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Chemical Bond. We hope the ideas here show how VB concepts can provide additional qualitative and quantitative understanding of transition-metal systems. The systematic studies on the first two rows of TM hydrides carried out with Dr. J. B. Schilling (now at Amoco Research Center) and Prof. J. L. Beauchamp[5a–c] (Caltech) led to the concepts that form the basis of this review. The similar studies on the third row TM hydrides with M. J. Brusich[5d] (now at IDA) are combined here with the earlier ones to provide an overview of MH^+ bonds for all three rows. Some of these concepts go back to the earliest GVB calculations on TM complexes carried out in collaboration with Dr. T. H. Upton (now at Exxon), Dr. C. F. Melius (now at Sandia Livermore Laboratory), Dr. B. D. Olafson (now at BioDesign, Inc.) and M. J. Sollenberger, M.D. (now in private practice). The calculations have been supported by the National Science Foundation (Grant No. CHE-8318041). G.O. is grateful to NATO for a fellowship supporting part of his stay at Caltech. In addition, the computer resources (Alliant FX8/8 and DEC VAX 8650) were funded by ONR/DARPA, NSF-MRG, ONR-SRO, and DOE-ECUT.

Model Reactions for Characterizing the Acidity of Solid Catalysts

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Solid acid catalysts are the backbone of major processes of refining and of petrochemistry: cracking, hydrocracking, reforming, isomerization, and disproportionation of aromatics. These catalysts, in the near future, should also play a significant role in the synthesis of functional compounds.[1] The participation of natural acid solids (in particular clays) as catalysts in the formation of petroleum is also well-known.[2]

There exist a large variety of solid acids:[3] natural clay minerals, mounted acids (H_3PO_4 mounted on diatomaceous earth), cation-exchange resins (Nafion), oxides (alumina) and mixtures of oxides (silica–alumina), salts ($MgSO_4$), and zeolites. The acidity of these solids even within a class can be completely different: Some solids can be considered as superacid while others have a very reduced acid strength.

In reactions occurring by acid catalysis, the activity, stability, and selectivity of acid solids are obviously determined to a large extent by their surface acidity (i.e., the number, nature, strength, and density of their acid sites). The acidity required for catalyzing the transformation of reactants into valuable products or into byproducts can be quite different. Indeed, certain reactions demand very strong acid sites while others can be catalyzed by very weak acid sites.[4] The rate of certain bimolecular reactions depends on the space between acid sites probably because their catalysis requires several acid sites.[5–9] However, for skeletal transformations of hydrocarbons, the rate depends essentially on the Brönsted acidity of the catalysts.[4,10] Good correlations have been obtained between the concentration of Brönsted sites and the rate of cumene dealkylation,[11,12] xylene isomerization,[13] toluene[14] and ethylbenzene[15,16] disproportionation, *n*-hexane cracking,[17] etc. Apparently, the Lewis acid sites alone are not active in these reactions. However, it has been shown that Lewis acid sites in the vicinity of protonic sites can increase their strength and consequently their activity.[18] The dependence of catalytic properties on the acid properties of solid catalysts is often more complex for the reactions of functional compounds. The acid sites (Lewis and/or Brönsted) and base sites, which coexist in adjacent positions on the surface of acid catalysts, participate together in most of these reactions[3] (acid–base bifunctional catalysis).

The rate and selectivity of reactions that do not occur by acid catalysis can also be affected by acidity. This has been shown in the case of oxidation of hydrocarbons on transition-metal oxides. Acid–base properties of

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[1] Hoelderich, W. F. *Zeolites, Facts, Figures, Future*; Jacobs, P. A., Van Santen, R. A., Eds.; Studies in Surface Science and Catalysis 49; Elsevier: Amsterdam, 1989; pp 69.93.

[2] Tissot, B. P.; Welte, D. H. *Petroleum formation and occurrence*; Springer-Verlag: Berlin, 1978.

[3] Tanabe, K. *Solid Acids and Bases*; Academic Press: New York, 1970.

[4] Guisnet, M. *Catalysis by Acids and Bases*; Imelik, B., et al., Eds.; Studies in Surface Science and Catalysis 20; Elsevier: Amsterdam, 1985; pp 283–297.

[5] Bierenbaum, H. S.; Partridge, R. D.; Weiss, A. H. *Adv. Chem. Ser.* **1973**, *121*, 605–617.

[6] Martin de Armando, M. L.; Gnep, N. S.; Guisnet, M. *J. Chem. Res., Synop.* **1981**, 8–9; *J. Chem. Res., Miniprint* **1981**, 243–255.

[7] Guisnet, M.; Avendano, F.; Bearez, C.; Chevalier, F. *J. Chem. Soc., Chem. Commun.* **1985**, 336–337.

[8] Giannetto, G.; Sansare, S.; Guisnet, M. *J. Chem. Soc., Chem. Commun.* **1986**, 1302–1303.

[9] Jacquinot, E.; Raatz, F.; Macedo, A.; Marcilly, C. *Zeolites as Catalysts, Sorbents and Detergent Builders*; Karge, H. G., Weitkamp, J., Eds.; Studies in Surface Science and Catalysis 46; Elsevier: Amsterdam, 1989; pp 115–125.

[10] Benesi, H. A.; Winquist, B. H. C. *Adv. Catal.* **1978**, *27*, 97–182.

[11] Turkevich, J.; Ono, Y. *Adv. Catal.* **1969**, *20*, 135–152.

[12] Jacobs, P. A.; Leeman, H. E.; Uytterhoeven, J. B. *J. Catal.* **1974**, *33*, 17–30.

[13] Ward, J. W.; Hansford, R. C. *J. Catal.* **1969**, *13*, 154–160.

[14] Aonuma, T.; Sato, M.; Shiba, T. *Shokubai* **1963**, *5*, 274–277.

[15] Karge, H. G.; Ladbeck, J.; Sarbak, Z.; Hatada, K. *Zeolites* **1982**, *2*, 94–102.

[16] Karge, H. G.; Hatada, K.; Zhang, Y.; Fiedorow, R. *Zeolites* **1983**, *3*, 13–21.

[17] Ward, J. W. *J. Catal.* **1968**, *10*, 34–46.

[18] Mirodatos, C.; Barthomeuf, D. *J. Chem. Soc., Chem. Commun.* **1981**, 39–40.

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these oxides either influence the adsorption and the desorption rates of reactants and products or are responsible for side reactions.[19]

The acidity of solids often plays a significant role when they are used as supports of catalytic species (e.g., metals and sulfides). Interaction of the support with the active components (support effect) can influence their catalytic properties. Moreover, for certain reactions, new paths involving the joint participation of the acid sites and other type sites can occur (polyfunctional catalysis[20]). Numerous examples are to be found in the processes of refining and petrochemistry: e.g., reforming and hydrocracking.

Given the great use and great variety of acid solids, it is very important to derive accurate methods for characterizing their acidity and predicting their value as catalysts. The methods most frequently used are based on the chemisorption of basic compounds. These methods have been reported in numerous reviews.[3,10,19,21,22] The most suitable, i.e., adsorption of bases followed by calorimetry or thermodesorption of stable bases followed by gravimetry or volumetry, give the total number of acid sites (Lewis + Brönsted) and their distribution according to their strength but do not differentiate between protonic and Lewis acid sites. Therefore, this information is not enough to allow prediction of the catalytic properties of a given solid unless the solid belongs to a coherent series in which only one parameter has been changed (e.g., percentage of the protonic exchange of a zeolite). Only certain physicochemical techniques such as IR spectroscopy of a solid on which pyridine is desorbed as a function of temperature can give this information. Indeed, there are IR bands characteristic of pyridine adsorbed on Brönsted sites (1545 cm^{-1}) and of pyridine adsorbed on Lewis sites (1440–1465 cm^{-1}).

However, the best method for characterizing industrial acid catalysts seems to be through model reactions.[4,19] Indeed, operating conditions similar to those of industrial processes can be chosen, which is not the case for chemisorption methods carried out mostly under vacuum and at room temperature. Obviously, the more the model reactions (and the operating conditions) are representative of the industrial transformation, the more correct the catalyst evaluation but unfortunately the more expensive and time consuming.

However, model reactions are not only useful for controlling the suitability of industrial catalysts. As will be shown in this Account, model reactions also constitute an efficient means for characterizing the surface acidity of solids, i.e., the nature, strength, and density of the sites.

Nature of Surface Sites of Amphoteric Oxides

Double-bond shift and cis–trans isomerization of olefins are very facile (rapid) reactions. Because of its simplicity (there are only three isomers) and selectivity (side transformations are generally insignificant), *n*-butene isomerization is one of the model reactions most used for the characterization of solid catalysts. The stereoselectivity of the reaction depends on the mechanism. For purely acid catalysts such as silica–alumina[23] or protonic zeolites,[24] isomerization occurs via carbenium species, and 1-butene transforms into a practically equimolar mixture of *cis*- and *trans*-butenes. For purely basic catalysts, isomerization occurs through allylic carbanions, the cis isomer being definitely favored (the cis/trans ratio is equal to 4 on MgO[25]). Moreover, on basic catalysts, there is no direct cis–trans isomerization. However, for most of the oxides, the situation is more complex. Indeed, acid and basic sites coexist on their surface and can be active either separately or together (acid–base bifunctional catalysis) for butene isomerization.[26]

The various reactions and hence the various active sites can nevertheless be distinguished by means of tracer techniques. This was shown for various oxides, SiO_2–Al_2O_3,[24] Al_2O_3,[27–29] MgO,[25] TiO_2,[30] by using [2,3-D_2]- and [1,4-D_6]-*cis*-butenes as reactants. Only the case of alumina will be developed. This simple oxide has a complicated surface on which coexist various sites: hydroxyl groups, incompletely coordinated aluminum atoms, and negatively charged oxygen atoms whose properties depend on their environment. Thus, there are five kinds of OH groups differing by the number of adjacent oxide ions (from 0 to 4). The pretreatment temperature determines the degree of dehydroxylation of the surface and hence the site distribution.[31,32]

The isomerization of deuterated *cis*-butenes was carried out at temperature T_R between 85 and 250 °C on alumina that had been pretreated under nitrogen flow at various temperatures T_P (300–580 °C). The isotope distributions in 1- and 2-*trans*-butenes were obtained by plotting the amount of each deuterated species against the percentage of conversion and extrapolating the curves to zero conversion. The absence of isotopic dilution of the hydrogen atoms of the catalyst surface was verified by including the reactants in a large slug of propylene: the isotope distributions remained unchanged. Isotope effects were determined by comparing under the same operating conditions the rates of formation of each isomer from deuterated and from light *cis*-butenes.[28,29]

For $T_P < 500$ °C and whatever the value of T_R, three reactions were observed (Table I): (i) double-bond shift with exchange of a deuterium atom in the allylic position between the butene molecule and alumina, i.e.,

$$CD_3CH{=}CHCD_3 \xrightarrow{-D,\ +H} CD_2{=}CHCH_2CD$$

(ii) cis–trans isomerization with exchange of a deuterium atom in the vinylic position, i.e.,

$$cis\text{-}CH_3CD{=}CDCH_3 \xrightarrow{-D,\ +H} trans\text{-}CH_3CH{=}CDCH_3$$

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[19] Kijenski, J.; Baiker, A. *Catal. Today* **1989**, *5*, 1–119.

[20] Weisz, P. B. *Adv. Catal.* **1962**, *13*, 137–190.

[21] Forni, L. *Catal. Rev.—Sci. Eng.* **1973**, *2*, 65–115.

[22] Jacobs, P. A. *Characterization of heterogeneous catalysts*; Delannay, F., Ed.; Chemical Industries 15; M. Dekker, Inc.: New York and Basel, 1984; pp 367–404.

[23] Perot, G.; Lemberton, J. L.; Guisnet, M. *Bull. Soc. Chim. Fr.* **1977**, 357–361.

[24] Mihindou-Koumba, P. C.; Lemberton, J. L.; Perot, G.; Guisnet, M. *New J. Chem.* **1984**, *8*, 31–35.

[25] Lemberton, J. L.; Perot, G.; Guisnet, M.; Maurel, R. *Bull. Soc. Chim. Fr.* **1976**, 359–361.

[26] Medema, J. *J. Catal.* **1975**, *37*, 91–99.

[27] Perot, G.; Guisnet, M.; Maurel, R. *J. Catal.* **1976**, *41*, 14–21.

[28] Guisnet, M.; Lemberton, J. L.; Perot, G.; Maurel, R. *J. Catal.* **1977**, *48*, 166–176.

[29] Lemberton, J. L.; Perot, G.; Guisnet, M. *J. Chem. Res., Synop.* **1979**, 94–95; *J. Chem. Res., miniprint* **1979**, 1290–1297.

[30] Lemberton, J. L.; Perot, G.; Guisnet, M. *Proc. Int. Congr. Catal, 7th* **1980**, 993–1005.

[31] Peri, J. B. *J. Phys. Chem.* **1965**, *69*, 220–230.

[32] Knozinger, H.; Ratnasamy, P. *Catal. Rev.—Sci. Eng.* **1978**, *17*, 31.

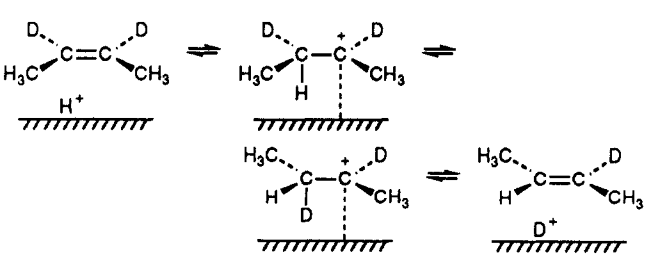
Table I
Isomerization of Deuterated *cis*-Butenes on Alumina. Effect of Drying and Reaction Temperatures (T_P and T_R)

			starting material					
			[2,3-D_2]		[1,4-D_6]		poisoning effect	
T_P, °C	T_R, °C	products	ID,[a] %	IE[b]	ID, %	IE	NH_3	CO_2
500	250	1-butene	100 (D_2)	1.0	100 (D_5)	1.8	yes	no
		trans-butene	25 (D_1) 75 (D_2)	1.2	100 (D_6)	1.6	yes yes	no yes
580	250	1-butene	100 (D_2)	1.0	95 (D_5) 5 (D_6)	1.6	yes	no
		trans-butene	50 (D_1) 50 (D_2)	1.4	100 (D_6)	1.3	yes yes	no yes
580	85	1-butene	100 (D_2)	1.0	100 (D_6)	3.0	yes	yes
		trans-butene	100 (D_2)	1.0	100 (D_6)	3.0	yes	yes

[a] ID = isotope distribution. [b] IE = isotope effect.

and (iii) cis–trans isomerization without exchange.

Reaction iii was poisoned both by NH_3 and by CO_2 (Table I), which shows that it occurs through acid–base bifunctional catalysis. The significant isotope effect observed in the allylic position (2.5) indicates that a C–H bond scission occurs in this position, the intermediates being allylic species. The active sites are probably exposed aluminum ions, weakly acid, associated with neighboring oxide ions which are weakly basic (due to the proximity of the anionic vacancy). These aluminum and oxide ions would be too weak to act separately. Isomerization therefore occurs with the simultaneous intervention of these centers, which precludes the formation of 1-butene from 2-butene. The rates of the reactions occurring with exchange (i and ii) were not modified by CO_2 but were reduced to the same extent by NH_3 (Table I). This shows that these reactions occur through the same mechanism involving protonic acid sites (but not basic sites) as active sites and carbenium ions as intermediates. In agreement with this, a significant isotope effect (1.8) was found in the allylic position for double-bond shift and in the vinylic position for cis–trans isomerization. An interesting point is that through this mechanism *cis*-butene-d_2 leads exclusively to *trans*-butene-d_1. This means that both the addition of a proton of alumina to *cis*-butene and the abstraction of a proton from the *sec*-butyl carbenium ion occur on the side of the molecule facing the catalyst surface[28] (stereospecific mechanism). This stereospecificity is obviously a particularity of heterogeneous catalysis.



The same reactions were observed at 250 °C with alumina pretreated at 580 °C, cis–trans isomerization without exchange being, however, more significant. Moreover, a very small percentage of double-bond shift occurs without exchange. The activity of this alumina was about 10 times greater than after pretreatment at 500 °C, which made it possible to study butene transformation at lower reaction temperatures T_R. A decrease in T_R caused a strong decrease in the proportion of isomerization with exchange (greater activation energy). For T_R = 85 °C, only double-bond shift and cis–trans isomerization without exchange were observed. Both reactions occurred with the same significant isotope effect in the allylic position (3.0) and were poisoned by CO_2 and by NH_3 (Table I). Whatever the poison, the rates of the double-bond shift and of the cis–trans isomerization were affected to the same extent. These reactions occur therefore through the same allylic intermediates formed on acid–base pair sites. Since these sites are stronger than those of alumina pretreated at $T_P < 500$°C, π-allylic species as well as σ-allylic species are formed. These species allow both double-bond shift and cis–trans isomerization.

The transformation of selectively deuterated butenes allows, due to the reactions observed, determination of the nature of the active sites: protonic sites or acid–base pair sites. This model reaction is therefore well-adapted for the characterization of the sites of amphoteric solids. Its complexity is but apparent. Indeed, the synthesis of the labeled butenes[33] and the analysis of the reaction products by mass spectrometry are simple. It must be emphasized that it was only by using deuterated reactants that the existence of protonic acid sites on the alumina surface was proved. Indeed, IR bands corresponding to pyridinium ions were never observed after adsorption of pyridine on alumina.[34]

Characterization of the Acid Strength of Protonic Sites

Model reactions can also be used for characterizing the strength of the active sites of a given solid provided a relation between their rate and the acid strength is established. To obtain this relation, two procedures have been generally employed: measurement of the activity (i) of a series of solids differing by the strength of their acid sites and (ii) of one solid whose acid sites are poisoned to different degrees. The change in the activity of protonic acid sites as a function of their strength was established for a large range of reactions (Table II) by using the second procedure.[35] Three criteria guided the choice of the reactions:

1. The reactions chosen were known to occur through catalysis on protonic acid sites without participation of basic sites or of Lewis acid sites.

2. The reactants or the products did not cause any modification of the catalyst acidity. This is why hy-

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[33] Plouzennec-Houé, I.; Lemberton, J. L.; Perot, G.; Guisnet, M. *Synthesis* **1983**, 659–661.

[34] Knozinger, H. *Adv. Catal.* **1976**, *25*, 184–271.

[35] Bourdillon, G.; Gueguen, C.; Guisnet, M. *Appl. Catal.* **1990**, *61*, 123–139.

Table II
Hydrocarbon Transformations. Reaction Temperature T_R

reactant	T_R, °C	reactions
3,3-dimethyl-1-butene	200	skeletal isomerization
cyclohexene	200	skeletal isomerization hydrogen transfer[a]
2,2,4-trimethylpentane	350	cracking
2,4-dimethylpentane	350	isomerization cracking
2-methylpentane	400	isomerization cracking
n-hexane	400	isomerization cracking
o-xylene	350	isomerization disproportionation[a]
1,2,4-trimethylbenzene	350	isomerization disproportionation[a]

[a] Bimolecular.

drocarbon reactions were used exclusively, compounds with functional groups or their transformation products (e.g., alcohols and water) often modifying the acidity of the catalyst (e.g., transformation of Lewis into Brönsted acid sites by water). However, the formation of heavy secondary products (coke) which causes catalyst deactivation by blocking access of the reactant to the active sites or by poisoning them cannot be totally avoided. The deactivation was hence limited due to an adequate choice of operating conditions. Consequently the initial rate was able to be determined accurately.

3. The reactions differed largely by their rate and therefore required sites of very different strengths for their catalysis. For instance, the isomerization of 3,3-dimethyl-1-butene occurs rapidly at low temperatures on weak acid catalysts such as alumina whereas the isomerization and cracking of *n*-hexane occur at high temperatures and/or on very strong acid catalysts. The difference between the reaction rates was so great (at 350 °C, 3,3-dimethyl-1-butene is about 200 000 times more reactive than *n*-hexane) that different temperatures (Table II) had to be chosen to avoid diffusion limitations.

Pyridine, stable up to at least 550 °C, was chosen as a poison. The catalyst employed (a stabilized HY zeolite) presented protonic sites with very different strengths. It had not only a large number of weak acid sites but also very strong ones (conserving pyridine quasi irreversibly adsorbed above 550 °C). The strength of the active sites was characterized by the temperature up to which they conserved the adsorbed pyridine. Indeed, the stronger the acid site, the more difficult to desorb the basic poison.

Figure 1 shows how the rates of the slowest and fastest reactions studied (3,3-dimethyl-1-butene and *n*-hexane transformations at 200 and 400 °C, respectively) changed as a function of the temperature of pyridine desorption T_D. For all reactions, the higher T_D, the greater the residual activity A_R (ratio of the activities of the poisoned to the fresh catalysts). The minimum strength that an acid site requires to be active can be estimated by means of T_{D0}, i.e., the value of T_D above which the activity can be measured. A great difference (300 °C) was found between the values of T_{D0} for 3,3-dimethyl-1-butene isomerization (T_{D0} = 220 °C) and *n*-hexane transformation (T_{D0} = 520 °C). In general, the lower the rate of a reaction, the greater the strength required for its catalysis. However, the rates of aromatic transformations were greater than expected from the T_{D0} values (Figure 2). This could be due to the greater basicity of aromatic hydrocarbons. The concentration of adsorbed intermediates would be therefore greater and the apparent reaction rate higher though the rate constant of the limiting step is probably smaller.

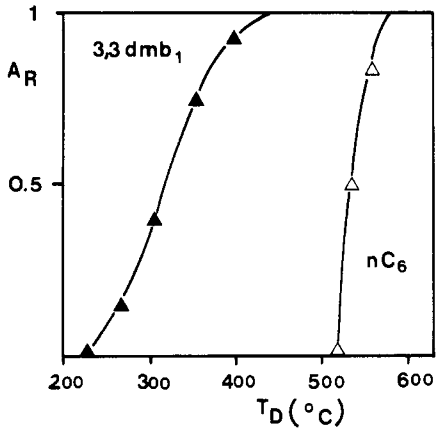

Figure 1. Influence of the temperature of pyridine desorption (T_D) on the residual activity (A_R) of HY for the transformation of 3,3-dimethyl-1-butene (3,3dmb$_1$) and of *n*-hexane (nC$_6$).

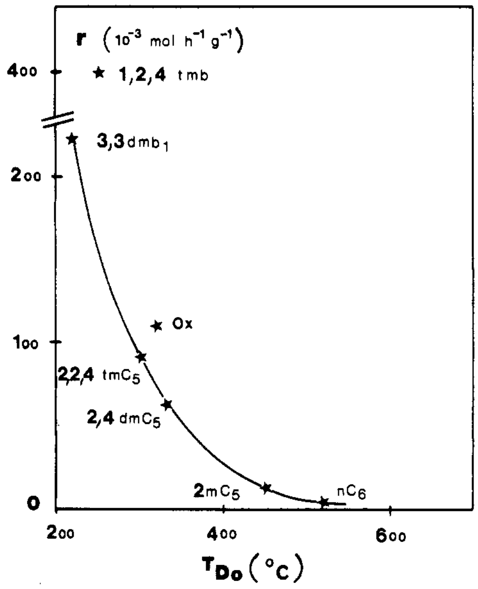

Figure 2. Transformations of various hydrocarbons on a stabilized HY zeolite. Reaction rate *r* versus acid strength required. T_{D0} = minimum temperature of pyridine desorption for measurable rate. nC$_6$ = *n*-hexane; 2mC$_5$ = 2-methylpentane; 2,4dmC$_5$ = 2,4-dimethylpentane; 2,2,4tmC$_5$ = trimethylpentane; ox = *o*-xylene; 1,2,4tmb = 1,2,4-trimethylbenzene; 3,3dmb$_1$ = 3,3-dimethyl-1-butene.

A fact that may seem strange is that with the most facile reactions A_R became close to 1 for relatively low T_D values (400–420 °C for 3,3-dimethyl-1-butene isomerization (Figure 1)), which seems to show that strong acid sites were not active in these reactions. This is due to the procedure employed: the activities of the fresh and poisoned catalysts were compared after 30 min of reaction. During this period of time, a significant amount of coke was formed, causing deactivation of the zeolite. It was demonstrated elsewhere that the first coke molecules were formed on the strongest acid sites.[36] Indeed, a decrease as a function of coke content in the

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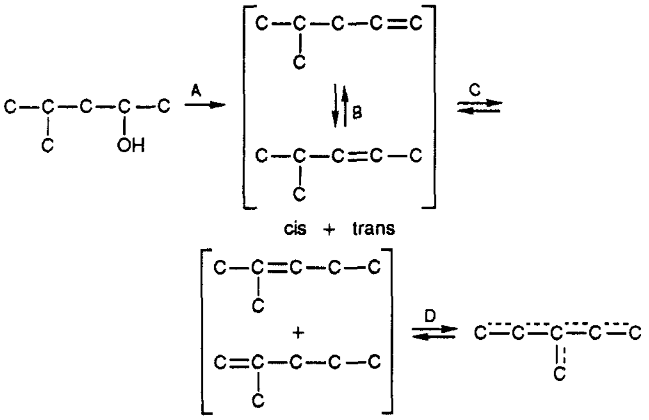
(36) Magnoux, P.; Cartraud, P.; Mignard, S.; Guisnet, M. *J. Catal.* **1987**, *106*, 235–241.

number and strength of the acid sites of coked Y zeolite samples was shown by ammonia adsorption followed by calorimetry. The strongest sites (for which the heat of NH_3 adsorption was the greatest) were the first affected while the weakest acid sites were practically not affected. Therefore the deactivation that occurred during the first 30 min of reaction did not hamper in any way the measurement of A_R for T_D values close to T_{D0}.

This series of reactions can be used to characterize the strength of acid solids. Thus, a solid that catalyzes only the isomerization of 3,3-dimethyl-1-butene has only weak protonic sites capable of retaining pyridine adsorbed at least up to 220 °C (T_{D0} for this reaction) but below 250 °C (T_{D0} for the transformation of 1,2,4-trimethylbenzene). A solid that can catalyze the whole series of reactions presents very strong active sites capable of retaining adsorbed pyridine at least up to 520 °C.

Other series of reactions have been proposed for characterizing the acid strength of solids.[37–40] However, each series comprises reactions that either involve reactants or products capable of modifying the acidity of the catalyst or can be catalyzed by sites other than protonic acid sites. The result is that these series are suitable only for the characterization of acid solids similar to those used for establishing the classification in acid strength. This is in particular the case for the successive transformations of 4-methylpentanol which have been classified by Damon et al.[38,39] as functions of H_R (the acidity function introduced by Deno et al.[42] for acid solutions).



Reaction A leads to water, which can transform Lewis sites into Brönsted sites, and reactions B and C can be catalyzed by acid, acid–base, and even base sites.

Since the rate of a reaction depends on operating conditions, this must also be the case for the acid strength required for catalysis. This was actually found for cyclohexene transformation. The higher the reaction temperature (hence the greater the reaction rate), the lower the T_{D0} value.[42] It is therefore possible with one single reaction carried out at various temperatures to characterize the strength of the protonic sites of acid catalysts. This effect of operating conditions on the acid strength required for catalyzing a reaction also shows that the conditions in which model reactions are carried out must be clearly specified.

Besides the simple determination of the acid strength of solids, the distribution in strength of their sites can be obtained. For this, Yoneda proposed a method he called "regional" analysis.[43] He classified the acid sites into different "regions" according to their strength characterized by H_0 values (H_0: Hammett acidity function[44]). The average intrinsic activity of the sites of each "region" was evaluated from the overall rates on a series of catalysis. However, this method does not allow differentiation between Brönsted and Lewis acid sites. To make this differentiation possible, the distribution of protonic sites of the stabilized HY zeolite used for obtaining T_{D0} values was determined by adsorption of pyridine followed by infrared spectroscopy. This technique, whose limitations were emphasized in the case of alumina, is perfectly adapted for the characterization of the acidity of solids possessing many acid sites such as stabilized HY zeolites. From the changes of the number of protonic sites and of the activities of the stabilized HY zeolites as functions of T_D, the intrinsic activities of the protonic sites were evaluated as a function of their strength.[45] The average turnover number value N of protonic sites from which pyridine desorbs between T_{D1} and T_{D2} is equal to

$$N_{T_{D1}}^{T_{D2}} = \frac{\Delta A}{\Delta n}$$

where Δn is the number of protonic sites from which pyridine desorbs between T_{D1} and T_{D2} and ΔA the activity resulting from these sites.

Obviously, this calculation is valid only when the reaction considered requires only one acid site for its catalysis. This is generally the case for monomolecular reactions but not from bimolecular reactions, which seem to require several acid sites for their catalysis.[5–9] Moreover, because of the deactivating effect of coke on the strongest acid sites, only the sites for which T_D was close to T_{D0} were considered. N increases significantly with the acid strength. Thus a site with T_D = 300 °C isomerizes about 10 times more molecules of 3,3-dimethyl-1-butene than a site with T_D = 240 °C.

The distribution of the protonic sites of a given catalyst can be obtained from $N = f(T_D)$ and from the activity of the catalyst in various reactions. This is shown below in the simple example of a catalyst active for 3,3-dimethyl-1-butene isomerization (T_{D0} = 220 °C) and for 1,2,4-trimethylbenzene isomerization (T_{D0} = 250 °C) but inactive for isooctane cracking (T_{D0} = 300 °C). Its inactivity for this latter reaction means that the catalyst has no protonic sites capable of retaining pyridine adsorbed above 300 °C. The rates of 3,3-dimethyl-1-butene and 1,2,4-trimethylbenzene isomerizations (r_1 and r_2) can be written as

$$r_1 = \bar{N}_1{}_{220}^{250} \times n_{220}^{250} + \bar{N}_1{}_{250}^{300} \times n_{250}^{300}$$

$$r_2 = \bar{N}_2{}_{250}^{300}\, n_{250}^{300}$$

in which the values of r_1, r_2, and $\bar{N}$ are known. From

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(37) Misono, M.; Saito, Y.; Yoneda, Y. *Proc. Int. Congr. Catal., 3rd* **1964**, 408–421.

(38) Damon, J. P.; Bonnier, J. M.; Delmon, B. *Bull. Soc. Chim. Fr.* **1975**, 449–452; *J. Colloid Interface Sci.* **1976**, *55*, 381–387.

(39) Damon, J. P.; Delmon, B.; Bonnier, J. M. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 372–380.

(40) Jacobs, P. A. *Carboniogenic Activity of Zeolites*; Elsevier: Amsterdam, 1977.

(41) Deno, N. C.; Berkheimer, H. E.; Evans, W. L.; Peterson, H. J. *J. Am. Chem. Soc.* **1959**, *81*, 2344–2347.

(42) Gallet, A. Ph.D. Thesis No. 231, Université de Poitiers, 1986.

(43) Yoneda, Y. *J. Catal.* **1967**, *9*, 51–56.

(44) Hammett, L. P.; Deyrup, A. J. *J. Am. Chem. Soc.* **1932**, *54*, 2721–2727.

(45) Bourdillon, G. Ph.D. Thesis No. 208, Université de Poitiers, 1985.

these equations it is easy to deduce n_{220}^{250} and n_{250}^{300}, i.e., the distribution in strength of the protonic acid sites of the catalyst.

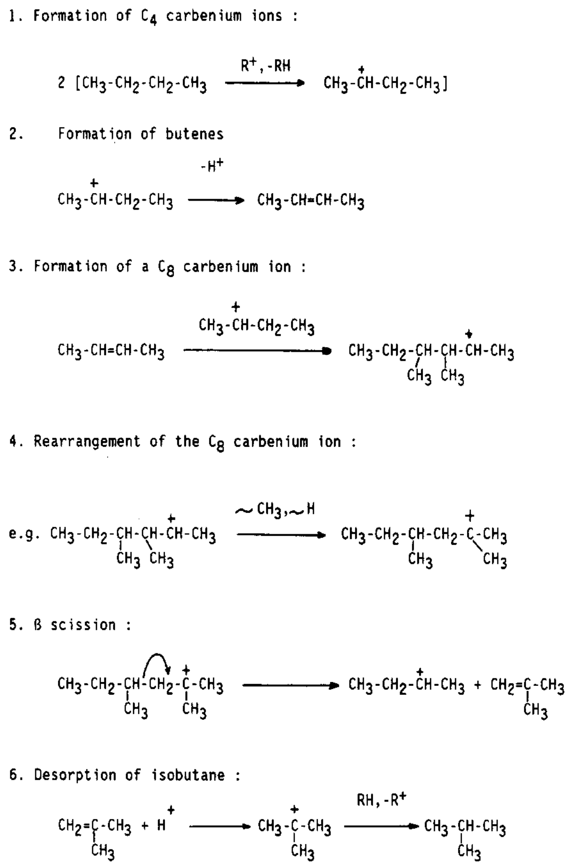
Characterization of the Density of the Acid Sites

The strength of the protonic sites is not the only parameter that determines their intrinsic activity. Their density (or inversely the distance between sites) seems to be an important parameter in the case of certain bimolecular reactions. This effect of site density on the activity, well-known in metallic catalysis (the so-called structure-sensitive reactions[46]), was shown only recently in acid catalysis due to the use of zeolites. Indeed, in these perfectly crystallized solids, the location of the acid sites is well-known and the site density can be easily modified through ion exchange or dealumination. However, other characteristics of the acidity will be affected also. Thus the strength of the acid sites will increase or remain constant according to the degree of dealumination.[47]

n-Heptane cracking was studied at 350 °C on two protonic Y zeolites with framework Si/Al ratios to 3 (HY3) and 35 (HY35).[8] The total number of acid sites, deduced from the unit cell formula, was equal to 25 × 10^{20} (HY3) and 2 × 10^{20} (HY35) per gram of zeolite. Although the acid sites of HY35 were stronger than those of HY3, their cracking activity was about 7 times smaller, which can only be explained by an effect of the site density. Moreover, the selectivities of the zeolites were completely different. For HY3, the product distribution was the one than could be expected with the classical carbenium ion chain mechanism, i.e., a quasi-equimolar mixture of C_3 and isoC_4 with a low olefin/alkane ratio. For HY35 there were besides C_3 and C_4 large amounts of C_1, C_2, and hydrogen, the cracking products being mainly olefinic (olefin/alkane = 2.5). However, in both cases, pyridine poisoned the active sites, which were therefore acidic, the poisoning effect being more pronounced on HY35, the zeolite that had the strongest acid sites. A monomolecular mechanism with carbonium ion intermediates was proposed to explain the product distribution on HY35. The change in mechanism could be due to the difficulty of forming carbenium ions through intermolecular hydride transfer on the isolated sites of low alumina content zeolites.[8]

The study of *m*-xylene transformation on the same zeolites shows that while the density of acid sites practically did not affect the isomerization rate, it had a significant effect on the rate of disproportionation into benzene and trimethylbenzenes. The disproportionation activity of the sites of HY35 was 30 times lower than that of HY3. It was concluded that the bimolecular reaction of disproportionation demanded adjacent acid sites for its catalysis while the monomolecular reaction of isomerization could occur on isolated acid sites.[48]

Contrary to C_5^+ alkane isomerization, butane isomerization on acid catalysts does not occur intramolecularly but through a disproportionation process. This was shown by (i) the simultaneous formation of C_3 and C_5 in equimolar amounts,[49] (ii) the reaction order equal to 2 with respect to butane both for isomerization and for the formation of C_3 + C_5,[49] and (iii) the ^{13}C content of the products resulting from [1-^{13}C]- or [2-^{13}C]isobutane transformation[50] (these products contained not only monolabeled species but also nonlabeled and bilabeled species).



R^+ : preexisting carbenium ion ; ~CH_3 : alkylshift , ~H : hydride shift

Figure 3. Mechanism of *n*-butane isomerization on H mordenites.

A mechanism involving as the rate-limiting step the formation of a C_8 carbenium ion through alkylation of a molecule of butene by a butyl carbenium ion was proposed. This C_8 carbenium ion underwent rearrangement steps and then *β* scission (Figure 3).

The butane transformation rates were measured over a series of protonic mordenites prepared by dealumination.[7] The Si/Al ratio of the samples varied from 7.5 to 110 and the total number of acid sites from 11 to 0.8 × 10^{20} per gram of zeolite. There was practically no difference in strength between the acid sites of the various samples. However, the activity per acid site depended very much on the sample. The greater the Si/Al ratio (hence the lower the density of the acid sites), the smaller their activity. The mordenite activity being roughly proportional to the square of the total number of acid sites, it was suggested that butane disproportionation required two acid sites for its catalysis.[7] This is in good agreement with the mechanism proposed above (Figure 3), which implies the formation of two carbenium ions in C_4 (step 1), one that is transformed into butene (step 2), the other reacting with butene to form a C_8 carbenium ion (step 3).

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(46) Boudart, M. *Adv. Catal.* **1969**, *20*, 153–166.

(47) Barthomeuf, D. *Mater. Chem. Phys.* **1987**, *17*, 49–71.

(48) Benamar, A.; Miloudi, A.; Gnep, N. S.; Guisnet, M., to be published.

(49) Bearez, C.; Chevalier, F.; Guisnet, M. *React. Kinet. Catal. Lett.* **1983**, *22*, 405–409.

(50) Bearez, C.; Avendano, F.; Chevalier, F.; Guisnet, M. *Bull. Soc. Chim. Fr.* **1985**, 346–348.

The rate of bimolecular reactions being dependent on the acid site density, and that of monomolecular reactions being independent, the ratio of these rates can be used for the characterization of the acid site density. Obviously it will be easy to use one single model molecule transforming through two main reactions: one bimolecular and the other monomolecular. In every case, the rate ratio will be characteristic of the acid site density only if the rates depend in the same way on the acid strength. It is the case for the disproportionation and the isomerization of xylenes[35] and the disproportionation/isomerization rate ratio which characterizes very well the acid site density.

Conclusions

Model reactions constitute an efficient means not only for checking the suitability of solid acids as catalysts but also for characterizing all the parameters of the surface acidity:

1. Thus through isomerization of [2,3-D_2]- and [1,4-D_6]-*cis*-butenes, the existence on the alumina surface of three different types of active sites (Brönsted acid sites and weak and strong Lewis acid–base pair sites) responsible for three different reactions was demonstrated. Physicochemical methods that are usually employed for characterizing the acidity of solids did not succeed in detecting the protonic acid sites of alumina.

2. The strength of the protonic acid sites of solids can be estimated by measuring their activity in a series of hydrocarbon reactions that were previously classified as functions of the acid strength required for their catalysis. The great difference in the rates of the chosen reactions (hence in the minimum strength the acid sites must possess to be active) makes it possible to characterize solids with weak acidity as well as those with very strong acidity.

3. The intrinsic activities of the protonic sites were determined, as functions of their strength, in monomolecular reactions of the series. The distribution in strength of the protonic sites of a given solid can be established from this information and from the activity of the solid for the reactions.

4. The density of the acid sites of a solid (or the distance between these sites) can be estimated from the ratio of the rates of a bimolecular (demanding) reaction and of a monomolecular reaction requiring for their catalysis acid sites of similar strength.

A certain number of conditions must, however, be satisfied in order to obtain valid information.[4] Obviously, the operating conditions of the model reactions must be rigorously similar to those for which relations between rates and acid site properties were established. The rate or the selectivity of the reaction must be measured on the solid catalyst before any modification of its surface (e.g., by coke deposit). Obviously, it is necessary to check that the reaction is not limited by external or internal heat or mass transport phenomena.[51] Thus diffusion limitations inside porous catalysts can be considered as negligible for isothermal reactions if the dimensionless group rR^2/cD_e is smaller than 1. r is the reaction rate, c the concentration of the reactant, R the radius of the catalyst particles, and D_e the effective diffusivity of the reactant in the porous catalyst. Moreover, the reactant must be free of any impurities that have either an inhibiting or a promoting effect.

An important point to emphasize is that only the *active* sites can be characterized. Thus model reactions proposed for characterizing the strength and density of the acid sites occurring on Brönsted acid sites give information concerning only these sites. It is a great challenge to develop model reactions for characterizing Lewis acid sites and above all acid–base pair sites which play a significant role in many reactions of functional compounds.

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(51) Smith, J. M. *Chemical Engineering Kinetics*; McGraw Hill Book Company: New York, 1970.