CATALYSTS, SUPPORTED

1. Introduction

The field of heterogeneous catalysis of organic reactions covers an enormous undertaking, including the conversion of the primary source of almost all the organic compounds known (oil and gas) to a range of functional intermediates that are then used to prepare the vast array of chemical products used in everyday life. The field can be split into two distinct areas—heterogeneous catalysis of gas-phase reactions and of liquid-phase reactions. The former is a well-known and long established field, representing some of the largest chemical processes known—the cracking and other conversions of crude oil and gas which lays the foundation for the remainder of organic chemistry. These processes are typically

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high temperature, high energy processes, operating on a megaton scale, and typically use zeolites as catalysts. These processes are very well described in a series of books and reviews as well as in other chapters of this work (see *Catalysis, Molecular Sieves, Supported Catalysts*) (1–5).

This contribution, therefore, relates specifically to the use of heterogeneous catalysis to the synthesis of fine chemicals. The vast majority of these systems operate under moderate temperatures and in the liquid phase, although there are a few that take place in the gas phase.

2. Preparation Methods for Inorganic Supported Catalysts

There are several methods for the preparation of supported catalysts such as those described in this article (6). One of the key concepts is the maximization of surface area; this is normally achieved by having a very porous support material, and the methods below aim to either generate materials with high surface areas, or to coat pre-formed high surface area supports with small amounts of catalytic species. In the latter case, it is important to note that the surface area of a typical commercially available support material such as alumina or silica is in the range 100–600 m^2/g^1. On the other hand, a crystalline solid such as potassium fluoride (KF) or zinc chloride will have a surface area of $<1\ m^2/g^1$.

Given that the exposed surface area is where reaction takes place, it is clearly very important not to overload the material to the point where microcrystals are formed on the surface although there may be instances where microcrystals are a necessary feature of the catalyst (eg, in epoxidations using supported silver catalysts) (7). The formation of the high surface area supports (which often may have catalytic activity themselves) is typically carried out by the condensation of inorganic precursors in the presence of a structure directing agent, whose role is to control the formation of a porous or layered structure and thus maximise the surface area.

Mechanical and thermal properties are also very important features of supports (8–10). Mechanical attrition of particles in the aggressive environment of a large chemical reactor must be allowed for and may cause changes in performance on reuse (this is especially important when a solid is used in a high shear stirred tank reactor). Many commonly used support materials have more than adequate thermal stability to cope with the temperatures commonly encountered in liquid phase-organic reactions. Some materials are sensitive, however, notably those that are organic polymer based (eg, acid resins) or have some surface-based organic functionalities (eg, sulfonic acids). The key properties of some of the more widely used support materials are given in Table 1.

2.1. Coating Pre-Formed Supports. The simplest method, and often the most appropriate, is wet impregnation, where a solution of the material to be supported is dissolved in a solvent and mixed with the support. The incipient wetness technique involves filling the pages of the support with a solution of the reagent. Removal of the solvent then leads to the supported catalyst. The degree of dispersion depends on several factors such as the rate of removal of solvent—too

Table 1. **Some Widely Used Support Materials**

Support	Surface area (m^2/g)	Pore size (nm)	Comments
commercial silicas	300–600	2–20	widely available moderate-large pore volumes wide pore-size distribution.
synthetic silicas (micelle-templated)	to >1000	~2 to ~10	can have narrow pore size distribution and large pore volumes
alumina	100–300+	various (broad distributions)	commercial materials are widely available synthetic, narrow poresize distribution materials are as yet, less well established (less stable)
montmorillonites	50–300	<1 to >10	natural clays have small intermamellar-spacings but can swell pillared clays provide large (>1 mm) spacing; acid-treated clays are amorphous and often mesoporous
zeolitic materials (inc. MCMs)	to ~1000	<1 to >1	narrow pore distribution original zeolites are microporous and may be unsuitable for many liquid phase organic reactions larger pore materials including MCMs are more suitable
carbons	to > 1000	various	complex surface chemistry can complicate applications synthetic mesoporous carbons are among recent innovations
organic polymers (Inc. resins)	[a]	various[a]	limited thermal and chemical stability in many cases but often inexpensive newer materials such as Nafion-based have many proven applications

[a] Generally not reported and may be meaningless due to swelling on applications.

rapid can lead to precipitation of clusters of catalyst, leading to reduced accessibility and possibly pore blockage. For many of the smaller pore size catalysts, it may be sensible to allow a period of a few hours contact time to allow ingress of the solution into the pores (incipient wetness), but for many catalysts this is not always necessary. Loading is also a critical factor. Too high a loading can again lead to clustering (microcrystals) and reduced activity, too low can lead to the need for a larger quantity of catalyst than is optimal. In general, 1 mmol catalyst per gram of support is an upper limit, but the situation can be complicated by factors such as a strong interaction with the support (9). In this case, there may be a small number of sites where there is a particularly advantageous interaction between the support and the catalyst, leading to unusually high activity. In these cases, a very low loading may be required, with additional material making very little difference to the overall activity of the supported catalyst.

Choice of solvent is important, and is especially critical in strongly acidic systems such as supported $AlCl_3$, where the extreme sensitivity and reactivity of the catalyst limits the choice of solvent to simple aromatics such as benzene and chlorobenzene. Posttreatment of such catalysts is also vital, partly to remove loosely bound material that can desorb easily during reaction and contaminate the liquid phase, and partly to enhance the activity of the catalyst. Thorough washing with solvents is generally enough, and the problem can be mitigated by appropriate choice of loading. Increases in activity are often brought about by heating of the catalyst (usually to 100–150°C), which serves to remove the last traces of solvent and water from the catalyst. More extreme heating usually is detrimental, but in the case of clayzic (11) a reaction between the support and the zinc chloride is effected by heating to 280°C, which leads to a dramatic increase in activity. Similarly, sulfated zirconia is prepared by treating ZrO_2 with sulfuric acid, and then calcining at high temperature.

Organic species can be supported onto oxide surfaces by grafting species such as $(RO)_3SiR^1$, where R^1 is the catalytic site or precursor thereto. The RO groups are typically methoxy or ethoxy, and these form M–O–Si bonds to the surface of the support. It is rare that all three RO groups are replaced with M–O–Si linkages, but singly and doubly bound species are easily formed, with the latter being more stable to thermolysis and solvolysis. Physisorbed material can also be formed, depending on the nature of the R' groups and the surface. This must be removed by appropriate washing before use.

Other techniques have also been used less frequently. These include grinding of two dry powders, or direct addition of both components to the reaction mix, where the supported catalyst forms in situ. Such approaches are occasionally of some value, but generally reproducibility is less good than with a carefully preformed system. Ion exchange can be an important method of preparation but is obviously limited to appropriate materials such as ion-exchange resins and solid acids that may be converted to sources of catalytically useful metal ions.

2.2. Formation of High Surface Area Supports/Catalysts. Catalysts can also be prepared by (co)-precipitation of oxide precursors, often brought about by a change in pH (eg, in the case of silica, sodium silicate can be partly protonated on decreasing pH from ~12 to ~10; the SiOH units formed readily condense to form SiOSi units and eventually silica) or by hydrolysis of alkoxides $M(OR)_n$. This route is typically carried out in water or aqueous alcohols, and can be used to prepare catalytic systems with one or more M atoms present. When this is the case, it is important to control the relative hydrolysis rates of the two different M alkoxides. Fortunately, the hydrolysis rates of many such species are well understood, and usually a combination of variation of the R group (larger = slower hydrolysis) and/or the use of bidentate systems such as acetylacetone is sufficient to match the hydrolysis rates of the two components so that a uniform material can be prepared.

An extension of this approach allows the incorporation of organic functionality directly into an inorganic framework. Catalysts based on the co-condensation of $Si(OR)_4$ and $R'Si(OR)_3$ can be achieved such that an organic–inorganic hybrid material is formed, where R' represents the active site of the catalyst, or a precursor thereto, or may be a group that modifies the polarity of the surface, improving adsorption–desorption phenomena and improving the activity of the catalyst. In these methods, it is important that the materials formed have a high surface area, in order to allow access to as much surface per unit mass catalyst as possible (in optimum cases surface areas of $\sim$1000 m^2/g can be achieved) and it is also critical that the pores in the material are sufficiently large enough and are open enough to allow free movement of the reactants and products (12). This is generally achieved by the use of templates, molecules that are added to the synthesis mixture and that encourage the formation of the solid around them, and that are subsequently removed. For microporous materials such as zeolites, the templates are normally quaternary ammonium salts, and the pores formed are very small (in general <1 nm). These microporous systems can accommodate small organic molecules readily, but exclude larger organics, limiting their usefulness. Larger pores can be achieved by the use of micellar templates or liquid-crystal phases, using aggregates of molecules such as quaternary ammonium surfactants, long-chain amines, or block polyethers as structure directing agents. In this way, standard, well-understood micelle chemistry can be used to tailor pore sizes of 2–10 nm, allowing access to the majority of organic molecules. For purely inorganic materials, high temperature calcination steps are usually used to remove template, but for organic–inorganic hybrid materials, lower temperature solvent extraction methods are used. These have the advantage of allowing recovery of the template and subsequent reuse, reducing the cost of the material.

While these template assisted formations of high surface area oxides are now well established and lead to a range of materials with various pore systems (such as MCM-41—which has a hexagonally stacked series of relatively straight cylindrical pores, and MCM-48, which has a three-dimensional network of interconnecting pores), nontemplated methods are also known, which lead to structured and regular materials. Hydrotalcites are one such class of compounds, where a layered structure, reminiscent of the clays, is formed—again by alteration of pH.

Many of these methods lead directly to powdered solids that are directly usable in stirred tank reactors and that can be readily separated from reaction mixtures by centrifugation. However, some systems lend themselves to processing as films or monoliths, which may be more appropriate for use in continuous reactors by immobilisation onto, eg, a metal support or even, in some cases, the formation of a membrane.

3. Supported Catalysts as Solid Acids

Solid acids are generally categorised by their Brønsted and/or Lewis acidity, the strength and number of these sites, and the morphology of the support (eg, surface area, pore size). The synthesis of pure Brønsted and pure Lewis solid acids as well as the control of the acid strength are important objectives (13). Pure Lewis acidity is hard to achieve with hydroxylated support materials especially

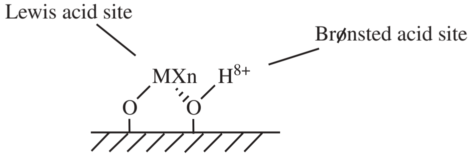


Fig. 1 Brønsted acidity on an hydroxylated support material enhanced by complexation with a neighboring supported Lewis acid.

as a result of polarization of those groups by supported Lewis acid centers such as shown in Figure 1.

Pure Lewis acidity can be important in maximizing selectivity in rearrangement reactions such as those of epoxides whereas Brønsted acidity can be necessary in some Friedel-Crafts reactions and reactions at sterically hindered sites. With acid strength, high acidity is often necessary for alkylations and esterifications while lower strength sites are preferred for acetal formation and hydrolysis reactions. In addition, the steric constraints imposed by the porous structure of many solid acids can influence reaction pathway although actual shape selective catalysis is largely restricted to microporous materials rather than the mesoporous solid acids favored in many liquid-phase organic reactions.

Acids are the most widely used catalysts in organic chemistry with applications covering all major sectors from petrochemicals to pharmaceuticals. The most commonly used include H_2SO_4, HF, $AlCl_3$, and BF_3 and are typically soluble in the organic reaction medium or remain as a separate liquid phase.

At the end of the reaction, such acids are normally destroyed in a water quench stage and require subsequent neutralization thus consuming additional (alkaline) resource and producing salt waste. These increasingly important environmental issues are incentives to utilize solid acids, which stay in a separate and easily recoverable phase from the organic components throughout the reaction. Acidic resins and clays have a proven track record in organic chemicals manufacturing but here we will consider newer solid acids that can substitute environmentally threatening soluble and liquid acids.

3.1. Supported Lewis Acids. The most widely used Lewis acid is aluminium chloride and its immobilization onto typical support materials such as clays, aluminas, and silicas has been widely studied (14–21). This can be achieved from the vapor phase or from a suitable solvent (both aromatic hydrocarbons and chloroaliphatics have been suggested), but in all cases we can expect some combination of physisorbed and chemisorbed, and various levels and types of acidic sites on the surface species (Fig. 2).

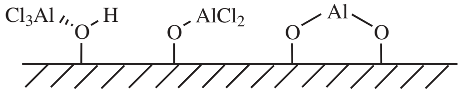


Fig. 2. Possible surface species formed on reaction of $AlCl_3$ with a hydroxylated support material.

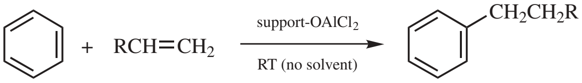


Fig. 3. Formation of alkylbenzenes using supported aluminium chloride as catalysts (r.t. = room temperature).

Catalysts of this type have been shown to be active in reactions including *n*-alkanes isomerizations, aromatic alkylations and oligomerizations and polymerization of unsaturated hydrocarbons (21,22). The use of monodisperse mesoporous solids (eg, 24 Å micelle templated silica) has been shown to give enhanced selectivities, eg, in terms of the degree of ring monoalkylation in the reaction of benzene with alkenes (up to 100% with >C14) although it is not clear if this is due to shape selectivity (largely unproven in pores larger than that in microporous zeolite materials) or diffusional factors (Fig. 3) (17). The proportion of the particularly important linear alkylbenzenes compares well with more traditional homogeneous catalytic methods. These are more active catalysts than the solid acids now being introduced into commercial alkyl benzene plants.

Supported Lewis acids, including supported aluminium chloride, has been described as good catalysts for the oligomerization of mixed refinery feedstocks leading to hydrocarbon resin products (Fig. 4) (21,23). This methodology can avoid the need for a water quench step (necessary in the familiar homogeneous Lewis acid continuous stirred tank reaction method) and enable catalyst reuse. These novel heterogeneous systems can also be expected to lead to new products with different and potentially useful properties such as softening point, molecular weights, and a degree of cross-linking.

Supported complexes of boron trifluoride can be used to make aromatic resins in this way (24). These catalysts are actually believed to be largely Brønsted acidic due to the use of alcohols (or other protic molecules) as cocatalysts (Fig. 5). The catalyst has also been reported as being active in other reactions typically catalyzed by homogeneous BF_3 including phenol alkylations and Claisen condensation reactions.

Commercial Friedel-Crafts catalysts based on supported Lewis acids have been developed for use in typical batch reactions. These include acid clay

$$\begin{array}{l} \text{unsaturated/saturated} \\ \text{aliphatic and/or aromatic hydrocarbon} \end{array} \xrightarrow[\text{RT or higher (no solvent)}]{\text{supported Lewis acid}} \text{hydrocarbon resins}$$

Fig. 4. Production of hydrocarbon resins using refinery feedstocks supported Lewis acid catalyst.

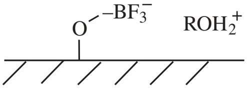


Fig. 5. Active species in supported boron trifluoride complexes.

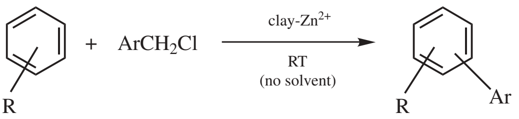


Fig. 6. Benzylations of aromatic substrates catalyzed by commercial acid clay supported zinc(II) catalyst.

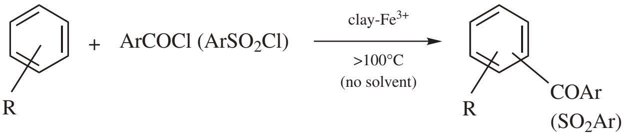


Fig. 7. Benzoylations and sulfonylations of aromatic substrates catalyzed by commercial acid clay supported iron(III) catalyst.

supported zinc(II) salts for use in reactions including benzylations (Fig. 6) and iron salts for the more demanding benzoylations and sulfonylations (Fig. 7) (25).

The reactions are best carried out in the absence of solvent, adding to their environmental credentials. Acid clay supported zinc salts have also been reported as catalysts for aromatic brominations (with some improvements in selectivity compared to normal homogeneous reactions) and the rearrangement of α-pinene oxide to the valuable perfumery intermediate campholenic aldehyde Fig. 8) (26). The last of these is especially demanding on the control of the acidity, since for any Brønsted acidity catalysis, there are several other reactions resulting in a complex product mixture.

3.2. Supported Heteropoly Compounds. Heteropolyacids supported on silica have been claimed to show commercially viable activity and catalyst lifetime for the manufacture of ethyl acetate from ethylene and acetic acid (27). One of the major current commercial routes to ethyl acetate is based on $PdCl_2/CuCl_2$ catalysis (the Wacker process), but this has a number of drawbacks, including the use and subsequent disposal of high concentrations of HCl. A solid acid catalyst could be a viable option and when comparing a range of materials including clays, acid resins and zeolites to $H_4SiW_{12}O_{40}$-silica, the last of these is clearly the most active (330 $g/L^1/h^1$ space−time yield). Careful choice of the catalyst and associated process conditions has made such a system a genuinely commercially viable option.

The hydrolysis of ethyl acetate can also be achieved using a supported heteropoly compound—$Cs_{2.5}H_{0.5}PW_{12}O_{40}$-silica (28). It is also important to note

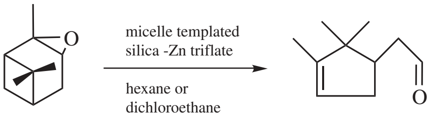


Fig. 8. The rearrangement of α-pinene oxide catalyzed by mesoporous silica supported zinc(III) triflate.

that the catalyst is unchanged at the end of the reaction. Supported heteropoly compounds are also active in the formation of methyl *tert*-butylether (MTBE) (29,30) with a selectivity of 95% particularly using dodecatungtophosphoric acid-K10 clay the dehydration of diols, the oligomerisation of propene, and the etherification of phenethyl alcohol with alkanols (31). Their industrial potential is further illustrated by a substantial recent patent literature that covers reaction applications including the isomerization of nonenes, the formation of *tert*-butylacrylamide (as a replacement for H_2SO_4), the formation of alkyl diphenylamine (as a replacement for $AlCl_3$), and polyisobutylene (as a replacement for BF_3 and $AlCl_3$) (31). Several types of support material have been proposed and while silica (especially mesoporous silica) and acid-treated clays are especially popular, others, including alumina and zirconia have been reported to be effective in some reactions.

3.3. Supported Sulfur(VI) Acids. The widespread importance of sulfuric acid and other sulfur(VI) acids, notably methanesulfonic and triflic acids, has encouraged a substantial amount of research into heterogeneous analogues and not insignificant commercial application, notably via polymeric acidic resins.

Modern mesoporous silicas and other materials have been successfully functionalized by sulfonic acid and their activity proven in a number of important reactions including esterifications, transeseterification and alkylations (32,33). A good example of this is the use of sulfonic acid functionalized MCM-41 as a catalyst for the liquid-phase condensation of phenol with acetone to form the commercially important bis(phenol)-A with high selectivity (Fig. 9) (34). Reaction occurs at a reasonable rate at temperatures as low as 70°C, which can be contrasted with the same support modified with the heteropolyacid 12-tungstophosphoric acid that is only catalytically active in this reaction at >120°C when reaction selectivity is relatively poor (35). It is also important to note that there is negligible loss of sulfur from the solid sulfonic acid after reaction.

Bisphenol-A is manufactured on a commercial scale using sulfonic acid-modified polystyrenes. Acidic resins have been used for a range of other commercial scale chemical processes including ester hydrolysis, olefin (eg, propylene) hydration, alcohol dehydration and the reaction of olefins with alcohols (notably the reaction of methanol with isobutylene to give MTBE (31). Commercially, MTBE is produced using a macroporous sulfonic acid resin catalyst in the liquid phase (36,37).

More speciality, applications for sulfonic acid resins include the preparation of perfumery-grade methyl anthranilate from the reaction of methanol with anthranilic acid. Numerous other esterifications have also been show to be effectively catalyzed be these solid acids (31).

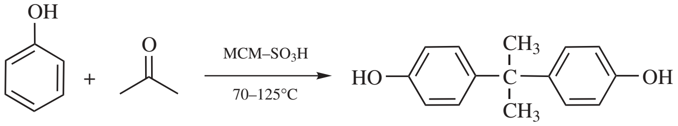


Fig. 9. The preparation of bisphenol-A using a sulfonic acid functionalized mesoporous solid.

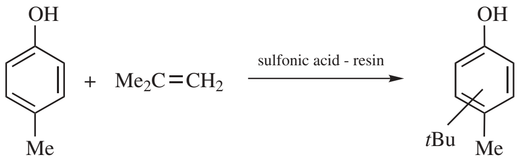


Fig. 10. Alkylation of cresol catalyzed by a sulfonic acid resin.

Polyfluorinated sulfonic acids are considerably stronger Brønsted acids than the conventional styrene-based materials (ΔH_0 ~10). They are also more thermally robust. Successful applications of these strong solid acids include the bimolecular conversion of alcohols to ethers. An interesting development in this context is the preparation of composites of silica with fluorinated sulfonic acid resins (eg, Nafion) (38,39). These can be considered as effectively being higher surface area forms of the highly acidic polymer with a commensurate increase in catalytic activity of up to 10^3 and allows catalysis of reactions not normally considered possible for conventional ion exchange resins. Thus a nafion resin/silica catalyst is active for the alkylation of benzene with C_{12} olefins to give the very large scale detergent intermediate dodecylbenzene. Its particularly important to note that very little branched alkylates on other by-products are formed. Selectivity in this application is very good although the catalyst is significantly less active in such alkylations than supported aluminium chloride or sulfated zirconia.

The alkylation of phenols such as the tertiary-butylation of *p*-cresol is a very important process in the manufacture of numerous chemical products including fragrances, antioxidants, herbicides, and insecticides (40). Sulfonic acid resins have replaced homogeneous and liquid acids in many of these processes especially where the alkylation is not too difficult (Fig. 10).

For more challenging systems, the more acidic fluorinated analogues may be more suitable. Similarly, olefin isomerisations require the more acidic materials to achieve reasonable reaction rates, eg, the Nafion-silica composites 200 times more active than plain Nafion resins and ~50 times more active than the zeolitic solid acid H-ZSM-S in the isomerization of 1-dodecene to its linear isomers (31,39).

Rather than fix a sulfur(VI) acid function to a support with a hydrocarbon or perfluorocarbon linker group, attempts have been made to support H_2SO_4 directly onto a support materials. The most successful of these is sulfated zirconia (SZ), which in many practical applications provides a mixture of Brønsted and Lewis acid sites (Fig. 11) (41).

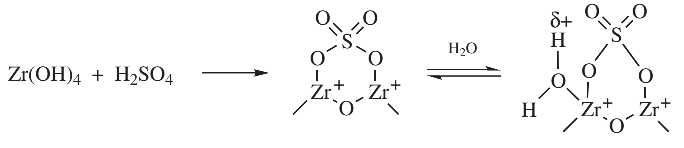


Fig. 11. Formation of sulfonated zirconia and the effect of water.

While many of the supported applications for SZ are in the vapor phase (where Lewis acidity can be expected to dominate) an increasing number of reports show it to be an effective Brønsted solid acid on mixed Brønsted/Lewis solid acid in some liquid phase reactions. The activity of SZ is, however, highly dependant on the temperature of activation. Thus the alkylation of benzene with olefins is readily catalyzed via optimized SZ at room temperature and with excellent selectivity to alkylation (vs digomerization, good selectivity to monoalkylation (>90%), and reasonable selectivity in the formation of the normally preferred 2-isomer (43%). The importance of pore size and pore volume, is very evident. Microporous SZ is blocked by high molecular weight by-products and shows little activity on reuse in a batch reaction. Mesoporous SZ retains its activity and while it will eventually become blocked, it is possible to reactivate the catalyst by a combination of solvent extraction and thermal treatment (Fig. 12) (42).

SZ has also been shown to be active in some Friedel-Crafts acylation reactions (41,43). The SZ will catalyze the benzylation of benzene (and other aromatic substrates) without solvent at moderate temperatures. Unlike $AlCl_3$, the SZ is genuinely catalytic in such reaction although rates or reaction are slow (but SZ does seem to be significantly more active with activated substrates such as anisole). A particularly important advantage is that a water quench is not needed at the end of the reaction (SZ can be removed by filtration, eg).

Loss of activity on moving from a homogeneous acid to a heterogeneous analogues is a frequent cause for concern and has undoubtedly delayed the commercial uptake of many supported catalyst systems. One way around this problem is through the utilization of a moving bed of the liquid catalyst wherebye the catalyst slowly moves over the surface of a support while reactants are fed through the mixed-catalyst bed (Fig. 13) (31).

One example of this reactor technology at work is in the very large scale butane alkylation reaction (*n*-butene and isobutane to isooctane) using CF_3SO_3H as the (moving) catalyst. Excellent activity can be achieved (100% conversion to the desired alkylates) along with good selectivity (up to 80% C_8). When

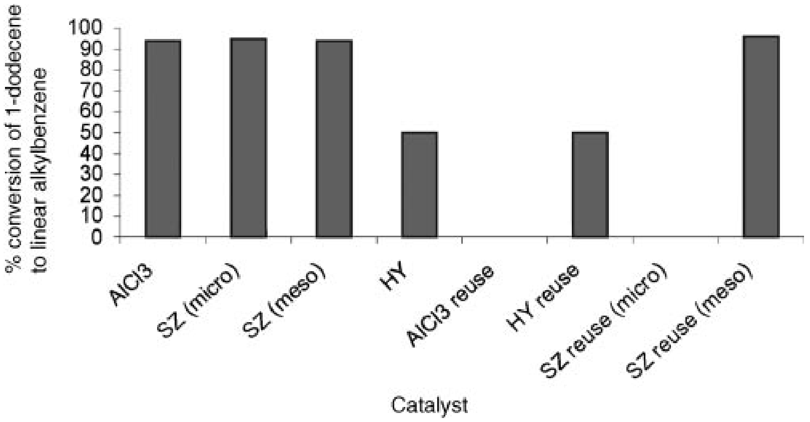


Fig. 12. Comparisons of the effectiveness and reusability of different catalysts for the production of linear dodecyclbenzenes from the reaction of benzene with 1-dodecene at 35°C.

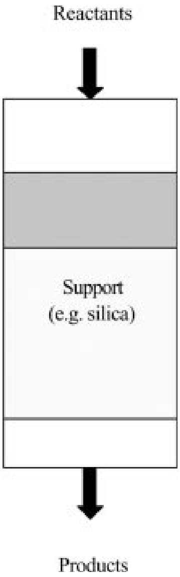


Fig. 13. Moving bed of the liquid catalyst.

the catalyst elutes from the support, it can be recycled. This pseudo-solid-acid technology offers health and safety advantages over the conventional HF and H_2SO_4-based methods.

3.4. Acid Catalysis by Zeolites. The use of zeolites as acid catalysts is one of the most prominent area of gas-phase catalysis, predominantly in the field of catalytic cracking. In recent years, some applications have begun to emerge in the field of fine chemicals synthesis, mostly in the liquid phase, but with one or two important exceptions.

The acid sites of zeolites comes about by the presence of Al atoms in tetrahedral sites in the oxide lattice. This leads to an overall negative charge on the lattice that can be balanced by a range of cations, including the proton. The acid strength of a zeolite is a complex function of the aluminium content, with acid strength ranging from moderate (high number of Al sites giving a large number of moderately acidic sites) to superacidic (low amount of Al leading to a small number of extremely acidic centres). Extension of this concept to the mesoporous "analogues" of zeolites does not appear to be feasible, and mesoporous molecular sieves (eg, MCM-41) seem to have very modest acidity.

The channels of zeolites can accommodate benzenoid systems, given that there are no meta or ortho substituents. These are barely large enough to fit inside (or form inside) the channels of the zeolites. Choosing a zeolite capable of absorbing benzene or a monosubstituted benzene might therefore lead to the possibility of highly selective para substitution under Friedel-Crafts conditions. Such work has been carried out with some success. Nitration using H-ZSM-5, H-ZSM-11, and H-beta is known where benzene, toluene and halobenzenes can be nitrated in excellent yield and para-selectivity (44). Selectivities up to 98% were achieved. Halogenation is also possible in excellent selectivity, with zeolites also being useful in retarding over-halogenation (more of a problem than with nitration) (45). Friedel-Craft alkylations are also documented using zeolites, and here selectivity is also controlled by the pore constraints of the catalysts chosen (46). Friedel-Crafts acylation is possibly the most challenging of these processes, with traditional acylations not being strictly catalytic. Nonetheless, progress has been made, and mildly acidic zeolites have been shown to be sufficiently active to effect the reaction. The acylation of toluene can be carried out using a Ce-exchanged Y-zeolite at 150°C, giving excellent para selectivity and yields that increase from low with short-chain acids (not acid chlorides!) to excellent for longer chain acids (47). The much more activated anisole has been acylated using a range of zeolites, with H-beta and HY being the most active (48). Rhodia curently operate a process that uses this technology to prepare 4-acetylanisole (49). Other activated substrates such as thiophene (50) and 2-methoxynaphthalene (51) have also been extensively studied. 4-Acetyl isobutylbenzene, a key intermediate in the synthesis of ibuprofen, has also been manufactured by the zeolite-catalyzed acylation of isobutylbenzene with H-beta zeolite in excellent yield and selectivity (52).

The Beckmann rearrangement of cyclohexanone oxime has been the subject of a substantial amount of research using zeolitic catalysts (53). Selectivity is excellent and catalyst lifetime can be very long, when a cofeed of carbon dioxide or methanol and water are used.

4. Basic Catalysts

Solid base catalysts are less well developed than solid acids, but nonetheless represent an important class of catalysts. They range from simple solids such as alumina, which has some basic activity, through more complex inorganic species such as zeolites, hydrotalcites, "blue alumina", and to the newer organic–inorganic hybrid materials, based on silica/amine composites. Basicity ranges from very mild, typical of simple amines, through to superbasic ($H^- > 37$).

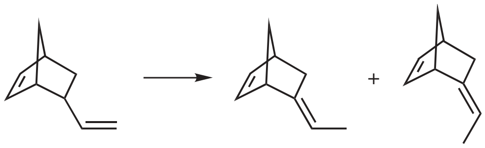
$$H^- = pK_{BH} + \log_{10}[B^-]/[BH] \tag{1}$$

One generic difficulty inherent in the handling and use of basic catalysts (particularly with the most basic systems) is the presence of acidic impurities in the atmosphere. Both water, and especially CO_2 can poison basic catalysts very rapidly, and possibly irreversibly. In the case of reversible adsorption of CO_2, the temperature-programmed desorption of CO_2 can be used as a measure of base strength. In the case of KF-alumina, the very rapid adsorption of CO_2 from the atmosphere may be the cause of the wildly differing reports of its base strength in the early days of research into its properties. Despite this problem, even the most basic of materials can be and are used on an industrial scale.

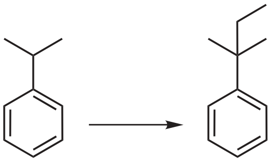
4.1. "Blue Alumina". An interesting and very basic material, which is finding industrial application, is based on the reaction of alumina first with NaOH, and then, in a high temperature step, with sodium metal, to produce the strongly basic "blue alumina".

The basicity of this material is exceptionally high, with $H^- > 37$. Its preparation involves the treatment of gamma alumina with sodium hydroxide, forming $NaAlO_2$. In a second step, this is treated at high temperature with sodium metal, leading to the superbasic solid. The potassium analogues are similarly superbasic. The basicity of these materials are such that they are extremely sensitive to air, water, and CO_2, but nonetheless they are used on a commercial scale for alkene isomerisation and for the side-chain alkylation of alkylaromatics. A range of patents, mostly to Sumitomo, describes such transformations, two of which are discussed below.

Superbases can be used to bring about the thermodynamic isomerization of alkenes, giving the most stable isomer. One example is the isomerization of 5-vinylbicyclo[2.2.1]hept-2-ene to 5-ethylidenebicyclo[2.2.1]hept-2-ene (54) an important component of ethylene–propylene synthetic rubber. The reaction proceeds at −30°C in the presence of catalysts, giving the product cleanly. The endo/exo ratio appears to be related to the temperature of the reaction (lower temperature gives higher selectivity to the endo isomer) but not to the endo/exo ratio of the reactant.



The alkylation of alkyl aromatics at the benzylic position is an important class of reaction, which can often give different isomers when compared to acid catalyzed routes. Such superbase-catalyzed alkylations are used industrially in the production of isobutylbenzene from toluene and propene. The alkylation of cumene with ethylene gives the pentylbenzene shown below in 99% yield under very mild conditions (54), this concept can be extended to the preparation of alkenyl substituted benzenes by using alkenes as alkylating agents (55). Substituted pyridines are also accessible via this route (56).



4.2. Zeolites. While the majority of zeolites have pore sizes that are too small to allow all but the smallest molecules to enter, and are consequently of little use in organic synthetic applications, a few examples exist where larger pore zeolites have been used as supports in base catalysis. The limited reaction space of the smaller zeolites becomes even more constrained by the requirement for a (normally) large counterion such as Cs, which is required to increase the basicity of the framework oxyanion sufficiently to allow good activity. Simple ion-exchange allows the formation of ion pairs between the M^+ and the framework O^-. This leads to moderately basic catalysts, with the Cs^+ containing material being most basic (57). More powerfully basic sites are obtained when the zeolites are loaded with salts that, upon thermal decomposition, give small clusters of Group I (I A) or (II A) oxides (58). These much more basic materials must be kept free of water and carbon dioxide, both of which reduce their basicity considerably. The latter appear to be capable of catalyzing reaction types similar to blue alumina, while the former have been studied for their activity in mild-base catalyzed condensation reactions (eg, Knoevenagel).

Reviews on zeolites written with a slant toward their organic chemical applications are available (59). Also see the Bibliography for more background information.

4.3. Hydrotalcites. Hydrotalcites are another group of catalysts that are proving efficient as medium-to-strong basic catalysts. As catalyst supports, they have been used in the synthesis of the superbases described above (56), but they are also interesting in their own right. Hydrotalcites are lamellar solids consisting of layers of mixed oxides, typically Mg and Al, but others are also known. The structure contains (partly) exchangeable anions such as hydroxide and carbonate that gives basicity to the structure and, combined with their lamellar structure, leads to them being referred to sometimes as anionic clays (60). Surface areas are generally $\sim 100-250\ m^2/g^1$ depending on thermal pretreatment/rehydration.

A range of C–C bond-forming reactions are known to be catalyzed by hydrotalcites and related materials (61,62). In particular, aldol reactions have been extensively studied (62), and the conversion of *n*-butyraldehyde to 2-ethylhexenal has been the subject of much work (63). There also exist patents describing the use of hydrotalcites as catalysts for the formation of alkoxylated alcohols and related products, of use as nonionic surfactants, by oligomerization of alkylene oxides (64) and to the preparation of crystalline stereoregular poly(propylene oxide) using a similar route (65).

Ni–Al hydrotalcites have been shown to have excellent properties for the industrially important reduction of nitriles to primary amines. The combination of basic character with reducing centers plays an important role in minimizing the production of secondary amines (66).

4.4. Metal Oxides. Metal oxides all have the potential for their surface oxygen atoms to act as basic sites. In practice, those with divalent cations are the most basic, and therefore the most studied. Tri- and tetravalent cations can give materials with basic sites, but these are often relatively mildly basic, and acidic sites can also be present. Such materials are very interesting for processes that require the presence of both types of sites, and an example is given below.

Of the divalent oxides, it is found that basicity increases as expected in the order $MgO < CaO < SrO < BaO$. Some sites with $H^- > 26$ are found on the most strongly basic of these. These catalysts are very good at abstracting protons from allylic positions, making them very effective catalysts for alkene isomerisation, as discussed in the section on “blue alumina”.

Zirconium oxide possesses both mildly basic and mildly acidic sites, and this makes it particularly suitable for certain reaction types. Industrial processes exist for the hydrogenation of aromatic carboxylic acids to aldehydes (67), and for the formation of vinylcyclohexene from 1-cyclohexylethanol (68). The formation of diisobutyl ketone from isobutyraldehyde has been practiced industrially for a quarter of a century (69). All of these processes are enhanced by the presence of both acid and basic sites on the surface of the catalyst.

4.5. KF-alumina. KF-alumina is the most studied of a group of MF-support catalysts, most of which are characterized by a strong interaction (or a much more fundamental reaction) between the two components. This leads to novel basic sites; in the case of KF-alumina this can be represented by the equations below:

$$12\,KF + Al_2O_3 + 3\,H_2O \rightarrow 2\,K_3AlF_6 + 6\,KOH$$
$$6\,KF + 2\,Al_2O_3 \rightarrow 3\,K_3AlF_6 + 3\,KAlO_2$$

These catalysts are active in a wide range of organic reactions (70). The basicity is such that many CH acids such as nitroalkanes and methyl ketones can undergo C–C bond-forming reactions such as Knoevenagel, Michael, and aldol reactions.

4.6. Organic–Inorganic Hybrid Catalysts. A range of mildly basic catalysts for fine chemicals synthesis exist, where the basic centre is an amine or diamine group, attached to a silica matrix via a short hydrocarbon spacer. Two routes exist to these compounds, including grafting with $(RO)_3Si(CH_2)_3NH_2$ onto amorphous silica or the newer micelle templated silicas such as MCM-41 (71). The second route involves the direct cocondensation of a silica precursor with the trialkoxyaminopropyl silane under micelle templating conditions (72). This latter route is more efficient with respect to the silane used, and the template can also be recovered and reused, making this method a relatively cheap and simple route to these compounds. The basicity of these materials is relatively mild, and thus these materials are being investigated for the condensation of C-acids such as diketones, dinitriles and ketoesters. Activity in Knoevenagel and Michael reactions, as well as aldol and related condensations is generally good.

4.7. Ion-Exchange Resins. Ion-exchange resins, which are often used in acid catalysis, are much less commonly utilized in base catalyzed processes. This is due to their limited thermal stability, with the quaternary ammonium hydroxide active sites being relatively easily destroyed by Hofmann degradation to the amine, alkene, and water. This finding is reported to occur at temperatures as low as 50°C, although some reports indicate that, in the carbonylation of methanol with CO, little loss of activity is found up to 70°C (73).

5. Supported Metal Complexes

The heterogenization of catalytically useful metal complexes is attractive both economically (by facilitating catalyst recovery and reuse or by enabling use of a fixed-bed catalyst reactor) and in the context of green chemistry (by simplifying reaction work-up and minimizing release of toxic metals into the environment) (74).

In principle, this can be achieved via immobilization typically on to a high surface area support material. However, limitations in the stabilities of supported metal complexes in liquid-phase reactions and uncertainties over possible parallel homogeneous catalysis due to leached metallic species makes this area controversial and still largely unproven (75).

A good example of these "hidden" complexities is the well-researched area of supported chromium complexes and their use in liquid-phase oxidations. While chromium(III) complexes are quite stable toward substitution of the metal, chromium(VI) is very labile and soluble especially in semiaqueous systems. Thus it has been conclusively shown that chromium aluminium phosphate, CRAPO, leaks chromium in reactions using aqueous hydrogen peroxide (76). This can be attributed to the formation of chromium(VI). In determining this a useful test for catalyst stability toward leaching has been developed. The so-called "hot filtration" test involves the filtration of the solid catalyst from the reaction mixture at reaction temperature, and then monitoring the filtrate for any further reaction of the organic substrate. This is an effective check on any homogeneous contribution to the reaction but does not rule out leaking of any inactive metallic species (this can only be determined by analysis of the filtrate but is limited by detectability of the metal). Numerous other attempts have been made to immobilize chromium for oxidation reactions including a commercial catalyst that appears to be based on Cr(VI) chemisorbed on alumina (25) and a chromium Schiffs base complex imprinted on a mesoporous silica surface (77).

While some of the reported activities of these materials in various oxidation reactions (notably the relatively facile ethylbenzene to acetophenone) are quite impressive and are based on good clean synthesis principles (no solvent, air as the only consumable source of oxygen), they are not stable in aqueous peroxide systems, and their stability in nonaqueous reaction mixture is questionable (though probably good enough to give very high turnover systems in moderate temperature alkylbenzene oxidations (75,77). Similar materials based on supported cobalt may have better long term potential (78) and also have value in other reactions such as allylic oxidations (79).

Other noteworthy attempts to develop genuine heterogeneous metallic catalysts for oxidation reactions include metalloporphyrinosilicas (prepared by methods including cocondensation with tetraethoxysilane) (80) and a mononuclear iron carboxylate complex immobilized on modified silica used to mimic the active site of methane monooxygenase. The latter catalyzes the room temperature oxidation of hexane using air although the reaction requires several auxiliaries (a mercaptan, acetic acid, and triphenylphosphine) Several other direct oxidations of alkanes using air, catalyzed by supported metal complexes have been reported including Fe-aluminophosphate (FeAlPU-31) for cyclohexane to adipic acid (81). This provides an interesting contrast with one of the current commercial routes (Table 2). Bifunctional molecular sieve catalysts have been reported as being effective for the one-step solvent-free production of cyclohexaneoxime and caprolactam using a mixture of air and ammonia (Fig. 14) (82).

Epoxidation reactions have been successfully catalyzed by an immobilized version of Jacobsens catalyst using NaOCl as the oxidation (82). This is interesting although long-term catalyst stability is again a likely problem.

Chemically modified (typically porous) solid supports can also make very effective ligands for palladium enabling a range of important reactions including amidations, carbon–carbon bond forming coupling reactions, hydrogenations,

Table 2. **Comparison of Traditional and New Heterogeneous Metal-catalyzed Methods for the Manufacture of Adipic Acid**[a]

	Traditional	New
method	nitric acid oxidation of a mixture of cyclohexanone and cyclohexanol >60°C, ~0.2 MPa; 60% HNO_3, V/Cu catalyst	direct conversion of cyclohexane; 100+ °C; 1–5 MPa air; Fe–AlPO catalyst
yield	90%	65%
major products	adipic acid, glutanic acid, succinic acid	adipic acid and cyclohexanone
by-products	NO_x . CO_2	glutanic and succinic acids
other factors	plant corrosion, health and safety concerns, expensive to recover catalyst	slow reaction
	health and safety concerns	
	expensive to recover catalyst	

[a] See Ref. 81.

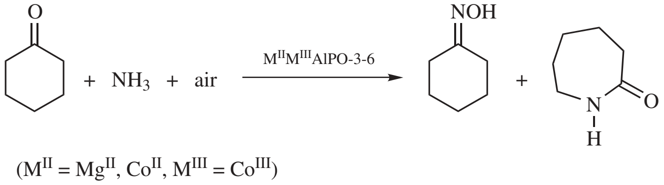


Fig. 14. The solvent-free production of cyclohexaneoxime and caprolactam using a solid catalyst.

and carbonylations. Apart from organic polymers, silicas and clays have been used as support materials. Silica modified with long chain bis-(diphenylphosphine) ligands can be used as a ligand for Pd(0) in the amidation of aryl halides (Fig. 15) (83).

Silica or clay supported mercaptans can also be used to bind Pd(0) and the resulting materials are catalytically active in the Heck reaction between aryl iodides and activated alkenes (84). Palladium supported on silica modified with pyridyl functions has also been used to catalyse Heck and Suzuki reactions (85,86) (Fig. 16). These catalysts have excellent turnover numbers (several thousand) and pass the “hot filtration test”, ie, the hot filtrates show no residual activity indicating that no active soluble palladium species are formed during the reactions.

Fig. 15. Amidation of aryl halides catalyzed by supported palladium (0).

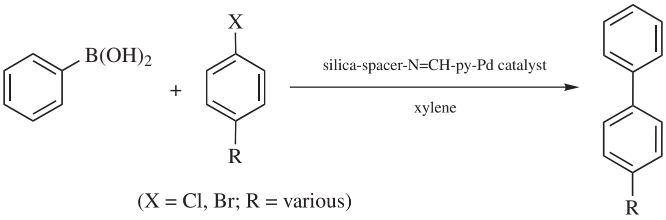


Fig. 16. Suzuki reaction to form biaryls catalyzed by silica supported palladium complexes.

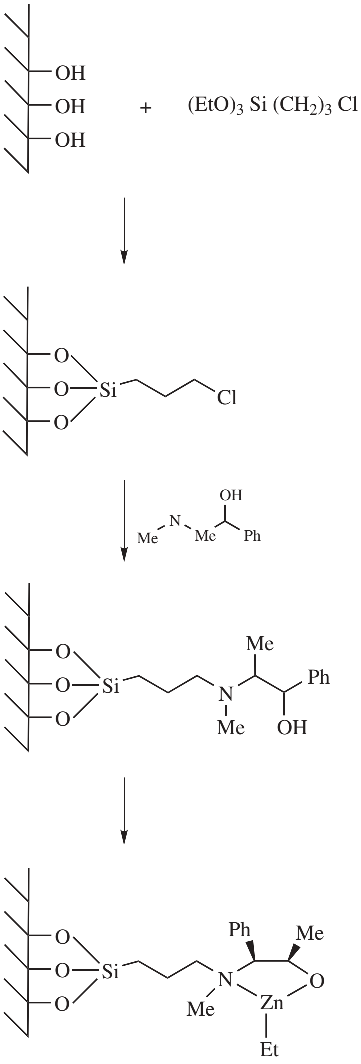


Fig. 17. Preparation of a solid chiral Zn catalyst for enantioselective alkylations.

A chiral palladium catalyst can be prepared using MCM-41 modified with 1,1-bis(diphenyl-phosphino)ferrocene ligand. Some regioselectivity and enantiometric excess is observed when using this catalyst in the allylic amination of cinnamyl acetate; the performance of the catalyst is superior to that of the homogeneous analogue (87). Another solid catalyst for enantioselective reactions is also based on MCM-41, this time modified with (−) or (+) ephedrine (88,89). The solid chiral auxiliary was then used in the enantioselective alkylation of benzaldehyde by diethylzinc to give the corresponding (*R*)- or (*S*)- 1-phenylpropan-1-ol (88). The preparation of the catalyst is shown in Figure 17.

Various other metals can be effectively immobilized on chemically modified supports, silica and clay supported rhodium complexes are good hydrogenation catalysts, eg, (90). Heteropolyacids have been used to enhance the solid-metal binding (91). Silica supported rhodium hydrides are efficient isomerisation catalysts (92). A good example of a supported ruthenium catalyst is that prepared from on sol–gel mixture containing *cis*-Cl(H)Ru(CO) (phosphine)$_3$ with $(EtO)_4Si$ and $[AllO\text{-i-}Pr)_3]$. The resulting material is quite stable and is active in the hydrogenation of *trans*-crotyl aldehyde with reasonable chemoselectivity to *cis*- and *trans*-crotyl alcohol (93). Osmium has also been effectively immobilised on a silica supported bis(cinchona) alkaloid and the very stable and reusable material that results is catalytically active in the asymmetric aminohydroxylation and dihydroxylation of alkenes (94).

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