sharing.

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3.1.3 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 spend the minimum number of words in recalling the main factors affecting the acid and basic strength of molecules.

If we compare the Lewis acid strength of molecules of the form MX_n 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 the 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 increase with the increase of the electron donating character of M.
2. When M is a metallic element, the basicity at O increases with the increase of the electropositive character of M (and with the ionic radius as well).

As far as the acid strength of the Brønsted acid HA is concerned, it is widely accepted that:

1. The acid strength increases with the increase of the electron withdrawing character of A.
2. The acid strength increases with the increase of stability of A⁻ (favored by hydrogen bonding interactions with the solvent or with other acid molecules).
3. The acid strength increases with the ability of A⁻ (conjugated base) to spread the negative charge over the whole moiety. Big size anions (A⁻) containing electronegative atoms or anions (A⁻) stabilized by resonance, can spread and delocalized efficiently the negative charge: hence they have very small basic character and consequently their conjugated acids, HA are very strong.

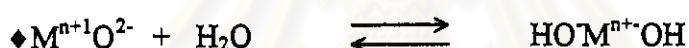
Point (1) is well illustrated by the greater acid strength of FSO₃H and CF₃SO₃H with respect to H₂SO₄; Point (2) is documented by the FSO₃H-SbF₅ superacid, where the acidity of FSO₃H is exalted by the interaction with the strong SbF₅ Lewis acid which stabilize the FSO₃⁻ anion through the formation of the FSO₃⁻-SbF₅ adduct. Point (3) is illustrated by the greater acidity of H(SbF₆) (HF.SbF₅) with respect to HF, because the size of the SbF₆⁻ anion is larger than that of F⁻. Effect (2) and (3) cannot always be distinguished.

3.1.4 Acid and base at 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 the 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 Brønsted 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 solids 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 Brønsted acidity.

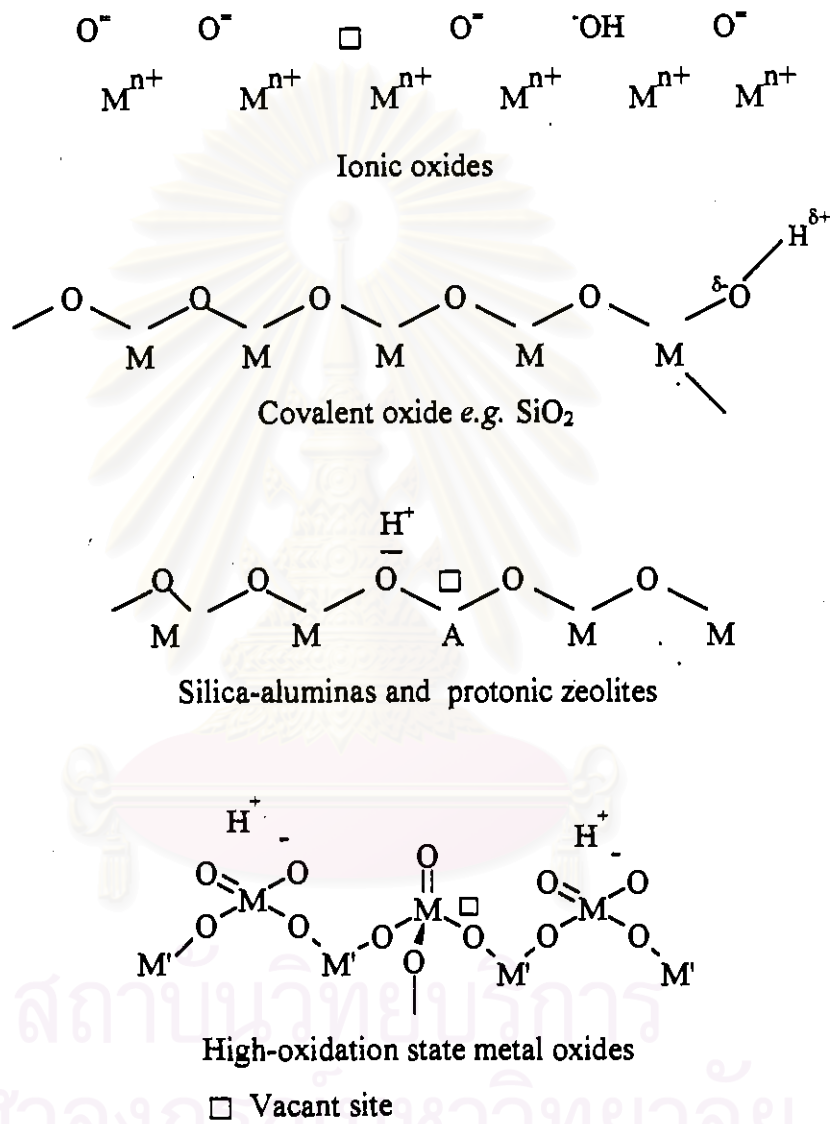


Figure 3.1 Structure of metal oxides

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.

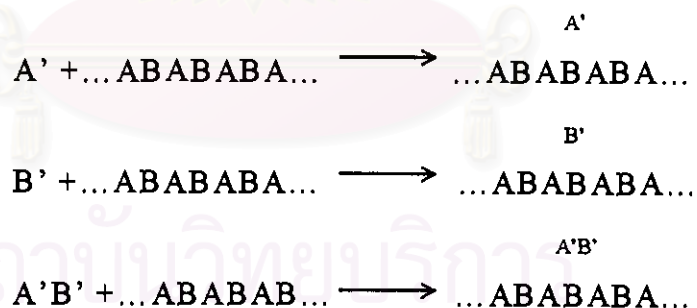
3.2 The measurement of the acid-base properties of surfaces [Parry 1963, Barzetti *et al.* 1996, Binet *et al.* 1996, Zecchina *et al.* 1998, and Busca 1998]

The measurement of the acidity of solid surfaces has been the aim of many studies. A variety of techniques has been used to measure acidity including the use of indicators [Benesi 1956], titration with bases using indicators [Benesi 1957], measurement of the quantity of chemisorbed ammonia at various temperatures [Webb 1957 and Barth and Ballou 1961], the use of the dealkylation rates [Johnson and Melik 1961], the use of isomerization and dehydration rates [Sidorov 1960], Calorimetric technique and the determination of IR spectrum of chemisorbed probe molecules [Parry 1963, and Solinas and Ferino 1998]. The application of many of these techniques has given conflicting and widely differing results on the same materials. Moreover, none of the methods except the last one distinguishes between protonic acidity (Brønsted) and aprotic acidity of the Lewis type. Some of the procedures also suffer from other disadvantages such as diffusion limitations and/or extraneous physical adsorption. In most recent IR spectroscopy studies of the acid-base properties of surfaces ammonia, pyridine, n-butylamine, triethylamine, or other

basic molecules have been used to characterize the surface acidity. 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 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 fulfils 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 Spectroscopic detection of the surface acid sites

The IR spectroscopic detection of surface acid-basic centers is based on the observation of the vibrational perturbation undergone by probe molecules when they adsorb on them. Adsorption on ionic oxides mainly involves acid-basic interactions. Basic molecules adsorb on acid sites while acid molecules adsorb on basic sites.

3.2.2.1 Spectroscopic detection and characterization of the surface Lewis acid sites

As already cited, coordinatively unsaturated cations exposed at the surface of ionic oxides give rise to surface Lewis acid sites. Basic molecules can, consequently, interact with these sites by forming a new coordination bond, so completing or increasing the overall coordination at the surface cation. The stronger are the polarizing power of the Lewis acidic cation (charge to ionic radius ratio) and the basic strength of the adsorbate, the stronger is the Lewis interaction. Upon this interaction, electrons flow from the basic molecules towards the catalyst surface. This electronic perturbation as well as the molecular symmetry lowering arising from this contact are the causes of a vibrational perturbation of the adsorbate. In most cases, the vibrational perturbation only consists in shifts of the vibrational frequencies, the more pronounced, the stronger is the interaction, *i.e.* the greater is the Lewis strength of the surface site. Consequently, the shift of the position of some very sensitive bands of the adsorbate upon adsorption can be taken as a measure of the Lewis acid strength of the surface sites. In Table 3.1, some data on the useful basic probe molecules are reported.

Table 3.1 Basic probes, their pK_a's and the position of their diagnostic vibration bands.

Base	Conjugated acid	pK _a	PA ^c	Sensitive bands (base)		Diagnostic band (acid)	
				Lewis acidity		Brønsted acidity	
				Mode	Position ^a	Mode	Position ^a
Piperidine	C ₅ H ₁₀ NH ₂ ⁺	C ₅ H ₁₀ NH ₂ ⁺	11.1	933		δNH ₂ ⁺	~1650
<i>n</i> -Butylamine	<i>n</i> -C ₄ H ₉ -NH ₂	<i>n</i> -C ₄ H ₉ -NH ₃ ⁺	10.9			δ _{sym} NH ₃ ⁺	~1540
Ammonia	NH ₃	NH ₄ ⁺	9.2	846	δ _{sym} NH ₃	δ _{as} NH ₄ ⁺	~1440
Pyridine	C ₅ H ₅ N	C ₅ H ₅ NH ⁺	5.2	912	v8a	v8a	~1640
					v19b	v19b	~1540
					v1(ring)		
Acetone	(CH ₃) ₂ C=O	(CH ₃) ₂ C=OH ⁺	-7.2	816	vC=O		
Pivalonitrile	<i>t</i> -C ₄ H ₉ -C≡N	<i>t</i> -C ₄ H ₉ -C≡NH ⁺	~-10		vCN		
Acetonitrile	CH ₃ -C≡N	CH ₃ -C≡NH ⁺	-10.4	783	vCN		
					FR ^b		
Nitric oxide	NO	[HNO] ⁺			vN=O		
Carbonmonoxide	CO	[HCO] ⁺		598	vC≡O		

^aRange cm⁻¹

^bFermi resonance doublet

^cProton affinity, Kcal/mol

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- Adsorbed pyridine as a probe for Lewis acidity

In spite of its toxicity, bad smell, low volatility and solubility in greases and rubber, giving rise to pollution of the vapor-manipulation ramps, pyridine is the most largely used basic probe molecule for surface acidity characterization. The adsorption of pyridine on catalyst surfaces can give rise at least to the four adsorbed species reported in figure 3.2.

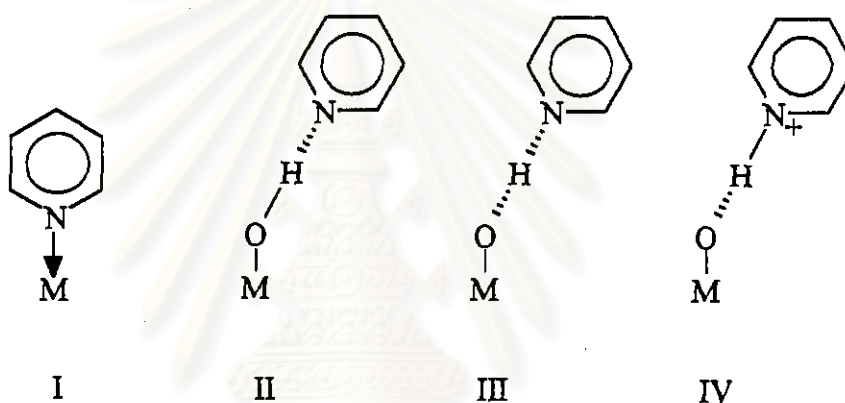


Figure 3.2 The adsorption of pyridine on catalyst surfaces

Species I is the product of the interaction of pyridine with Lewis acidic M cationic centers.

The pyridine molecule, C_5H_5N , is constituted by 11 atoms, so that 27 vibrational degrees of freedom ($3 \times 11 - 6$) correspond to vibrational modes. The usual notation of the vibrational modes of pyridine is derived from that of the parent molecule benzene, C_6H_6 , which has one atom more and consequently three additional vibrational modes. The lower symmetry of pyridine (point group C_{2v}) with respect to benzene (point group D_{6h}) gives rise to the splitting of all double degenerate vibrational modes of benzene into two non-degenerate vibrational modes (Table 3.2). Almost all vibrational modes of the pyridine molecule, strongly coupled, are sensitive to the strength of the interaction involving its nitrogen lone pair. However, some of

them are more sensitive than others. Accordingly, the 8a mode and the 19b mode (both mainly involving in-plane vibrations of the C₆ ring) are the most used in IR studies to evaluate the strength of the Lewis acid sites. Raman spectroscopic studies are also performed on adsorbed pyridine. The 1 mode, weak in IR band frequently masked by skeletal absorption, is very intense and accessible to Raman and is consequently used to characterize Lewis acidity with Raman spectroscopy of adsorbed pyridine. As shown on Table 3.2, some of the most sensitive bands of pyridine shift strongly (and also change of shape) when pyridine is protonated to form the pyridinium cation. This allows to distinguish coordinated from protonated pyridine easily. So, as it will be discussed further below, pyridine is largely used as a probe for both Lewis and Brønsted acidity.

In Table 3.3 the position of the most sensitive 8a mode of pyridine when coordinatively adsorbed on different oxide surfaces is reported. The position of this sharp band roughly correlates with the polarizing power of the adsorbant cation, PP, calculated as the charge to ionic radius ratio. In Table 3.3 some assumptions (mostly based on experimental data) have been made to improve this correlation. As for example, the adsorbing sites on CuO have been assumed to be monovalent Cu ions, according to the IR spectra of adsorbed CO that gave evidence of predominant monovalent Cu⁺ adsorbing sites.

The correlation evident in Table 3.3 allows to draw some interesting conclusions:

1. On ABO₃ perovskite-type oxides the adsorbing sites are assumed to be always the big A cation, the smaller B cation being likely not exposed at the surface. This leads to a significant difference in Lewis acidity between perovskite-type and ilmenite-type metatitanates. It is seen that the 8a and 19b sensitive modes of adsorbed pyridine are both significantly shifted upward in the ilmenites with respect to the perovskites.

2. In any case, in mixed oxides the counterions have always an effect. As for example, Ti and Zr cationic centers on the pyrophosphates are stronger Lewis acids than those on the corresponding oxides, and the acidity of Mg orthovanadate is intermediate between those of the pure oxides vanadia and magnesia.

3. It is still not clear why octahedral Al cations so weakly acidic (α -Al₂O₃ is a very inert surface) with respect to octahedral Fe and Cr cations.

4. The Lewis acidity of WO₃ and V₂O₅-based catalysts dose not correlate correctly with the others, because the polarizing power of W⁶⁺ and V⁵⁺ cations, calculated as above, is "overestimated". These values roughly correlate with the others if we calculate the polarizing power using the charge of wolframyl and vanadyl cations (WO⁴⁺ and VO³⁺) and the radius of W⁶⁺ and V⁵⁺.

The use of pyridine is also justified on the basis of its chemical stability on oxide surfaces. Transformation to α -pyridine on alumina and to dipyridyl on strongly activated alkali earth oxides and on oxidizing oxides only occurs at relatively high temperatures.

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Table 3.2 Position (ν , cm^{-1}) of the vibrational bands of pyridine and pyridinium ion as compared to those of benzene.

Point group D_{6h}				Point group C_{2v}						Assignments
Benzene C_6H_6				Pyridine C_5H_5N				Pyridinium $C_5H_5NH^+Cl^-$		
Sym	Notation	Act	ν (cm^{-1})	Notation	Sym	Act	ν (cm^{-1})	ν (cm^{-1})		
A_{1g}	1	R	992	1	A_1	IR, R	991	1009	ν_{CC}	
E_{2g}	8	R	1596	8a	A_1	IR, R	1583	1638	ν_{CC}	
				8b	B_1	IR, R	1577	1608	ν_{CC}	
E_{1u}	19	IR	1479	19a	A_1	IR, R	1481	1535	ν_{CC}, δ_{CC}	
				19b	B_1	IR, R	1436	1485	ν_{CC}, δ_{CC}	

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Table 3.3 Position (cm^{-1}) of the sensitive bands of adsorbed basic probe molecules on different catalyst surfaces (Lewis acid strength decreases from top to bottom).

Adsorbate	→	Pyridine	Ammonia	Pivalonitrile	Acetonitrile		Adsorbing site		
Mode	→	8a	$\delta_{\text{sym}}\text{NH}_3$	$\nu\text{C}>\text{N}$	$\nu\text{C}>\text{N}^b$		Type	PP	
Surface ↓	Structure ↓				I	II			
AlF_3	Crystalline	1627		2309-5			ivAl^{3+}	7.7	
$\gamma\text{-Al}_2\text{O}_3$	Def.spinel	1625	1295	2296	2330	2300	ivAl^{3+}	7.7	
		1615	1265				ivAl^{3+}		
		1595	1220				ivAl^{3+}	5.7	
		1622		2295			viAl^{3+}	7.7	
$\text{SiO}_2\text{-Al}_2\text{O}_3$	Amorphous	1625					ivAl^{3+}	7.7	
		NiAl_2O_4	Inv. spinel	1605				viNi^{2+}	2.8
		1595					ivAl^{3+}	5.7	
MgAl_2O_4	Norm. spinel	(1623)					ivAl^{3+}	7.7	
		1608					ivMg^{2+}	3.7	
ZnCr_2O_4	Norm. spinel	1614					ivZn^{2+}	3.3	
WO_3	Pseudocubic	1613	1275, 1222				viW^{6+}	6.9 ^a	
$\gamma\text{-Fe}_2\text{O}_3$	Def. spinel	1612	1230				ivFe^{3+}	6.1	
MgFe_2O_4	Inv. spinel	1612					ivFe^{3+}	6.1	
		1606	1172				viFe^{3+}	5.4	
ZnFe_2O_4	Norm. spinel	1612					ivZn^{2+}	3.3	
$(\text{VO})_2\text{P}_2\text{O}_7$	Crystalline	1610		2290	2328	2300	VO^{3+}	5.5 ^a	
V_2O_5	Crystalline	1608	1249	2280	2324	2296	VO^{3+}	5.5 ^a	
ZrP_2O_7	Layered	1610			2321	2294	Zr^{4+}	5.0	
TiO_2	Anatase	1610	1225	2285	2320	Mask	vTi^{4+}		
			1185	2260	2302	2274	vTi^{4+}	6.6	

Table 3.3 Position (cm^{-1}) of the sensitive bands of adsorbed basic probe molecules on different catalyst surfaces (Lewis acid strength decreases from top to bottom). (Continued)

Adsorbate	→	Pyridine	Ammonia	Pivalonitrile	Acetonitrile	Adsorbing site		
Mode	→	8a	$\delta_{\text{sym}}\text{NH}_3$	$\nu\text{C}>\text{N}$	$\nu\text{C}>\text{N}^{\text{b}}$			
Surface ↓	Structure ↓				I	II	Type	PP
$\alpha\text{-Fe}_2\text{O}_3$	Hematite	1608	1220, 1180		2310	2283	νFe^{3+}	5.5
MtiO_3	Ilmenite-type	1605	1210				νTi^{4+}	6.6
$\alpha\text{-Cr}_2\text{O}_3$	Eskolaite	1608	1200				νCr^{3+}	4.9
MgCr_2O_4	Norm. spinel	1607	1200				νCr^{3+}	4.9
ZrO_2	Baddeleyite	1606	1210, 1160				Zr^{4+}	~5.0
$\text{Mg}_3(\text{VO}_4)_2$	Crystalline	1605			2295	2268	νMg^{2+}	2.8
LaMO_3^{a}	Perovskite-type	1602-1596					La^{3+}	2.8
$\alpha\text{-Al}_2\text{O}_3$	Corundum	1597					νAl^{3+}	5.7
MgO	Periclase			2260	2307	2279	νMg^{2+}	3.7
		1595			2294	2254	νMg^{2+}	2.8
$\text{BaAl}_2\text{O}_{19}$	β -Alumina	1594					Ba^{2+}	1.4
MtiO_3^{d}	Perovskites	1595-2					M^{2+}	1.8-1.4
CuO	Tenorite	1592					νCu^+	1.0
$\text{K}_2\text{O-TiO}_2$	Anatase	1588	1143				K^+	0.7
Liquids		1583	1054	2236	2292	2254		

PP=polarizing power (charge to radius ratio)

^aM=Fe, Cr, Mn, Co

^bI and II=Fermi resonance doublet

^cM=Co, Ni

^dM=Co, Ni

^eM=Sr, Ba

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- Carbon monoxide and nitrogen monoxide as probes for the surface cationic centers

Carbon and nitrogen monoxide are very weak bases and are largely used for the surface characterization of cationic centers on metal oxide surfaces. The electronic structure of CO is described in Table 3.4 in correct terms [Jorgensen *et al.*1973] and in a simplified view. It implies a triple bond between C and O, according to the stretching frequency measured at 2143 cm^{-1} for the free molecule in the gas. In principle, the 14 electrons are distributed symmetrically between C and O atoms, so that the lower positive charge of the C nucleus with respect to O implies the formation of a dipole with the negative charge of the C nucleus with respect to O implies the formation of a dipole with the negative charge at the C atom, in spite of the lower electronegativity of C with respect to the O nucleus. For this reasons, the CO molecule tends to interact through the C end with cationic centers (figure 3.3). This interaction is rather weak, usually completely reversible by outgassing at room temperature and should be studied at room or lower temperatures (*e.g.* at liquid nitrogen, $-196\text{ }^{\circ}\text{C}$).



Figure 3.3 The adsorption of CO and NO on catalyst surfaces

According to theoretical calculations [Pacchioni *et al.*1991] this interaction is a simple polarization, with no formation of a true coordinative σ bond with the cationic center. This interaction tends to increase the CO bond order, so that the CO stretching frequency tends to increase upon of. Accordingly, the experimental measure of the CO stretching frequency for CO interacting with surface cations can be taken as a measure of the polarizing power of the cation or, in other terms, of its Lewis acidity (See Table 3.5).

Table 3.4 The electronic structure of carbon monoxide.

Notation	Occup.	Simplified not.
6 σ	—	σ^*
2 π	—	$\pi^*_y\pi^*_z$
1 π	$\uparrow\downarrow$	$\pi^*_y\pi^*_z$
5 σ	$\uparrow\downarrow$	σ
4 σ	$\uparrow\downarrow$	C 2sp hybrid
3 σ	$\uparrow\downarrow$	2sp hybrid
2 σ	$\uparrow\downarrow$	C 1s
1 σ	$\uparrow\downarrow$	O 1s

Table 3.5 CO stretching frequencies of carbon monoxide adsorbed at low temperature on closed shell cation oxides.

Catalyst	$\nu_{\text{CO}}(\text{cm}^{-1})$	Cation	PP
$\gamma\text{-Al}_2\text{O}_3$	2235,2210	IVAl ³⁺	7.7
	2200-2180	VAl ³⁺	5.7
TiO ₂	2226,2208,	VTi ⁴⁺	6.6
	2182		
ZrO ₂	2195,2170	Zr ⁴⁺	~5.0
ZnO	2192,2189	IVZn ²⁺	3.3
MgO	2158,2149	VIMg ²⁺	2.8
La ₂ O ₃	2155	La ³⁺	2.8
V ₂ O ₅	—	No interaction	
Gas	2143		

However, when the cation or the metal atom contains, besides empty orbitals, also full of partly filled d-type orbitals, they can interact with the empty π^* -type orbitals of CO via a π -type electron backdonation from the metal to CO stretching frequency is decreased by this last interaction. In this case, the interaction can become very strong and very stable metal-carbonyl complexes can be formed. The experimental CO stretching frequency in this case is a complex function of the electron accepting power of the cation (Lewis acidity) and of its π -type electron donating power. Accordingly, the CO stretching frequency of CO adsorbed on several transition metal cations is very informative on the oxidation state of the adsorbing ion, but cannot be taken as a measure of its Lewis acidity. For this reason, the use of CO as a probe for surface acidity is limited to closed shell cation oxides (Table 3.5).

However, also some closed shell cations like V^{5+} and W^{6+} do not give rise to detectable adsorption. This allowed us to evaluate the coverage and the dispersion of the surface oxide species in V_2O_5 - TiO_2 and WO_3 - TiO_2 catalysts. Zecchina and coworkers (1996) largely used CO as a probe of the surface sites in many oxide systems in relation to their morphology and sintering treatments.

Nitrogen monoxide has one electron more than CO, so that the same electron configuration could apply with the additional electron in an antibonding π^* -type orbital. The bond order is decreased to 2,5 and this is reflected in the lower stretching frequency (1875 cm^{-1} for NO gas). Thus, the NO molecules is a radical and this makes its reactivity by far higher. It easily dimerizes to N_2O_2 , is easily oxidized to NO^+ , to nitriles NO_2^- or to NO_2 . NO can also easily disproportionate and its thermodynamically unstable towards decomposition to N_2+O_2 . This makes this molecule very reactive so that its successful use as a probe for cationic centers is limited.

Anyway, NO can also interact with surface metal centers on metal oxides, giving rise to surface nitrosyl species. In homogeneous complexes, nitrosyl species can be either linear or bent (figure 3.3). Linear species generally form over cationic

sites and are characterized by ν_{NO} higher than the gas, while bent nitrosyls are formed mainly over reduced centers and are characterized by ν_{NO} lower than the gas. In the former case the main interaction is between the N 2sp hybrid orbital and empty orbitals of the metal cation so that NO is depleted of electrons. The rise of the ν_{NO} frequency can be taken as a measure of the Lewis acidity of the adsorbing cation.

When the cation of the metal atom contains, besides empty orbitals, also full or partly filled d-type orbitals, they can interact with the π^* -type orbitals of NO molecule, via a π -type electron backdonation. This gives rise to bent nitrosyls, where N is likely sp^2 hybrid and the NO stretching frequency is decreased. In this case, the NO stretching frequency does not correlate with acidity.

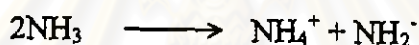
In any cases, sometimes a good correlation exists between the adsorbed species produced by contact with CO and NO. In both cases a main band is observed, with a smaller component at higher frequency. Possible assignments for such bands are reported in Table 3.6, where the subscripts indicate the overall coordination of the Ti cation after adsorption.

Table 6 Assignment of the bands of surface carbonyls and nitrosyls on TiO_2 -anatase.

CO adsorption			NO adsorption			Assignment
ν_{CO}	$\Delta\nu_{\text{CO}}$	$\Delta\nu_{\text{CO}}/\nu_{\text{CO}}$	ν_{NO}	$\Delta\nu_{\text{NO}}$	$\Delta\nu_{\text{NO}}/\nu_{\text{NO}}$	
2226	+83	0.039	1935	+60	0.031	IVTi ⁴⁺ ←CO
2205	+62	0.029	1913	+39	0.020	VTi ⁴⁺ ←CO
2186	+43	0.020	1900	+25	0.013	VITi ⁴⁺ ←CO
2143			1875			Gases

- Other basic probes for the spectroscopic characterization of Lewis acidity

Other basic probe molecules can be used for probing surface Lewis acidity. Other N-containing molecules, that are in water stronger bases than pyridine, like piperidine [Hughes *et al.* 1967], n-butyl amine [Ramis *et al.* 1989] and ammonia [Tsyganenko *et al.* 1975], can be successfully used too. However, they present in most cases, some disadvantages. Piperidine and n-butyl amine do not present very sensitive bands in a “clean” spectral region to be easily used to evaluate the basic strength. Ammonia can be very useful, although in some cases it is too reactive and gives rise to reactive adsorption. This is the case of its adsorption on alumina, where a complex spectrum is obtained likely due to a disproportionation reaction like



Moreover, the transformation of ammonia to amide species NH_2^- , imido-species, NH , and hydrazine species, $\text{NH}_2\text{-NH}_2$, as well as its oxidation to N_2 , N_2^- and N_3^- species is well-documented. Ammonia is a good probe for acidic non-oxidizing or poorly oxidizing, surfaces [Ramis *et al.* 1992].

The use of less basic organic probes like ketons and nitriles is also limited by their reactivity (enolization, polymerization, etc.). However, the spectroscopic features of the molecularly adsorbed species give rise to a picture that correlates quite well with what is obtained by pyridine and/or CO adsorption, as it can be deduced from Table 3.3. Nitriles are largely used in acid catalysts characterization [Busca *et al.* 1985, Busca *et al.* 1989, and Odenbrand *et al.* 1992].

3.2.2.2 Spectroscopic detection of the surface Brönsted acid sites

The fragments arising from the dissociative adsorption of water on the surface of metal oxides give rise to hydroxy-groups that are potentially more or less active Brönsted acid sites. Such surface hydroxy-groups can be detected, directly, recording the IR spectra of the oxide catalyst powders in the region $3800\text{-}3000\text{ cm}^{-1}$, where the O-H stretching modes (νOH 's) fall. Although the position and shape of the νOH bands of such surface hydroxy-groups is informative on their coordination, these data do not give straightforward information on their Brönsted acidity. In fact, as for example, the position of the νOH band over a basic catalyst like MgO, of a weakly acidic catalyst as amorphous silica and of a strong Brönsted acidic catalyst like silica-alumina is almost the same ($3745\pm 3\text{ cm}^{-1}$). Moreover, very acidic catalysts like, for example, sulfated zirconia and titania do not present any definite sharp νOH band, while others, like zeolite ZSM-5 and silica-alumina, show sharp νOH bands. These facts are due to two main reasons:

1. The νOH frequency depends not only from the O-H bond strength, but also from the nature of the M-O(H) bond, *i.e.* from the element(s) to which the OH is bonded.

2. In any case, even for OH's bonded to the same element, the function νOH versus acidity is not necessarily linear but can present a maximum .

3. The state of the OH groups at the surface also depends on the basic strength of the oxide ions. In fact, in very covalent structures, like for silica alumina and zeolites, where oxygens are almost not basic, the acidic OH's are responsible for rather sharp and well-defined bands while when the nearest oxygen are more or less basic, the acidic OH's give rise to H-bondings, with a shift down and a broadening of the νOH band.

4. It seems also likely that the location of the acidic OH's inside a zeolite cavity can also be responsible for a shift down and broadening of the νOH band. This seems necessary to justify the location of the "acidic" OH band in zeolite HZSM-5 at 3610 cm^{-1} , rather broad, with respect to the position of the "acidic" OH of amorphous silica-alumina at 3742 cm^{-1} , very sharp.

3.2.2.3 Spectroscopic characterization of the surface Brönsted acid sites

- The basic strength method

The presence of Brönsted acid sites can be detected "indirectly" by studying the interaction of bases of appropriate strength and by monitoring the formation of the corresponding protonated species. This is done most frequently using again pyridine as the adsorbed probe molecule. On the titanates the 8a, 8b, 19a and 19b bands of coordinated molecular pyridine are observed, more or less shifted, as usual, towards higher frequencies. No traces are found of pyridinium cations. On the contrary, on GeP_2O_7 the observed spectrum is definitely different, with a split broad band at $1640, 1628\text{ cm}^{-1}$, another broad band at 1548 cm^{-1} and a very strong band at 1492 cm^{-1} . This spectrum is typical for pyridinium cations, as compared with the spectrum of pyridinium chloride (Table 3.2). According to these data we can conclude that titania is a purely Lewis acidic material while GeP_2O_7 is a purely Brönsted acidic solid. Most frequently, solids can be both Lewis and Brönsted acidic. The interaction of pyridine with silica-alumina, the bands at 1597 and 1446 cm^{-1} are due to the 8a and 19b modes of pyridine molecules interacting via H-bonding with the weakly acidic surface hydroxy-groups of the catalyst (species II and/or III in figure 3.2) while the bands at 1623 and 1455 cm^{-1} are due to the same modes of pyridine molecularly coordinated on Al^{3+} cations, acting as Lewis acid sites (species I in figure 3.2).

The bands at $1639, 1547$ and 1492 cm^{-1} are the most intense modes of pyridinium cations, associated to a total proton transfer from the Brönsted acidic surface OH group to the basic molecule (species IV in figure 3.2). According to these assignments, outgassing at $100\text{ }^\circ\text{C}$ causes the disappearance of the bands at 1597 and

1446 cm^{-1} (due to H-bonded pyridine), while the other, strongly held species are not perturbed. However, stronger bases than pyridine can be protonated in part on alumina. For example, piperidine adsorbed on $\gamma\text{-Al}_2\text{O}_3$, the evident band at 1650-1610 cm^{-1} is absent on the spectrum of the "free" base and is due to the scissoring mode of the $\text{-NH}_2\text{-}$ group of dialkylammonium cations (in this case, piperidinium cations). Thus, the acid strength of the surface Brønsted sites on solid surfaces can be evaluated by the basic strength of the molecules they are able to protonate. In this respect, the question arises of whether the basic strength scale to be used is that applied in water solution (*i.e.* the pKa scale) or in the gas phase (*e.g.* the proton affinity scale) which are not coincident (see Table 3.1). In particular it appears that in the gas phase pyridine is more acidic than ammonia, while the contrary is true in water. Ammonia is more easily protonated than pyridine on oxide surfaces (see Table 3.7) so is apparently more basic.

- The hydrogen-bonding method

As discussed above, the strength of the acid-base interaction depends on the acid strength of the acid as well as on the basic strength of the base. When the base is sufficiently strong, a Brønsted acid protonates it (species IV in figure 3.2), but when the base is too weak the interaction results in a hydrogen bonding (species II in figure 3.2). In intermediate cases, the proton transfer can be only partial so that a "symmetrical hydrogen bonding" occurs (species III in figure 3.2). These two situations can be detected and distinguished spectroscopically from protonation and interaction with Lewis sites. In fact, in both these cases the spectrum of the adsorbed base is only weakly perturbed with respect to the liquid, but in the same sense as for interaction with Lewis sites. Moreover, hydrogen bonding causes the shift down and the broadening of the HO stretching bands of the surface OH groups. Simple hydrogen bonding gives rise to the formation of well-defined although broad OH stretching bands, and the shift of the maximum of the νOH band upon interaction can be taken as the H-bonding interaction. If the same base is used, this shift measures that acid strength of the protonic center. Very weak bases, that cannot ordinarily be protonated, like nitriles or benzene, can be used for this purpose. Low temperature

adsorption of even weaker "bases", like CO of ethylene [Chambellan *et al.* 1992], are also useful experiments in this respect.

The formation of a stronger "symmetrical" hydrogen bonding causes the formation of an almost continuous absorption in the overall spectrum, giving rise to three maxima and two minima, the so-called ABC contour arising from Fermi resonance type interactions. The minima correspond to the first overtones of the in plane, δOH , and the out of plane deformation modes, γOH , of the MOH group. This phenomenon occurs when the interaction of the base with the OH group is intermediate between H-bonding and a true Brønsted acid-base interaction.

- The olefin polymerization method

Olefins and dienes are very reactive towards the electrophilic attack of Brønsted acid, and can undergo proton-catalyzed cationic polymerization. This phenomenon occurs the faster, the stronger is the Brønsted acid, the more electron-rich is the olefinic double bond and (in a low-temperature range) the higher is the temperature. Thus, the polymerization rate follows the order: 1, butadiene > isobutene > propene > ethylene. Very strong acids, like zeolite HZSM-5, sulfated titania and zirconia, supported WO_3 , cause the polymerization at room temperature. Less acid surfaces, like $\text{MoO}_3\text{-TiO}_2$ and silica alumina, do not cause ethylene polymerization but are able to polymerize propene and isobutene. Moreover, very strongly acidic surfaces like HZSM-5 zeolite allow polymerization + skeletal isomerization of olefins, like 1-butene with the production of polyisobutene. A Brønsted acidity scale for solid acids measured using this method is reported on Table 3.7, where a comparison of the three methods we proposed can be made. It seems evident that the olefin polymerization method can discriminate between very strong Brønsted acid solids, while the H-bonding.

Table 3.7 Evaluation of the Brønsted acid strength of surface hydroxy-groups on catalytic materials by different IR techniques.

Catalyst	Protonation of					$\Delta\nu\text{OH}$ nitriles	Behavior with <i>n</i> -butenes at r.t.	Polymerization of			
	AN	Py	NH ₃	RNH ₂	Piper			Ethylene	Propene	Isobutene	1, 3-butadiene
HZSM5	yes	yes	yes	yes	yes	ABC	Polymerization+ isomerization	yes	yes	yes	yes
TiO ₂ -SO ₄	no	yes	yes	yes	yes	ABC	Polymerization	no	yes	yes	yes
Silica-alumina	no	yes	yes	yes	yes	ABC	Polymerization	no	yes	yes	yes
H ₃ PO ₄ -SiO ₂	no	yes	yes	yes	yes	ABC	Polymerization	no	no	yes	yes
AlF ₃	no	yes	yes	yes	yes	>500					
B ₂ O ₃ -Al ₂ O ₃	no	no	yes		yes	480-420 330-280	Butoxide traces	no	no	dimer	yes
Silicated-alumina	no	no			yes	480-280 330-280	$\Delta\nu\text{OH}$ 200-300				
γ -Al ₂ O ₃	no	no	yes	yes	yes	450-400 330-280	$\Delta\nu\text{OH}$ 200-300	no	no	no	yes
am-SiO ₂	no	no	yes	yes	yes	400	$\Delta\nu\text{OH}$ 150-200	no	no	no	no
TiO ₂ -an.	no	no	no	no	no	<300		no	no	no	no
ZrO ₂	no	no	no	no	no			no	no	no	no
MgO	no	no	no	no	no	~250		no	no	no	no

AN = Acetonitrile

Py = Pyridine

Piper = Piperidine

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