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KEYNOTES IN ENERGY-RELATED CATALYSIS

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INTRODUCTION

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It is accepted today that the synthesis, structure elucidation and catalytic property assessment of ZSM-5 and other pentasil zeolites constitute a major milestone in the history of catalysis. These catalysts may indeed be viewed as providing an ultimate form of shape selectivity as the precise size and geometry of their pores are such that the hydrocarbons grown on their strong Bronsted acid sites cannot exceed the size of the small aromatics present in gasoline. Such a spectacular property, which is related to the so called product shape selectivity (ref. 1), is however not the only asset of these zeolites. What may be even more important for practical applications is the fact that the inner acid sites are protected against deactivation by polyaromatic coke. This property is associated with transition state restriction shape selectivity. In other words the monoaromatic carbenium ion cannot give rise to a diaromatic carbenium ion intermediate inside the ZSM-5 pore lattice due to steric constraints imposed on the size of the transition complex in this reaction. As a consequence, the rapid deactivation by coking observed for acid sites located in the wider cavities of large pore zeolites, and which is the origin of the great complexity of cat-cracker technology, does not happen with pentasil zeolites.

It is therefore not surprising that such possibilities have inspired many catalyst designers around the world, and have triggered a whole flurry of new ideas for the synthesis of novel catalysts produced by modifying the ZSM-5 as well as other zeolites. The aims of these modifications have been to affect acid sites, particularly their strength and spatial distribution, to tune-up specific shape selective properties by modifying the pore geometry, or to design multifunctional catalysts by associating the zeolite with some other catalyst. In this last case, the example which comes to mind is the preparation of a shape selective Fischer-Tropsch catalyst by combining a syngas conversion catalytic function with a ZSM-5 zeolite (ref. 2). There are however many more examples in the current literature and one can predict that many more will appear in the future. This book is an attempt to critically review the current trends in the various subfields of catalytic science which may serve as a rational basis for the design of such new kinds of catalysts. Among these subfields, catalysis by solid acids is of prime interest and is therefore the object of chapter 1. In this chapter the emphasis has been placed on the acidic properties of zeolites, their definitions and measurements, and their relation to structure and catalytic properties especially in the reactions of hydrocarbons. In addition, the various theoretical approaches to the description of

acidity in solids have been taken into consideration. These include quantum mechanical calculations as well as the Sanderson electronegativity approach. Chapters 2 and 3 both deal with solid catalysts in which surface acid sites are located in spatially restricted environments, namely pillared clays and heteropoly-acids respectively. These relatively new fields both have the potential to generate new experimental knowledge and new model systems for the comprehension of heterogeneous acid catalysis and shape selectivity. In that respect these first three chapters constitute a coherent ensemble.

As the shape selectivity of ZSM-5 provides a means for imposing a controlled deviation from the Anderson-Schulz-Flory molecular size distribution in Fischer-Tropsch syntheses, multifunctional catalysts combining ZSM-5 with a CO hydrogenation function are of significant interest. It was therefore considered appropriate to include in this book a chapter reviewing the current trends in carbon monoxide hydrogenation, and this is the object of chapter 4. Zeolites have also been utilized as supports for heterogenized homogeneous catalysts. One of the best examples of this is probably the heterogeneous counterpart for the Monsanto homogeneous methanol carbonylation catalyst, namely Y zeolite supported rhodium promoted by methyl iodide (ref. 3). Since many more new catalysts can be similarly designed, chapter 5 intends to give the reader an overview of the fast growing field of industrial homogeneous catalysis by transition metal complexes. Moreover, as the subject of chapter 5 is restricted to processes involving CO and H_2, chapters 4 and 5 all together may be viewed as a more or less complete coverage of catalytic reactions involving these two gases.

Chapters 6 and 7 also deal with complementary and sometimes overlapping subjects. Chapter 6 covers the field of metal clusters in all zeolites, whereas chapter 7 reviews the literature on the various chemical modifications specifically for the ZSM-5 zeolite. Zeolites have the ability to stabilize small metal particles and this is of fundamental significance in catalysis as a means of providing a stable and high dispersion of metal. Moreover, as small particles have surface properties different from those of the bulkier metal, unusual catalytic properties may be expected for metallic clusters. As these properties can be affected by interactions with the zeolite lattice or combined with its shape selective and acidic properties, many new solids can be prepared both as model or industrial catalysts. Similarly, many new catalyst preparations can be obtained by chemical modifications of zeolites. Isomorphous substitutions in framework positions, alumination and dealumination, post-synthesis modifications affecting acidity or pore geometry, partial or complete ion exchange and intimate combinations with dispersed foreign materials are all examples of such modifications.

With the possible exceptions of chapters 2, 3 and 7, the topics covered in this book have been the objects of previous monographs or review articles. The particular goal set for each chapter was therefore to present the personal views of

an expert, or a small group of experts, on the current state of the art and on the trends in his field likely to lead to important developments. The presentation and discussion of personal works were therefore encouraged. It is hoped that the gathering of these various keynotes in one volume, will provide an inspiration to the reader interested in the development of zeolite based catalysts for energy applications, and in particular will suggest to the new-comer to the field of cata- lyst design, methods to develop his own original orientations.

This book is intended for researchers and advanced students in the field of catalysis. At this point however the reader not familiar with this science and its numerous applications may wonder why catalysis by solid acids, like zeolites and the modifications of these solids, are of special relevance to energy applications. Acid catalysis, currently plays a major role in modern petroleum refining opera- tions. Such large scale processes as Fluid Catalytic Cracking, Catalytic Reforming, Alkylation, Olefins Oligomerization and many others, rely on the ability of acid catalysts to transform hydrocarbons.

Zeolites and modified zeolites are therefore obviously essential to the im- provement of existing processes and to technical innovations for the conversion of conventional crude oil. An example of recent such innovation is the Mobil lube dewaxing process which uses the molecular sieve properties of the zeolite ZSM-5 to selectively hydrocrack the n-paraffins in lubricating oils, thus diminishing their pour point. Another example of potential application is provided by the capacity of bifunctional catalysts like Pt HZSM-5 to convert small alkanes, like those found in liquid petroleum gas or in the natural gas liquids, to gasoline range hydrocar- bons.

Modified zeolites will also find numerous applications in the synthesis of chemicals now derived from petroleum, either by improving present processes or by using alternate sources of carbon. Examples are numerous in both cases. One can mention the Mobil-Badger process for benzene alkylation which uses ZSM-5 for the synthesis of ethyl benzene and replaces the now obsolete Friedel-Craft liquid phase alkylation. It has also been shown that para ethyltoluene could be produced by alkylation of ethylbenzene with methanol on modified ZSM-5 with a selectivity higher than 97%. Many other examples will be found in this book regarding the synthesis of oxygenated compounds such as alcohols, aldehydes, ketones and carbo- xylic acids, using small molecules like CO, H_2, C_2H_4, CH_3OH as reactants and it will be shown that in many cases the catalysts would be supported or hetero- genized over zeolite materials.

The methanol to gasoline process, demonstrated in the late seventies, was certainly a major technological breakthrough utilizing the zeolite ZSM-5. Indeed as methanol is synthesized from syngas, which way be derived from coal or natural gas, the MTG process opened a new indirect route to convert these two feedstocks into gasoline. Since that time, as discussed in Chapters 6 and 7, many

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modidications of ZSM-5 have been shown at laboratory scale to allow the direct conversion of syngas to gasoline. Other such modifications allow the conversion of methanol to small olefins. All these results provide possible routes for the up-grading of extremely abundant fossil carbon sources like coal and natural gas.

Moreover methanol conversion may be considered as only one example of a conversion of an oxygenated organic compound to hydrocarbons. ZSM-5 derived catalysts allow such conversions for a very large variety of such oxygenates and as a consequence they are of enormous potential use in the conversion of biomass derived compounds to hydrocarbons.

For all these reasons there is little doubt that zeolite based catalysts will play a major role in the future management of fossil fuels and biomass. It is hoped that this book will contribute to tomorrow's achievements in this area.

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Chapter 1

RELATION BETWEEN ACIDIC AND CATALYTIC PROPERTIES OF ZEOLITES

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· 1.1 ACIDITY DEFINITION AND MEASUREMENT

The acidity of solids is usually interpreted in terms of proton donor capacity - Bronsted acidity (ref. 1) or as electron acceptor capacity - Lewis acidity (2). Basic sites in solids can also be utilised in catalysis.

1.1.1 <u>Bronsted Acidity and Acidity Functions</u> (H_O, H_R)

In homogeneous systems (aqueous and non-aqueous) a quantitative measure of protic acidity may be provided by an acidity parameter (3). For a weak base 'B' the parameter H_O is defined as follows.

$$BH^+ \rightleftharpoons B + H^+ \tag{1}$$

$$K_{BH^+} = a_B a_{H^+}/a_{BH^+} = [B]/[BH^+] \, (a_{H^+} f_B/f_{BH^+}) \tag{2}$$

where a_i is activity, f_i activity coefficient and $[\ ]$ is concentration.

$$K_{BH^+}[BH^+]/[B] = a_{H^+} f_B/f_{BH^+} \tag{3}$$

and
$$H_O \equiv pK_{BH^+} - \log([BH^+]/[B])$$

$$= - \log(a_{H^+} \, f_B/f_{BH^+}) \tag{4}$$

In dilute solution ($f_B/f_{BH^+} = 1$) and $H_O \equiv pH$.

For equal concentrations of free and protonated base $H_O = pK_{BH^+}$ and, since for a weak base the equilibrium in (1) is on the product side, pK_{BH^+} is a negative number ($H_O < 1$). Extensive protonation of B gives $H_O < pK_{BH^+}$.

Some typical values of H_O for homogeneous solutions are given in Table 1.1

Table 1.1   HAMMETT FUNCTIONS$^{(a)}$ $-(H_o)$

Acid	$-H_o$	Classification
HCOOH	2.2	WEAK
H_3PO_4	5.0	
H_2SO_4 (98%)	9.36	STRONG
HSO_3F	12.8	
TaF_5 (10 mol%)/HF	18.85	SUPERACIDS
SbF_5 (10 mol%)/HF	24.33	

(a)   From ref 3

Typically (4,5) acids with $-H_o < 5$ are classified as weak acids.   Those with $-H_o$ = 8.2-12.8 as strong acids and for superacids $-H_o > 16.8$, although these divisions, especially that for classification of superacidity, are arbitrary.

Superacids were initially, and arbitrarily, taken as acids with H_o less than that for 100% sulphuric acid (4).   Superacids are usually produced by adding a stronger acid to an initially strong acid or more commonly by adding a strong Lewis acid to a strong Bronsted acid in order to shift the autoprotonation equilibrium (5).

$$2HA + L \rightleftharpoons H_2A^+ + LA^-$$

In such cases there is a substantial increase in acidity (decrease in H_o) over that of pure HA.

1.1.2 Hammett indicators and the H_o scale

For two bases B_1 and B_2 reacting with acid solutions having the same strength (from eqn (2))

$$K_{B_1H^+}/K_{B_2H^+} = ([B_1]/[B_1H^+])/([B_2]/[B_2H^+]) \Big/ (f_{B_1}/f_{B_1}H^+)/(f_{B_2}/f_{B_2}/f_{B_2}H^+) \quad (5)$$

and is constant at fixed temperature. Hammett (3) assumed that, when B_1 and B_2 are sufficiently similar in structure, the ratio of the activity coefficients in a given solution is constant so that the ratio of K values can be obtained from experimentally measured concentration ratios. If the strongest base in the series (B_1) can be protonated in pure water, where $f_i \approx 1$, then K_{BH^+} can be calculated from equn (2). The base B_1 and a weaker base B_2 can then be protonated in a stronger acid (eg dilute H_2SO_4) where $f_i \neq 1$ but the ratio of activity coefficients in equn (5) is unity. From measured values of $[B_i]$ and $[B_iH^+]$, $K_{B_2H^+}$ can be calculated from $K_{B_1H^+}$. The weaker base B_2 can be used to determine $K_{B_3H^+}$ for a weaker base, B_3, using a stronger acid solution. In this way a range of Hammett indicators have been developed which facilitate the measurement of H_o in homogeneous systems using equation (3) which requires that $[BH^+]$ and $[B]$ should be measurable. The initial Hammett indicators were substituted primary aromatic amines

$$R_iNH_2 + H^+ \rightleftharpoons R_iNH_3^+$$

but others have been developed. The validity of H_o functions determined in this way depends upon the assumption that the activity coefficient ratio for different bases is constant in a given acid solution. This assumption implies that a plot of $\log [BH^+]/[B]$ vs H_o is linear (slope = -1.0) for the series of bases. Other acidity functions have since been developed based on other indicators, for example alkyl carbinols (6) which dissociate as,

$$ROH + H^+ \rightleftharpoons R^+ + H_2O$$

and generate (7) the function H_R

$$H_R = pK_A - \log([ROH]/[R^+])$$

An extensive discussion of acidity scales is available (8).

1.1.3 Lewis Acids

Whereas Bronsted acid-base interactions involve a common proton-transfer process there is no corresponding common process to provide a unique basis for comparison of the strengths of Lewis acids. Consequently the strength, or coordinating power of a Lewis acid cannot clearly be defined and, experimentally, its strength depends on the particular Lewis base. Specific preferential interactions are found of the kind incorporated into the classification (9) of donors and acceptors as type 'a' or 'b' and subsequently to the more general classification (10) into 'hard' and 'soft' with the development of the principle of hard and soft acids and bases (HSAB principle). The HSAB principle states that hard acids 'prefer' to bind to hard bases and soft acids 'prefer' soft bases. In very general terms soft acid-soft base interactions involve a significant covalent contribution whereas hard acid-hard base interactions involve less covalent and more electrostatic interactions. Consequently, in aqueous solution, Al^{3+} (hard acid) will bind to F^- (hard base) in preference to triphenyl phosphine (soft base) whereas Ag^+ (soft acid) will preferentially bind to the phosphine.

Theoretical approaches to HASB interactions have been made (11) which, although they are not completely satisfactory, do result in representation of the interaction energy in terms of an electrostatic and a covalent term. Large values for the electrostatic term are associated with pronounced hard-hard interaction and large values for the covalent term are expected for strong soft-soft interactions. A semi-quantitative approach to such interactions utilizes the enthalpies (ΔH) of formation of donor-acceptor molecules to estimate parameters which may be used to estimate contributions to ΔH of mainly electrostatic (E_i) and mainly covalent (C_i) terms (12). Attempts to quantify complexation of Lewis acids and bases via the use of donor numbers (DN) and acceptor numbers (AN) have also been made (13).

As with Bronsted acids, superacids of the Lewis type are known. These are taken arbitrarily as those Lewis acids stronger than $AlCl_3$ (5). The difficulty, outlined above, in defining the strength of a Lewis acid means that a unique scale cannot be generated. However, it is evident that some Lewis acids (eg SbF_5, AsF_5) have a greater ability to ionize alkyl halides than, for instance $AlCl_3$, and consequently are much more effective catalytically. Additionally, in spite of the above difficulties, a wide range of experimental investigations have resulted in an order of relative Lewis acidity for the MF_n type acids (5).