The Concept, Reality and Utility of Single-Site Heterogeneous Catalysts (SSHCs)

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The Concept, Reality and Utility of Single-Site Heterogeneous Catalysts (SSHCs)

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Abstract

Very substantial advances have recently been made in the design and construction of solid catalysts and in elucidating both their mode of operation and the factors that determine their selectivity and longevity. This Perspective explains how and why such progress has been made. One important factor, the deployment of single-site heterogeneous and enzymatic catalysts, used either alone or in conjunction with other strategies, including metabolic engineering, enables a multitude of new products (for example, environmentally clean jet fuel) to be readily manufactured. In a practical sense SSHCs enable the advantages of homogeneous and to a lesser degree enzymatic catalysts to be united with those of heterogeneous ones. With the aid of the vastly increasing families of nanoporous solids, desired catalytically active sites may be engineered in atomic detail on their inner, accessible surfaces, thereby opening up new possibilities in synthetic organic chemistry – as in the smooth formation of C-C and C=N bonds in a number of intermolecular reactions – as well as in photocatalysts and in fluidized catalytic cracking of hydrocarbons.

1. Introduction

Seven years ago, two eminent US scientists published[1] the following statement: *"Given the enormous importance of catalysis in the production and storage of energy, in the production of petrochemicals and the materials derived from them, and in all biological and most geochemical processes, it is astonishing (and a little disheartening) how little is known of the fundamentals of catalysis: how catalysts operate, how to control them, and especially how to generate new ones."*

Such has been the rapidity and richness of progress registered in the intervening years that it can now be fairly asserted that many, but not yet quite all, of the inadequacies identified in this statement are no longer valid. As we describe below, there has recently been a splendid surge of new catalysts of desired functionality, and of new methods (based on increased knowledge of the nature and construction of novel nanostructures) for generating them.

Moreover, recent advances in metabolic and bioengineering, exemplified by the work of Arnold[2,3] and Keasling[4,5] and their associates, have already led to dramatic new ways of producing transportation fuels (especially jet fuel and diesel) and commodity chemicals. In addition, the combined use of bioengineering and inorganic solid-state catalysis – as described fully elsewhere[6] and outlined in Section 5.1 below – has paved the way to the construction of new catalytic reactors and biorefineries, some of which are already operational.

In the realm of those catalysts which consist of close-packed, continuous solids, typified by metals, alloys and the majority of oxides, halides and chalcogenides, the "descriptor" approach pioneered by Norskov and collaborators[7] has proved invaluable. Advances in density functional theory (DFT) mean it is now possible to describe, using these descriptors, catalytic reactions at surfaces with the detail and accuracy required in computational results that compare favourably with experiment. Theoretical methods can now be used to describe surface chemical reactions with precision and to understand variations in catalytic activity from one catalyst to another.[8] To be specific, Norskov *et al*[7] have recently demonstrated that the results of kinetic models based on DFT calculations agree very closely with experimentally determined ones in (a) the oxidation of CO over RuO_2, (b) the synthesis of NH_3 over Ru and (c) the decomposition of methanol over Pt. In addition, they have identified preferred catalysts for the important industrial process of selective hydrogenation of acetylene and the synthesis of ethylene oxide.

Another major advance is the identification of the role of structural defects and lattice strain, as described by Behrens, Schlögl *et al*[9], in industrial-scale catalysts such as the copper-catalyzed synthesis of methanol. Such work has enlarged our knowledge of both how this catalyst operates and how to control its activity, selectivity and longevity.

There have been other, quite major recent advances that also merit elaboration in response to the Crabtree-Whitesides statement, cited above. We shall quote just two.

First, dramatic improvements have been made in the production of zeolitic catalysts. Thus, workers like the Garcia-Martinez[10-11] and Pérez-Ramirèz[12,13] have succeeded, by post synthesis modification, to produce hierarchical zeolites in which mesopores are introduced to the intrinsic micropores originally present, thus making them capable of processing larger molecules than hitherto. Such newly designed catalysts are vastly superior to the traditionally employed fluid catalytic cracking (FCC) catalysts, which have been used on a massive (megatonne) industrial scale since their introduction in petrochemical processes some 50 years ago. It has been estimated that some 40 percent of all heterogeneous catalysts used industrially are zeolitic.[14]

Second, as a result of inspired application[15] of the principles of solid state chemistry, known, as emphasized elsewhere[16], to be crucially important in the discovery and improvement of new catalysts, great progress has been made in generating powerful new catalysts. Thus, the environmentally attractive method of producing Cl_2 (a vital component for the production of certain vinyl polymers and bleaching agents) from aerial oxidation of hydrochloric acid ($4HCl + O_2 \longrightarrow 2Cl_2 + H_2$), as was first done 180 years ago in the now defunct Deacon process, has been resurrected using a designed $CuCrO_2$ heterogeneous catalyst. This catalyst is closely-related to the mineral delafossite, and Pérez-Ramirèz *et al* [15] have shown it to provide an industrial method of producing Cl_2 that is superior to the environmentally aggressive and energetically demanding, as well as expensive, electrolytic method of manufacturing this gas.

Despite these spectacular recent successes, which do much to negate the claims of Crabtree and Whitesides[1], it must be conceded that if inorganic and physical chemists possessed a method for the design of new solid catalysts as reliable as that of site-directed mutagenesis in enzymology, many of the remaining unsolved problems that face the community of designers of heterogeneous catalysts would disappear, and the assembly of new catalysts could then become a pleasing constructional exercise.

Fortunately, the ease with which vast new kinds of open-structure solids can now be produced,[17-31] along with the chemical dexterity with which single-site catalytically active centres may be ever more readily engineered on to such solids,[32] has opened up a rich diversity of new, atomically well-defined and readily monitored (*in situ*) families of solid inorganic catalysts. This growing body facilitates the enlargement of single-site heterogeneous catalysts (SSHCs). And, to fix our ideas, it is prudent to recall that SSHCs are, *inter alia*, those in which the active centres are energetically equivalent and spatially isolated from one another, and are uniformly distributed over an internal and accessible surface which is exceptionally large (eg. *ca* 10^3 m^2g^{-1}) and three-dimensional (3D). SSHCs, as we shall summarize below, are ideal for numerous practical applications and model systems especially in the fields of green chemistry, clean technology and sustainable development. In particular, they offer a coherent strategy for the design of numerous new catalysts.

2. SSHCs: A Recapitulation

Nine years ago, SSHCs were the subject of a comprehensive review[29] and shortly thereafter a detailed account was given[30] of the advantages and future potential of SSHCs. That article[30] highlighted the enormous scope for chemical conversions (regio-, shape-, as well as stereoselective) that may be carried out within nanoporous solids, where pore openings *ca.* 30Å permit ready access of large reactant molecules into engineered active centres accommodated within the interior of the heterogeneous catalyst. Fuller details, including examples of industrial exploitation of certain asymmetric syntheses were given[31] in a short review that appeared in *2008*. Subsequently, in 2012, a monograph was devoted[32] to this topic. Dal Santo, Guidotti *et al* have also surveyed[33] the field of SSHCs for high chemo-, regio- and stereo-selectivity. The topic has become highly relevant for a variety of reasons, as outlined later in this perspective article. In addition to the design of a wide range of new, thermally-activated catalysts, photocatalysts, required as potential means of producing solar fuels and for the photo-degradation of contaminated waters and environmental pollutants, may also be fashioned using the approach of engineered single sites. It is especially significant that metal-organic frameworks (MOFs), as demonstrated recently by Clarke, Wright and co-workers[34] are exceptionally promising as convenient and superior water-compatible, recyclable heterogeneous versions of classic homogeneous catalysts (such as Sc triflate) for effecting C-C and C=N bond-forming intermolecular reactions. Such bond-forming processes are ubiquitous in synthetic organic chemistry. These topics are discussed in Section 6.1 below.

Many extensively used industrial chemical processes utilize SSHCs, but some are in urgent need of improvement, as, for example, in achieving a liquid-phase process for the Beckmann rearrangement of the oxime of cyclohexanone to the massively used – for the synthesis of nylon 6–caprolactam. Raja and co-workers[35] have recently announced a specific SSHC for the low-temperature (130° C) liquid-phase transformation of the above-named oxime to caprolactam, the precursor of nylon 6. This constitutes a major advance in applied catalysis. Other extensively used industrial chemical processes that currently utilize SSHCs include cracking of hydrocarbons, catalytic dehydration, isomerisation, alkylation, oligo- and polymerization. Deeper insights are continually being gained into the mechanisms of most of these processes.

In the wide sweep and long history of catalysis, however, the notion that heterogeneous catalysts can have well-defined single sites is relatively new. This fact is neatly illustrated in the important recent paper published by Kwak *et al* [36] who state:

"Owing to the heterogeniety of active centres in heterogeneous catalysts, it is frequently difficult to identify the specific sites that are responsible for the overall activity." These authors also contrast, as this author previously pointed out in Chapter 2 of his monograph,[32] the situation pertaining to many heterogeneous catalysts, and their distinction from enzyme catalysts, where the active centres have precisely defined coordination environments that *"are able only to accommodate intermediates relevant to the specific catalytic process."*[36]

3. Sequence of Ensuing Topics

In this perspective, we select a number of illustrative examples, several of considerable practical importance, that emphasize both the reality and increasing utility of SSHCs.

We begin by elaborating the recent work of Kwak *et al* [36] who have demonstrated the striking similarity in the mode of operation of the copper form of nitrite reductase enzymes and the Cu^{2+} ion-exchanged solid known as SSZ-13 (related to the mineral chabazite,[37]) that selectively catalytically reduces (SCR) NO in the presence of NH_3 and O_2, a key reaction in auto-exhaust catalysis. Subsequent examples highlight recent examples of single-site Brønsted acid catalysts, of Lewis acid SSHCs in which transition-metal ions are substituted in the framework sites of crystalline microporous and mesoporous structures or individual metal ions anchored to non-crystalline mesoporous supports like silica. The remarkable Lewis acid catalytic performance of Sc-centred MOFs (like MIL-100) offer enormous advantages, in synthetic organic chemistry. We also highlight the growing importance of SSHCs in photocatalysis; and, finally, a brief discussion of the putative role of individual metal atoms (on specific supports) as highly active single-site catalysts.

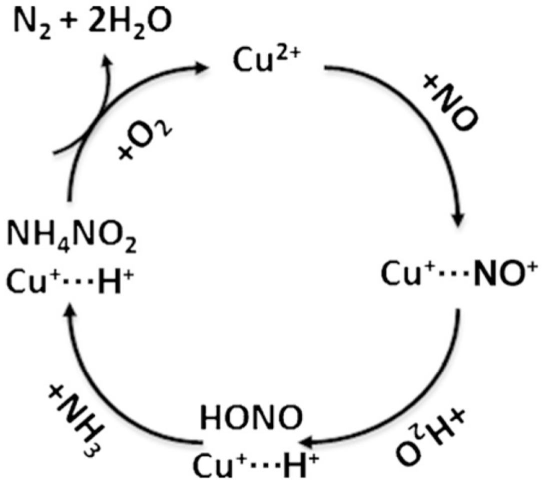
First we focus on the similarities between SSHCs in an inorganic solid catalyst on the one hand and a metallo-enzyme catalysts on the other.

4. The Kinship Between the Active Centres and Reaction Intermediates for N_2 Formation in the Selective Catalytic Reduction (SCR) of NO with NH_3 in an Auto-exhaust Catalyst and the Copper Form of the Nitrite Reductase Enzyme

After extensive exploration[38,39] in the use of Cu^{2+} ion-exchanged zeolites, such as ZSM-5, and zeolites Y and Beta for the SCR of NO, it has been found[39,40] that the small-pore synthetic zeolite known as SSZ-13 possesses remarkable hydrothermal stability of the kind needed to function as a viable catalyst in automotive emission control. (The traditional three-way auto-exhaust catalyst is completely inefficient for the conversion of NO to N_2 in the presence of excess oxygen, O_2, which is the situation that applies in so-called lean burn combustion engines that are the most appropriate option for fuel-efficient vehicles).

Using sophisticated versions of both FTIR and high magnetic field solid state (SS) magic angle spinning (^{15}N-MAS) NMR, Kwak *et al* [36] have identified side-on Cu^+-NO^+ complexes as the key intermediate in the SCR of NO over Cu-SSZ-13 zeolitic catalysts. Analogous intermediates have been observed and characterized in nitrite reductase enzymes and shown to be the critical intermediates in the formation of N_2 for anaerobic ammonium oxidation reactions[41].

Kwak *et al* [36], by combining their spectroscopic studies with earlier kinetic measurements, were able to propose the following reaction mechanism (Figure 1), in which the first step is the reduction of Cu^{2+} to Cu^{+} by NO, and the formation of the side-on $Cu^{+}...NO^{+}$ species, just as in the intermediates shown to be present in nitrate reductase enzymes.



Proposed mechanism for the selective catalytic reduction of NO with NH_3 over Cu-SSZ-13.

Figure 1. Proposed mechanism for the selective catalytic reduction of NO with NH_3 in the pressure of excess O_2 over the single-site catalyst Cu-SS2-13. (After Kwak *et al* [36])

In the presence of H_2O, the formation of HONO is facile; and it, in turn, can react with NH_3 to form ammonium nitrite, which subsequently decomposes thermally to yield N_2 and

H_2O. The catalytic cycle is closed by the reoxidation of Cu^+ to Cu^{2+} by O_2, which is present in the reactant gas in excess.

5. Brønsted acid SSHCs

These are the best known and most widely characterized SSHCs. In zeolitic acid catalysts the active centre is usually the acidic OH bond that bridges the tetra coordinated Si and Al sites in solids such as HZSM-5, mordenite and zeolite Y. Zecchina and co-workers have extensively investigated such SSHCs, especially in the context of the initiation and propagation of the oligomerization of ethene and propene.[42,43] Using fast FTIR spectroscopy, Zecchina *et al* identified the formation of short-lived hydrogen-bonded precursors formed by interaction of the alkene with the internal acidic Brønsted sites, followed by a protonation step and a chain-growth step, as depicted in Figure 2. For both the ethene and propene it is the protonation of the precursors that is the rate-determining step of the oligomerization process[44].

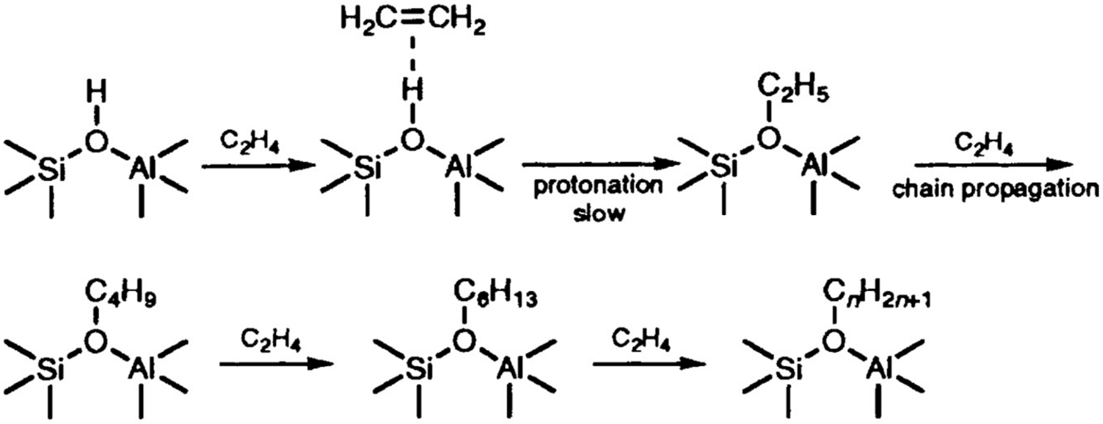


Figure 2. Mechanism of the process of polymerization of ethylene over H^+ ZSM-5, in which the slow step of protonation precedes the chain propagation. (After Spoto *et al* [42])

The reaction mechanism in this particular example of single-site Brønsted acid catalysis is simple and explicit, in contrast to the situation that pertains to the Brønsted acid-catalyzed methanol-to-olefin or methanol to hydrocarbon (MTO or MTH) transformations, which take place readily – and is used industrially – over other narrow-pore zeolites such as SAPO-34 or MAP-18 (see Chap 4 of Ref 32). In the "hydrocarbon pool" mechanism for the MTO and MTH processes proposed by Norwegian workers,[45,46] cationic pentacyclic[46,47] and (recently discovered[48]) heptacyclic carbenium ion transitory intermediates are present in the hydrocarbon pool that is an integral, but still somewhat enigmatic, intermediary in the formation of the first C-C bond (and subsequent production of hydrocarbons) from methanol.

5.1. The role of Brønsted Acid SSHCs in modern biorefineries designed to produce transportation fuels and commodity chemicals

Recent advances in biotechnology have made it possible to convert sugars into a wide variety of renewable chemicals.[3,49] Of the many molecular products now generated biotechnologically, isobutanol (2-methylpropan-1-ol) is exceptionally interesting. It turns out to be an excellent blend for petrol (gasoline), and also a precursor to C_4 petrochemical building blocks. It is especially promising as a transportation fuel because of its potential for high-yield production and compatibility with existing fuel infrastructures based on petroleum. Isobutanol is an energy-rich, low vapour pressure, high octane species that burns in a combustion enegine just like the conventional petrol (gasoline) without adversely affecting performance. Moreover, isobutanol is also readily dehydrated (by Brønsted acid catalysts such as HZSM-5) to butene. This butene can, in turn, be directly converted to produce hydrocarbon-based fuels (jet fuel, diesel and gasoline) as well as commodity chemicals and an array of polymeric materials – see Figure 3.

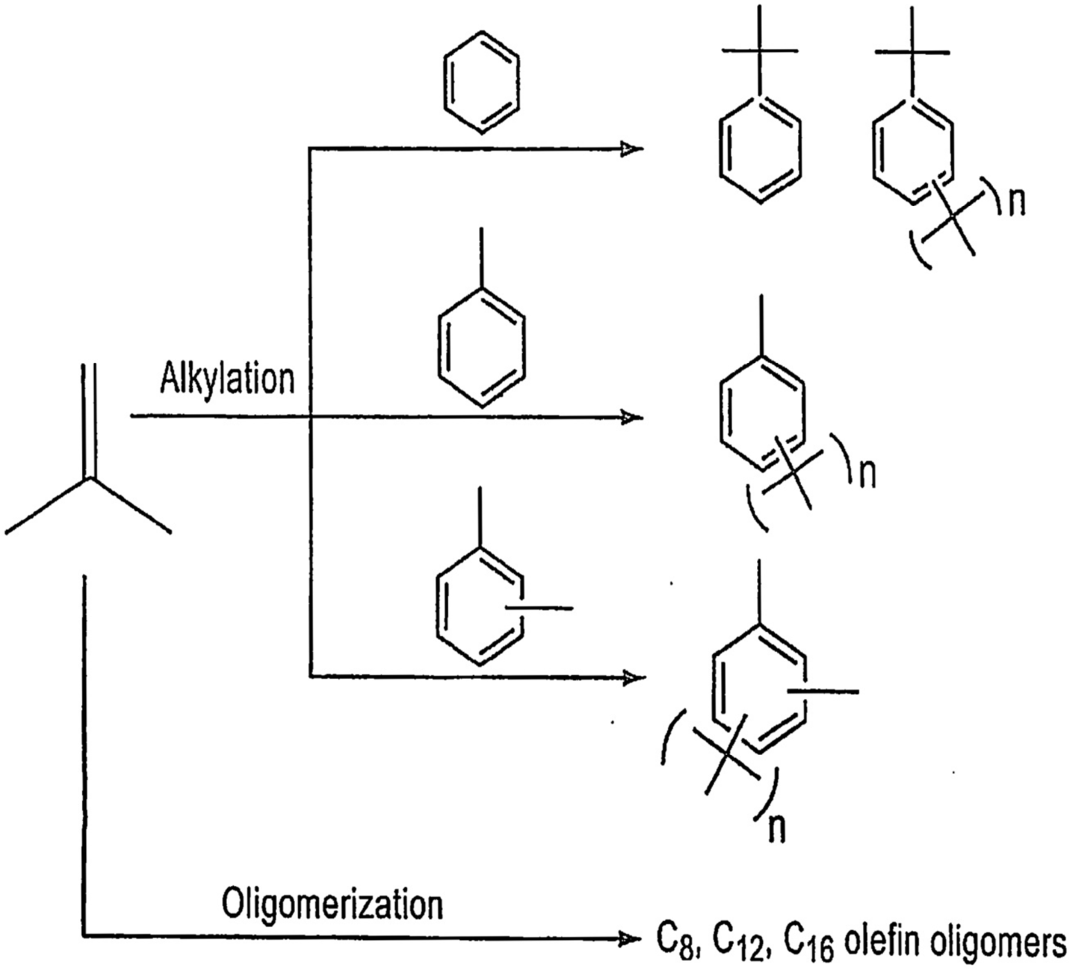


Figure 3. Brønsted acid catalysts readily convert isobutene, by alkylation, to both mono- and bi-substituted *t* butyl benzenes (top) and to olefin oligomers (bottom)

Very recent technological advances announced by the U.S. company, Gevo Inc (Englewood), show[50] the way in which, in its more general sense, sugars derived from biomass can be fermented with one or more species of microorganisms to form not just C_4 alcohols like isobutanol, but also one or more C_2 to C_6 alcohols, which then enables the following simple steps to be effected by proven (largely Brønsted acid) SSHCs:

- C_2-C_6 alcohols → C_2-C_6 olefins;

- Isolation (e.g. by selective adsorption) of one or more of these olefins;
- Oligomerization of one or more C_2-C_6 alkenes thereby forming one or more C_6-C_{24} unsaturated oligomers.

And it is readily feasible to hydrogenate portions of these products to form a selection of C_6-C_{24} alkanes. Using further embodiments of the Gevo Inc patents, recently announced,[51] it becomes possible to generate renewable jet fuel (see Figure 4), as well as renewable gasoline and renewable diesel fuel. The comparison in Figure 4 between the compositions of petroleum-derived jet fuel and renewable jet-fuel (which has zero sulphur content) is quite striking. This is also true of the comparison between the compositions of both diesel and gasoline when they are generated from renewable feedstocks.

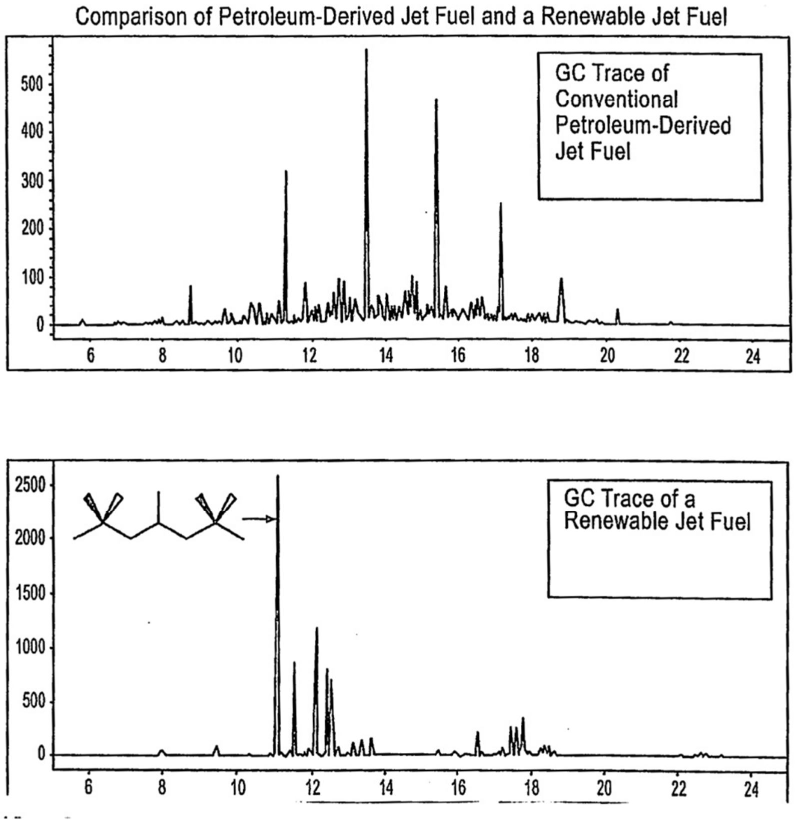


Figure 4. Jet fuel derived from renewable sugars are superior to those that are derived from petroleum. (After Gevo Co. Inc, US Patent 8,193,402B2, June 2012)

Industrial sugars from plant biomass now constitute a vitally important feedstock. The sugars can be fermented with customized microbes to produce chemical intermediates. BASF and its partners are for example currently pursuing production of 1,4-butanediol, acrylic acid and succinic acid in this way.

5.2. Brønsted Acid SSHCs and the Impact of Mesostructured Y Zeolite

Fluidized catalytic cracking is a massive industry. Thre are over 400 oil refineries in the world, some of which process as many as 940,000 barrels of oil per day (as in the Paraguana Refinery Center in Falcon, Venezuela[53(a)]). Zeolites are the centrepiece of FCC catalysts, the most effective being zeolite Y, exchanged with rare earth cations, the loosely attached protons, that constitute the single sites being in this case produced by cation hydroxyls[53(b)]:

$$(RE)^{3+}H_20 \rightleftarrows (RE)^{3+}OH^- + H^+Z^-$$

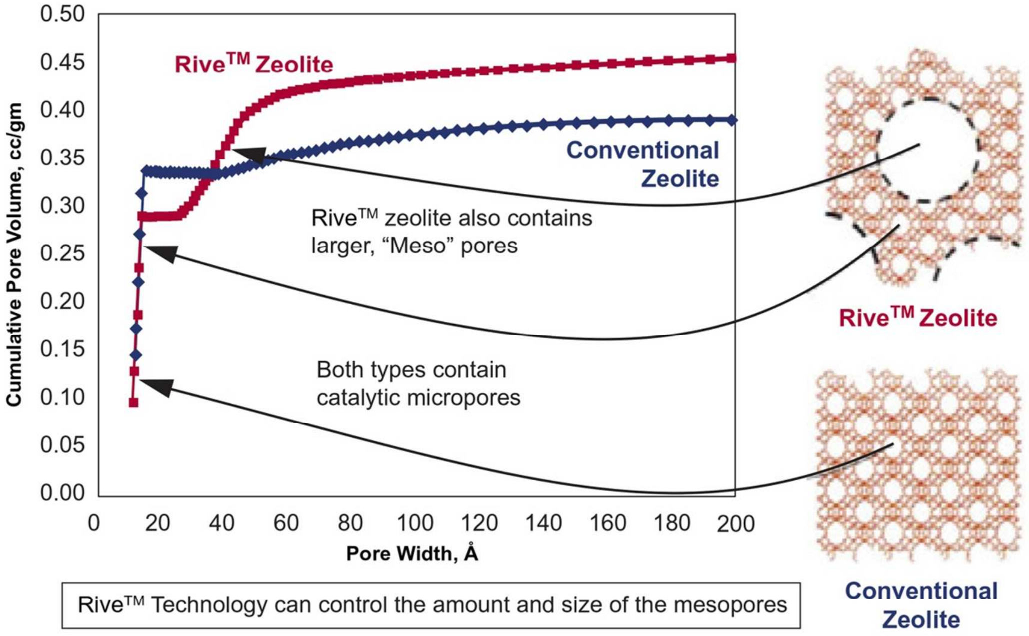
where RE is the rare-earth cation, typically La, and Z is zeolite Y.

Such is the colossal scale of FCC's that it is estimated that 500 K tonnes of the cracking catalyst are "consumed" each year – because the catalyst matrix (consisting of zeolite Y, kaolin (as a filler) and, typically, aluminium chlorohydrol (as a binder)) – are friable and lack sufficient attrition resistance. The unique properties of zeolite Y as the premier component of FCC catalysts are the following:

- High surface area and relatively large pores (*ca.* 7.4Å diameter);
- Strong Brønsted acidity;
- Outstanding thermal and hydrothermal stability; and, not least,
- Low cost of manufacture

But despite its widespread use in FCC, zeolite Y is not ideal, because its pore and cage diameters are too small to cope with many of the molecules that need to be "cracked". (At one time, it was thought that, when mesoporous silicas (developed in the US and Japan) made their dramatic entry, in the early 1990s, they might well revolutionize catalytic chemistry. Later, it transpired that mesoporous aluminium-containing silicas simply do not possess the hydrothermal stability to be used as cracking catalysts for hydrotreatment in place of zeolite Y.)

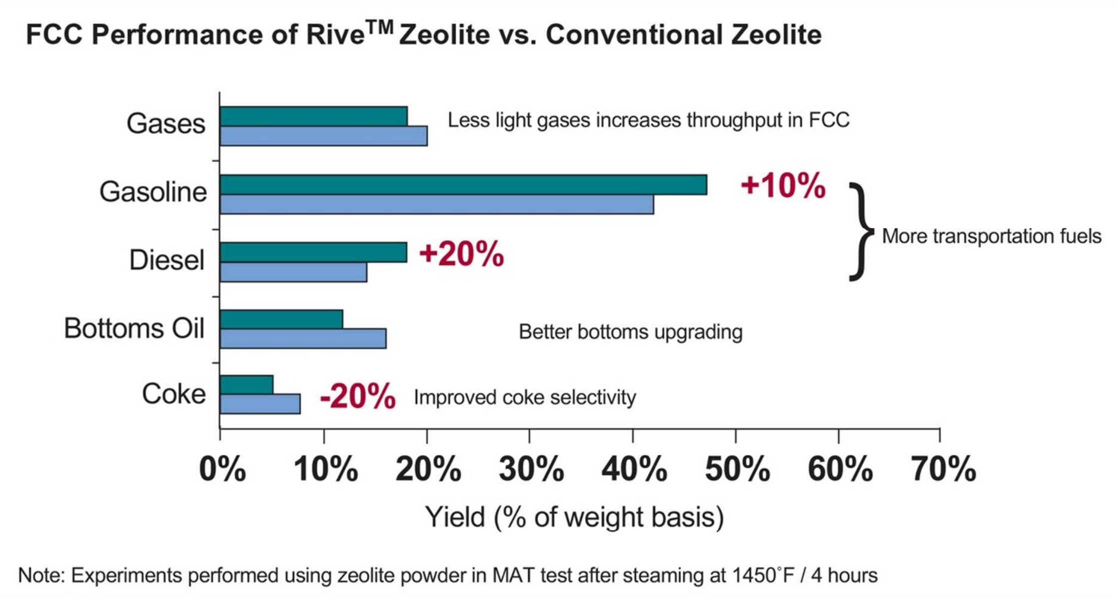
Now, however, thanks to inspired synthetic work by Garcia-Martinez[10,11], Pérez-Ramirèz[12,13] and Ryoo[52] mesostructured Y zeolite has been developed as a superior FCC catalyst both on the laboratory and industrial scale. Garcia-Martinez *et al* [10,11] introduced mesopores into zeolite Y (of low Si/Al ratios) by using a liquid-crystal template. The net result of their work is that their catalysts are more capable of cracking large hydrocarbon molecules, and allow valuable primary cracked products, like the molecules that make up gasoline and diesel, to escape more readily from the catalyst – before they are "overcracked" to less valuable light gases and coke. So successful is this new mesostructured catalyst that has become a so-called "drop-in" replacement for current FCC catalysts, and it now enables refiners to increase throughput (and profitability) without extra capital investment. This is an industrially dramatic advance! Figure 5 shows a pore size distribution typical of that used for catalytic cracking.



Argon Adsorption showing 40 Angstrom (Å) mesopores created in Y-zeolite.

Figure 5. Graph showing the cumulative pore volumes of (a) conventional cracking catalyst (blue) and (b) a meso-structured cracking catalyst, prepared by Rive (see text). (After Speronello *et al* [54])

This graph compares the cumulative pore volumes and pore diameters of the so-called Rive^{TM} Y-zeolite – it has been developed by Rive Technology Inc, New Jersey, USA – with conventional Y-zeolite as a function of pore diameter, and it shows that both types contain a large volume of micropores at <20Å diameter. However, the new (Rive) mesostructured zeolite also contains 0.15 ccg^{-1} of larger pores in a very narrow range at about 40Å in size. These 40Å pores (in the classic "meso" range stipulated by IUPAC) are unique to the Rive zeolite and are of crucial importance to achieving the superior cracking yields that are outlined in Figure 6. A comparison of the cracking yields of the conventional (ultra-stabilized zeolite-Y) and Rive (mesostructured) zeolite Y in a fluid bed test unit (at the National Center for Upgrading Technology in Alberta, Canada) is shown in Figure 6.[54] At equal 70 wt percent conversion gasoline yield, as well as distillate (light cyclo oil, LCO) yield, increased by 10 and 20% respectively, and there was a dramatic diminution (by 20%) in production of coke.



Note: Experiments performed using zeolite powder in MAT test after steaming at 1450˚F / 4 hours

Mesoporous Rive™ USY zeolite showed greatly improved cracking yields compared to standard USY.

Figure 6. The mesoporous Rive US Y zeolite catalyst shows significantly superior performance compared with the conventional cracking catalyst. (After Speronello *et al*[54])

Not only does the mesostructured zeolite Y catalyst exhibit excellent hydrothermal stability, it possesses a variety of other properties such as:

- Efficiency in the catalytic pyrolysis of biomass to produce bio-oils and other materials;
- Usefulness in the transesterification of vegetable oils;
- Methanol conversion to hydrocarbons (MTH). (See Section 5).

Moreover it is possible that this new mesostructured zeolite Y may also be utilized for less energy-intensive adsorptive separations as well as for the treatment of water.

In the interests of pedagogy, it is noteworthy that Garcia-Martinez's work has registered remarkable progress from laboratory-scale to the pilot-plant scale in which *ca* 30 tonnes of mesostructured zeolite Y were manufactured in a commercial plant utilizing regular equipment for such preparations.[10]

6. Lewis acid SSHCs

As long ago as 1983, Italian researchers had shown[55] that several heteroelements, such as Ti, Zr, Sn, Nb, Ta and V could be substitutionally incorporated into the framework sites of zeolites; but, unlike Al in natural zeolites, these elements do not introduce a charge imbalance. The classic example, TS-1 (with Ti^{IV} sites replacing some of the Si^{IV} sites in silicalite) has become the archetype of Lewis-acid catalyzed reactions[56] and of a wide range of important practical selective oxidation catalysts, especially for the epoxidation of alkenes, in the production of phenol from benzyne and aldehydes and ketones from primary and secondary alcohols, to name but a few.

The key factor here, as established early on by Ingallina *et al,* [56] is the activation of the H_2O_2 species on the Ti^{IV} active centre. (The mild amphoteric nature of Ti^{IV} centres framework-substituted in the open-structure aluminophosphate, ALPO-5 – see also Section 8 – has been harnessed in the selective oxidation of *c*-hexene to adipic acid using H_2O_2 as oxidant, a reaction that proceeds in a cascade fashion involving six, clearly identified sequence of intermediates.[57])

Nowadays, in the context of the selective conversion of biomass to fuels and chemicals,[58] there is also intense interest in utilizing Sn-containing open-structure (SSHC) catalysts for such reactions as:

- monosaccharide isomerization[59]
- retroaldol condensations[60]

- hydride shift reactions[61,62]
- Meerwin-Ponndorf-Varley-Oppenauer redox reactions[63]
- Bayer-Villiger oxidations[64] and
- Synthesis of 5-(hydroxymethyl) furfural from carbohydrates[65]

In particular, Sn atoms incorporated into zeolite beta have been shown to be highly active single-sites for these reactions. For a concise review of this field see Osmundsen *et al.*[58]

Just as Ti^{IV} Lewis acid centres grafted on to mesoporous silicas, such as MCM-41, prove effective for the epoxidation of *c*-hexene with alkyl hydroperoxides,[66] so also have Sn^{IV} Lewis acid centres grafted on to MCM-41 been found to convert trioses selectively to lactates.[67] Very recently, Tiozzo *et al* [68] have generated Nb^{V}-centred single sites on silica by grafting Nb $(C_p)_2$ Cl_2 onto silica surfaces in a manner comparable to that used by Maschmeyer *et al* [66,69] for Ti^{IV} (see Figure 7). The Nb complex undergoes nucleophilic attack by pendant silanol groups on the silica surface. A chemisorbed tripodally-grafted η^5-cyclopentadienylniobium moiety is formed, and, when calcined, it generates a 4-coordinate oxo-Nb^{V} species, which, upon hydration, is converted to a 6-coordinate Nb^{V} species. Prior to use in epoxidation, in a manner analagous to that described by Maschmeyer *et al*[66] and by Catlow *et al,* [69] for grafted tripodally-attached Ti^{IV} centres, the catalyst is calcined in dry air to remove the labile water molecules.

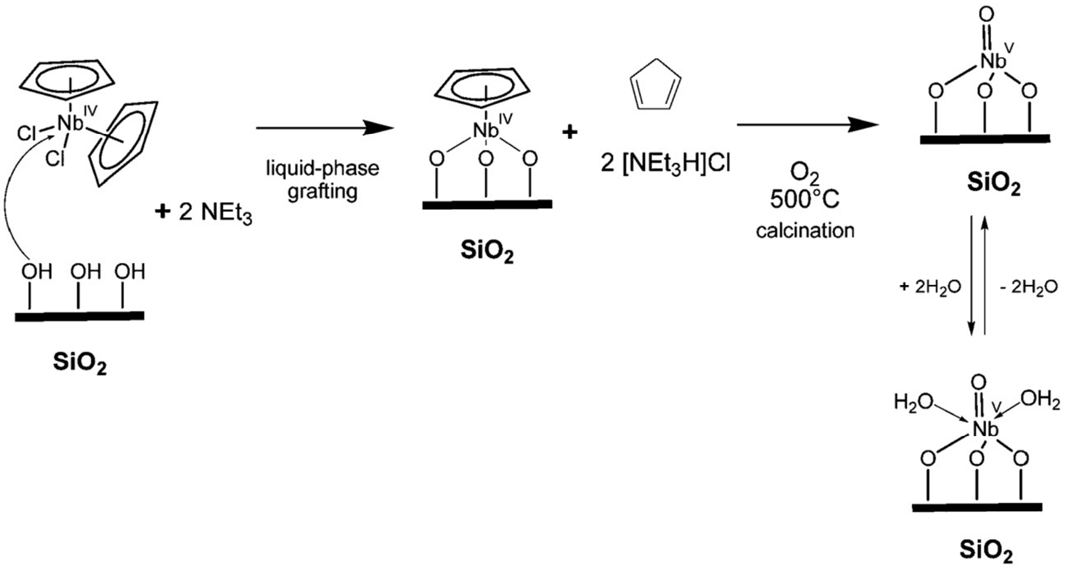


Figure 7. Scheme showing the procedure used by Tiazzo *et al* [68] to prepare the 4-coordinated SSH oxo-Nb^{V} epoxidation catalyst. (Compare the preparation of the 4-coordinated tripodal Ti^{IV} SSH epoxidation catalyst[66]).

The superiority of Zr Lewis acid active centres (over Sn, Ti, Nb and Ta) in the zeolite Beta structure for the rearrangement of β-pinene epoxide into myrtanol has been demonstrated by de la Torre *et al.*[70] It transpires that Zr-zeolite beta is a robust re-usable solid Lewis acid catalyst for this specialized reaction.

6.1 Single-site Lewis acid catalysts and their viability in synthetic organic chemistry

Here we summarize the recent work of Clarke and Wright[34] who, using scandium-based MOF structures of the MIL-100 family (see Figures 8 and 9), have shown the outstanding merit of these SSHCs for a wide range of organic chemical intermolecular reactions that entail the facile formation of C-C and C=N bonds. We first recall that MOFs offer high surface areas that can accommodate spatially well-separated active sites accessible via well-defined pore openings. They are, in other words, heterogeneous catalysts possessing possible

– as yet to be fully explored – shape-selectivity. Moreover, certain MOFs have the advantage over zeolites in that they exhibit greater chemical variability and also porosities that surpass those in the micro-range (as with zeolites) into mesoporous range, hence offering a greater scope to process larger molecular entities than those done by zeolites, (except for mesostructured zeolite Y). MOFs are, however, of lower thermal stability than zeolites, thereby making them better suited to the catalytic preparation of fine rather than bulk chemicals.[71]

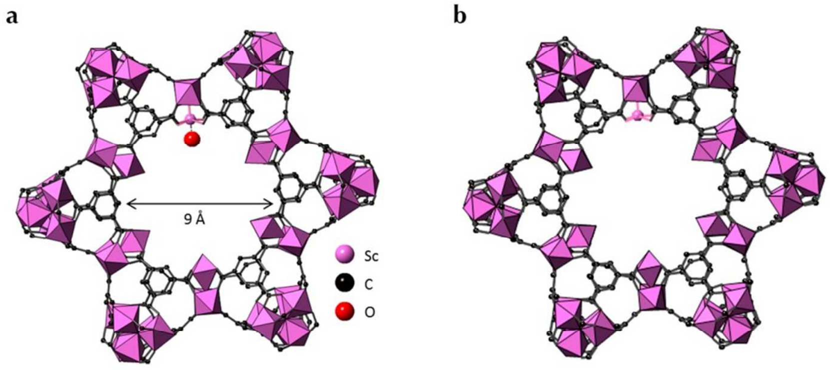


Figure 8. The essence of the Sc^{3+} form of MIL (100) metal-organic framework used by Clarke and Wright *et al* [34] to effect a variety of intermolecular C-C and C=N bond formation, by Lewis acid catalysis. These are of great value in synthetic organic chemistry. In (a) oxygen atom at the top denotes the H_2O molecule which can readily be displaced to produce a coordinatively unsaturated active Lewis acid site (centred on Sc^{3+}) shown in (b).

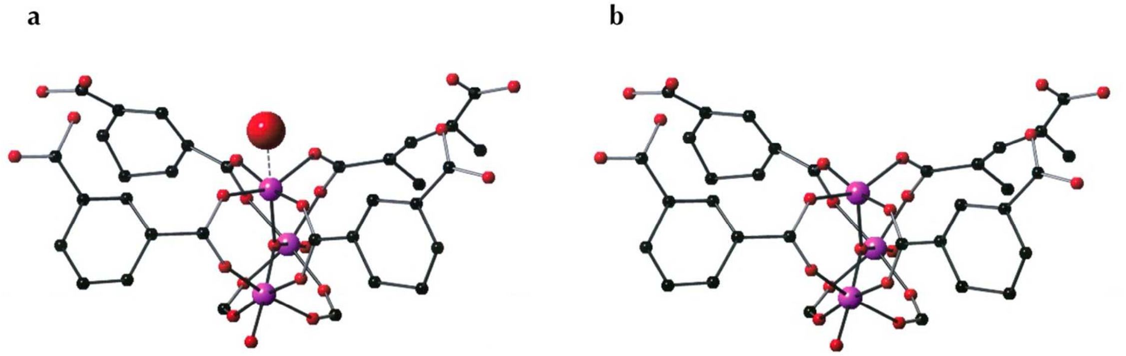


Figure 9. Greater detail of the MIL (100) structure used by Clarke and Wright *et al* for their Lewis acid catalyzed inter-molecular reactions for C-C and C=N bond formation. The Sc^{3+} active site before (a) loss of a sixth oxygen ligand and after (b) to yield an exposed Lewis acid centre.

One of the great advantages displayed by certain MOFs, including the MIL-100 family,[21] is that the metal cations that are integral to the framework can be made catalytically-active by removal of their solvent-ligands to leave a vacant coordination site as a Lewis acid (so long as the MOF remains porous). A conspicuous example is exhibited in the Lewis acid catalysis associated with the so-called HKUST-1, which possesses framework Cu^{2+} cations from which water can be removed to leave square planar coordinated Cu^{2+}, ripe for Lewis catalysis.[72] There have been several accounts of catalytic transformations within the pores of MOFs. Among the most up-to-date is that given by Furukawa *et al*[22]. In Furukawa *et al's* review, mention is made of methane oxidation to acetic acid in vanadium-based MOF-48. Whilst it is true that the catalytic turnover for this oxidation far exceeds that of the analagous homogeneous catalysts, the fact remains that the turnover is probably too low to be of practical value. The oxidation is also carried out with a sacrificial oxidant, an alkali persulphate salt.

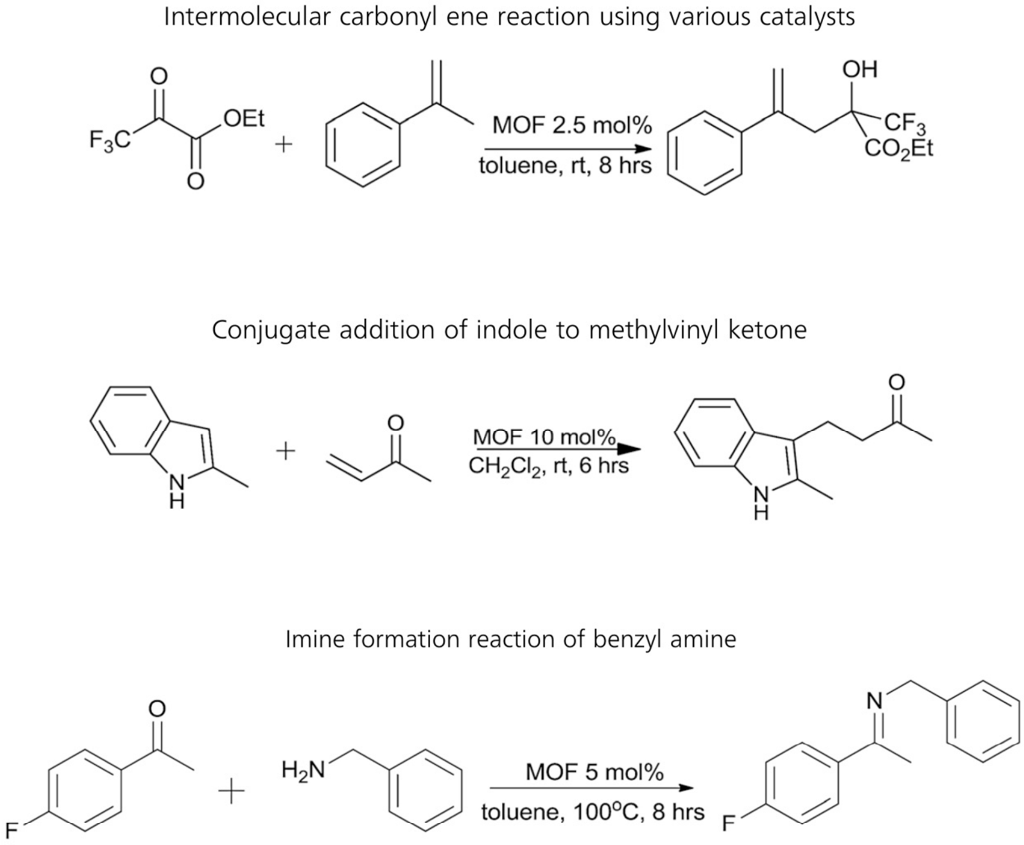
In the significant recent work of Clarke and Wright,[34] the starting point was the knowledge that homogeneous Sc triflate ($Sc(CF_3SO_3)_3$) is a very powerful Lewis acid catalyst, even in the presence of water, that has already led to major advances in synthetic organic chemistry, as evidenced by the work of Barrett *et al*,[73] Evans and Wu[74] and Kobayashi.[75] In the Sc form of MIL-100, the 6-coordinated central Sc^{3+} ion can readily lose one of its coordinated water molecules to leave 5-fold (i.e. coordinativity unsaturated) Sc cations that are strong Lewis acid centres. (Spectroscopic evidence by Otero Arean *et al* [76] bears this fact out).

Clarke, Wright *et al* [34] demonstrated three important examples of how Sc (MIL-100) can serve synthetic organic chemistry:

(a) **Intermolecular carbonyl-ene reactions.** This 100% atom-efficient reaction can be carried out with complete recovery of catalyst, and pure organic compounds can be produced without the necessity for additional steps of purification. This class of reaction takes place readily in the presence of the SSHC (Sc (MIL-100)) between a nucleophilic alkene and an electron-deficient aldehyde or ketone. (See top entry in Table 1).

(b) **Friedel-Crafts Michael addition reactions.** The addition of indoles and pyrroles to methyl vinyl ketone was the example taken by Clarke and Wright – see second entry in Table 1.

(c) **Imine synthesis from the condensation of amines with carbonyl compounds.** This is another synthetically useful reaction that is catalysed by the Sc (MIL-100) SSHC. (See third entry in Table 1). Here there are signs of shape-selectivity since some of the species involved in the reaction are rather too large to penetrate the 9Å windows (Figure 9) of the solid catalyst.



Intermolecular carbonyl ene reaction using various catalysts

Conjugate addition of indole to methylvinyl ketone

Imine formation reaction of benzyl amine

Table 1. Three classes of intermolecular reactions that form C-C or C=N bonds using SSH Lewis catalysts.

In summary, MIL-100 (Sc) is an excellent, rapidly regenerable and re-usable catalyst for a range of synthetically interesting C-C and C=N bond-forming reactions. This SSHC is readily prepared with high surface areas, has a 3D connected array of mesoporous cages and is stable in moist air and under the reaction conditions used for the conversions summarized in Table 1. The active sites in this catalyst are the Sc^{3+} cations that form part of trimeric units. Two out of three Sc^{3+} ions in each trimer are coordinated by water molecules. Clarke and Wright have succeeded[77] in incorporating Fe^{3+} ions along with Sc^{3+} ones in MIL (100) catalysts, and this new catalyst is capable of facilitating novel tandem reactions.

7. Surface Chromium Single Sites As Important Polymerization Catalysts

Apart from TS-1 and ZSM-5, the so-called Phillips Cr/SiO_2 catalyst for ethylene polymerization is one of the simplest industrial examples of SSHCs.[78,79] Unlike other widely used industrial single-site polymerization catalysts, the Phillips one is unique in that it does not require the use of an activator – such as alumoxane or aluminium alkyls as in the classic, immobilized zirconocene catalyst.

Zecchina and his associates have shed much light on this catalyst, in which the SiO_2 support to which the Cr active sites are grafted is amorphous.[78,79] The surface OH group react with a Cr precursor (such as chromic acid) forming surface chromate species (Figure 10). The activation process can be effected in two distinct ways: industrially, the surface chromates are directly treated with ethylene at *ca* 80-100 °C. After an induction period, reduced Cr^{II} sites are formed that are able to polymerize ethylene with high efficiency. In laboratory, model studies the surface chromates are first reduced to Cr^{II} by CO, with the attendant formation of CO_2 which is liberated. Zecchina established that a fraction of the Cr^{II} sites (Figure 10*c*) are then able to polymerize-ethylene at room temperature without an induction period. As well as the Zecchina group, those of Weckheuysen and Wachs[80] have also studied the structure of the Cr^{II} active site. At least three types of Cr^{II} species are present, differing in the number of available coordination vacancies. Although all these sites are able to form Cr^{II} $(C_2 H_4)_n$ complexes (with n = 1 or 2), only a fraction, it seems,[79] further evolve into catalytically active species and thus initiate ethylene polymerization. A possible explanation is that only the most protruding Cr^{II} precursors are reactive enough to form the active sites by interaction with ethylene.

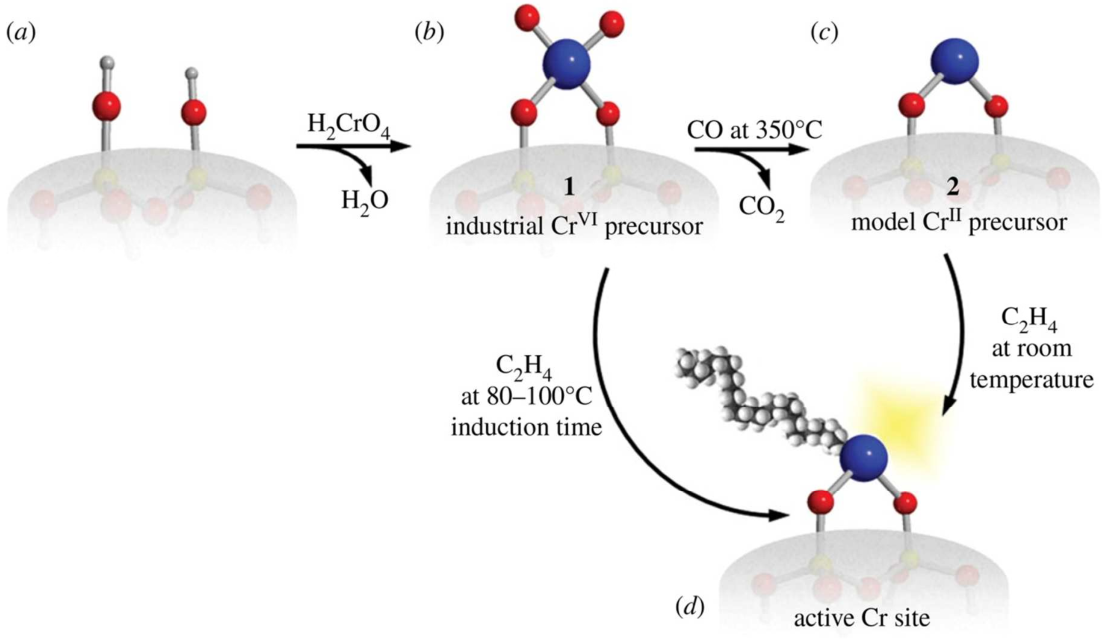
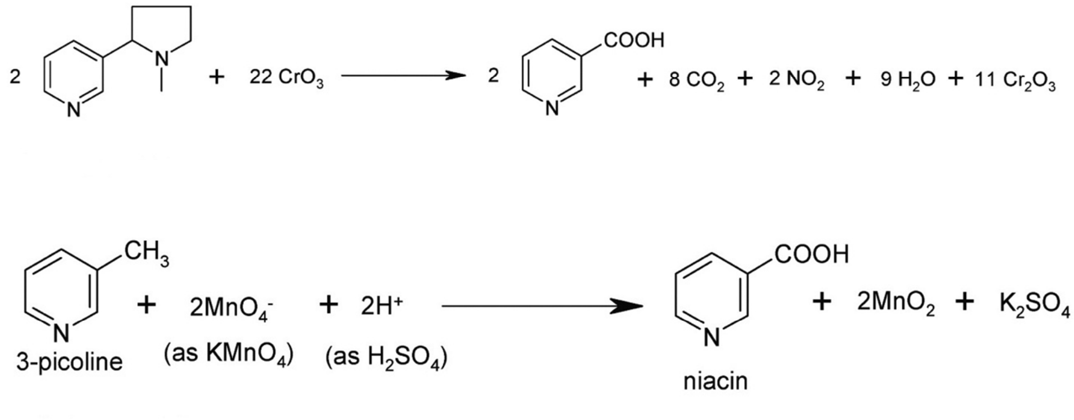


Figure 10. (*a-d)* Schematic (after Zecchina and Groppo[79]) of the preparation and activation of Cr/SiO_2 Phillips catalyst for the polymerization of ethylene following either the industrial (path *b-d*) or the model (path *c-d*) route. The surface chromates (species ***1**; b*) and the anchored Cr (11) sites (species ***2**; c)* are both precursors of the same active species (*d*). The structure of the Cr active centre is hypothetical and is based on an analogy with the structure of the active species in metallocenes and Ziegler-Natta catalysts; the active species contains a coordination vacancy available for the coordination of ethylene (coloured shadow). H, O, and Cr atoms are represented as small, medium and large spheres respectively. The SiO_2 surface is shown in grey. (After Zecchina and Groppo[79]).

Cr sites grafted on amorphous SiO_2 or mesoporous silica or zeolitic materials have also been investigated as examples of photocatalytic SSHCs. These are briefly discussed in Section 9 below.

8. SSHCs based on microporous aluminophosphates (ALPOs)

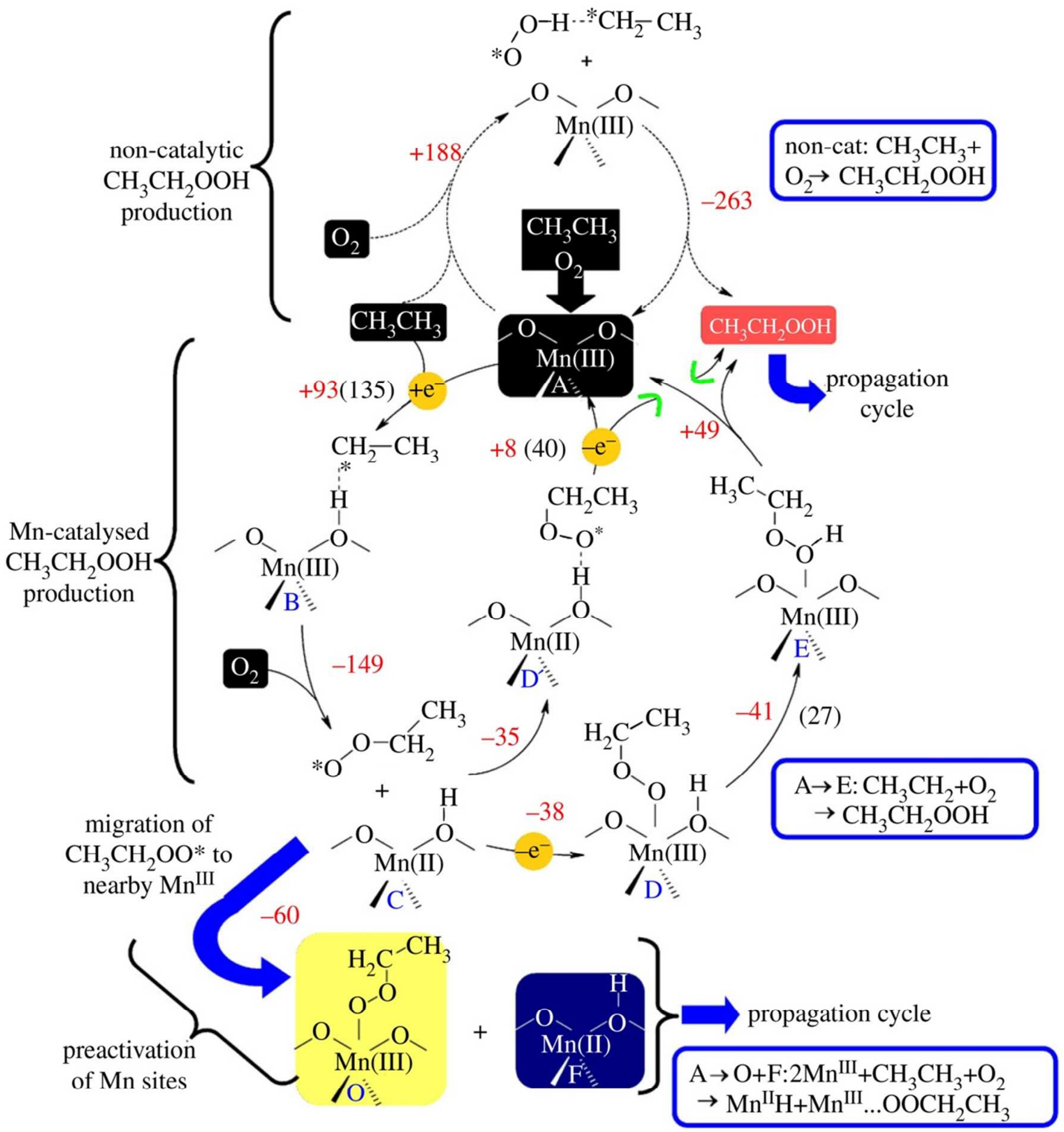
Much has already been written[29,32] on the utility of using transition-metal ions in high oxidation states (like Mn^{III}), framework-substituted in various ALPO structures, for selective oxidations of hydrocarbons (and other species) by molecular O_2, and also as a means of producing hazardous intermediates (like NH_2OH) *in situ* with such SSHCs.[81] In addition, key aspects of potential and actual industrial applications, such as the steps involved in the production of nylon 6[82] and in the benign syntheses[83] (using Mn^{III}-substituted ALPO-5 SSHC in both cases) of the vitamin niacin to replace the currently used, environmentally aggressive and stoichiometric preparations using hazardous solid oxidants like CrO_3 and $KMnO_4$ – see Scheme 1.



Scheme 1. (Top) Chromic acid oxidation of nicotine to nicotinic acid.

(Bottom) Oxidation of 3-picoline with permanganates.[32] Both these processes are environmentally aggressive.

Very recently, however, Cora *et al*,[84] have given an elegant quantum-mechanical quantitative interpretation of the aerobic selective (terminal) oxidation of hydrocarbons[85] in Mn-doped ALPOs with particular reference to (Mn) ALPO-5, where each active site is in precisely the same chemical environment. These workers (using so-called hybrid exchange density functional theory methods) have been able to identify short-lived intermediates and the overall pathways of conversion. Such information is, at present, inaccessible to experiment: high pressures of O_2 or air (*ca* 30-60 bar) are used in these selective oxidations. Cora *et al*'s calcuations[84] confirm all the experimental facts reported earlier.[85,86] In particular, that the aerobic catalytic oxidation proceeds via a radical mechanism on the Mn sites; and that both Mn^{III} and Mn^{II} ions are implicated in the overall conversion. Full details are contained in several papers by this group in which individual steps, like pre-activation[87] of the Mn sites, hydroperoxide decomposition[88] via their agency, the propagation[89] and regeneration[90] mechanisms are given. A summarizing account of all these processes is given in reference 84 from which Figure 11, showing the mechanism of preactivation is taken.



Preactivation mechanism for the production of CH_3CH_2OOH from RH and O_2 without (top) and with the assistance of Mn^{III} (middle). Boxed species represent initial catalyst and reactant molecules, and intermediates produced here which are necessary to initiate the propagation cycle (figure 3). Enthalpies and activation energies if any (in brackets) are shown for each elementary step in kJ mol^{-1}. (Online version in colour.)

Figure 11. Preactivation mechanism for the production of CH_3CH_2OOH from C_2H_6 and O_2 without (top) and with the assistance of Mn^{III} (middle). Boxed species represent initial catalyst and reactants, and intermediates produced which are necessary to initiate the propagation cycle (not shown). Enthalpies and activation energies if any (in brackets) are shown for each elementary step in kJ mol.[7] (After Cora *et al* [84]).

9. Single-Site Photocatalyst

Early on Anpo and his colleagues,[91,92] showed how highly dispersed Ti^{IV} ions in zeolite Y functioned as a tetrahedrally coordinated SSH photocatalyst. Figure 12 illustrates how such a single-site photocatalyst enables unwanted molecular species (e.g. NO and CO_2) to be destroyed photochemically. Other illustrations, involving the photocatalytic elimination of CO in the presence of H_2 – required to generate purer forms of the latter for use in fuel cells, for example – are shown in Figures 27 and 28 of reference 18.

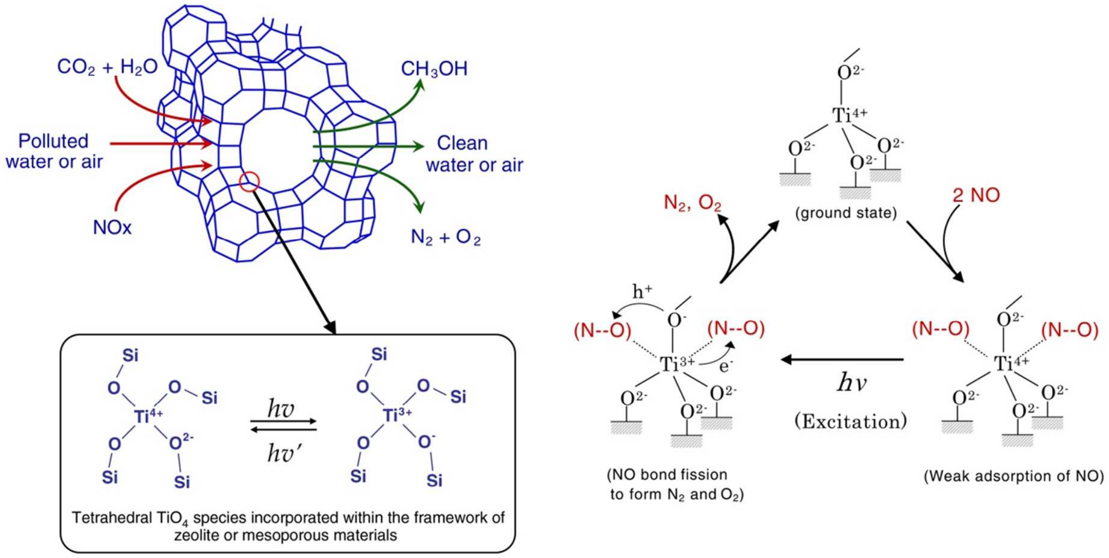


Figure 12. (Left) Schematic diagram of the highly dispersed TiO_4 species in tetrahedral coordination incorporated within a zeolite Y framework as a single-site photocatalyst.

The applications of single-site photocatalysts[93] involving isolated, tetrahedrally coordinated ions of Ti, V, Cr, Mo and W in silica matrices have been reviewed by Yamashita[94] and co-workers in 2008. They show that, as well as their utility in eliminating unwanted materials, this category of SSHCs is useful for the design of functional materials. An up-to-date analysis of such photocatalysts has recently been given by Che *et al.*[95]

9.1 Metal-organic frameworks for light-harvesting and photocatalysis

Recent claims[96] that MOFs have emerged as a versatile platform for developing SSH photocatalysts and to drive a range of reactions including Lewis acid/base catalysed reactions, redox reactions and asymmetric reactions bear out many of the examples cited earlier in this article. The charge-separated excited states of the chromophoric building blocks of the MOF created upon photon excitation, can migrate over relatively large distances to be harvested as redox equivalents at the liquid/MOF interfaces via electron transfer reactions or, alternatively, can directly activate the reactants that have diffused into the MOF channels for photocatalytic reactions. As emphasized earlier in this Perspective, MOFs serve as an ideal platform to design single-site photocatalysts by combining molecular functionality into the judiciously chosen solid (nanoporous) material. This fact has also been emphasized by Anpo and his colleagues.[97] There are, however, some disadvantages. For example, certain components of the MOFs used to date – such as the Ir complexes of Wang *et al* [96] – are prone to leach on use as photocatalysts. Moreover, the encouraging reports[96] concerning photocatalytic generation of H_2 and CO_2 reduction have been achieved (all with MOFs) with the use of sacrificial agents. A number of MoFs have modest hydrolytic and thermal stabilities, which will limit their use as practical catalysts. Also, many of them involve either expensive or relatively rare elements (Ir, Re, U, etc). And, finally, most MOFs do not possess strong mechanical properties – attrition resistance – or good processability or high electrical conductivity, all of which will hamper their incorporation into viable, useful solar devices.[96] When one contemplates the whole scenario pertaining to the generation of solar fuels, the tasks facing the community devoted to harnessing solar radiation for this purpose, are formidable as described in more detail elsewhere.[53(a)]

10. Supported Single Atoms of Metals as SSHCs

An early report by Sachtler[98] drew attention to the fact that an isolated atom, slightly charged, of Pd or Pt, loosely bound to the bridging (Brønsted acidic) OH group of a zeolite, could function as an effective catalyst. Since that time there have been several other reports[99,100] in which direct experimental evidence points to the catalytic effectiveness of single atoms located at specific sites on an appropriate support. One report, by Kwak and Szanyi *et al*,[101] concerns the structure of Pt on γ-Al_2O_3 supports, a widely-used hydrogenation catalyst. They concluded that, at low loadings of the noble metal on the oxide, the catalytic phase is atomically dispersed Pt and that it is localized, as individual atoms, on coordinatively unsaturated Al^{3+} centres in a 1:1 ratio ($Pt / Al^{3+}_{penta} = 1$). Very recently, Flytzani-Stephanopoulos *et al* [102] have shown that atomically dispersed Au-$(OH)_x$ species bound on TiO_2 catalyze the low-temperature water-gas shift reaction. It seems that such single sites (of both Au and Pt) are also effective as catalysts for this reaction on other oxide supports.

A particularly intriguing example of single metal atom catalysis, described by Sykes *et al*,[103] involves what they have termed single atom alloys (SAA), in which a solitary Pd atom, supported on metallic Cu leads to facile dissociation of reactants and weak binding of intermediates. These, in turn, give rise to efficient and selective catalysis. In particular, such SAAs allow of very selective hydrogenation of styrene and of acetylene (to yield olefins). Such reactions do not take place on Cu or on Pd metal alone. The energetic and pictorial representations are given in Figure 13.

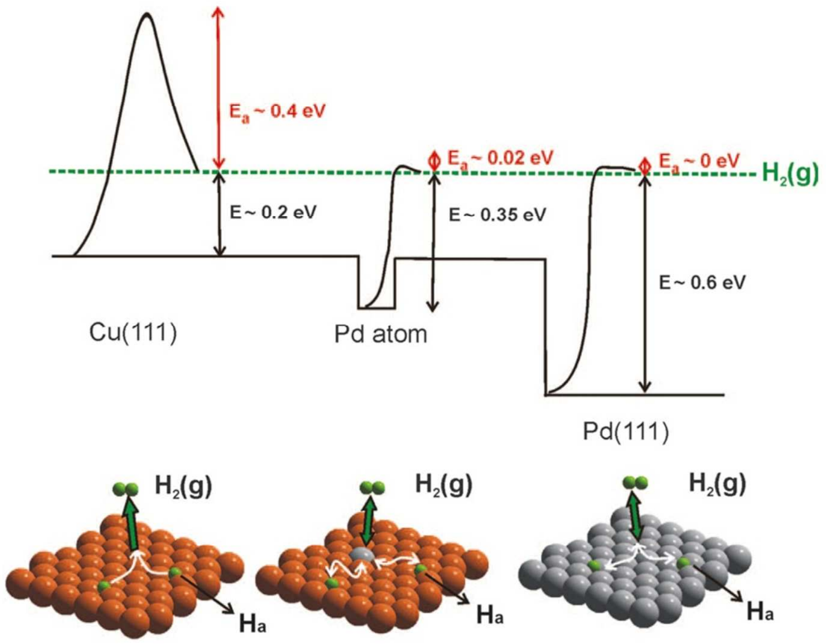


Figure 13. Potential energy diagram depicting the mode of action of a Pd single atom alloy surface compared with those of pure Cu (111) and Pd (111). Dissociative adsorption of H_2 on Cu (111) (orange) is a highly activated process. On Pd (111) (grey), H_2 dissociation is essentially barrierless, but the adsorbed atoms are bound strongly. For the isolated Pd atom, the dissociation carrier is low, H_2 is weakly bound, and it can spill over onto the Cu (111). (After Kyrfodau *et al* [103])

To date, no industrially applicable examples involving single metal atoms on an oxide, metal or other support have been reported.

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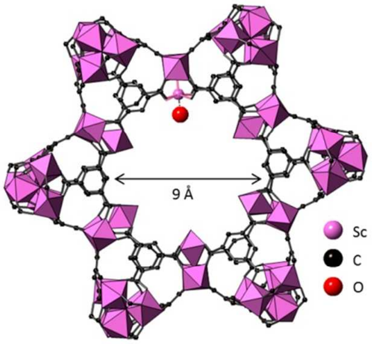
Table of contents entry:

The large-pores of this metal-organic framework allow bulky reactants to be catalytically converted at single-site active centres.

I dedicate this article to the memory of Professor Wynne Roberts, my friend of 65 years, who died on the 6th March 2014.



Biography:

J. M. Thomas has for many decades researched widely in solid-state, surface and materials chemistry. He is the author of numerous university texts and research articles on catalysis. The second edition of his book with W. J. Thomas, *Principles and Practice of Heterogeneous Catalysis* is shortly to be published. He was the first recipient in 1999 of the American Chemical Society Annual Award for ‘Creative Research in homogeneous and Heterogeneous Catalysis.’