

# Solid Acid Catalysts in Green Chemistry

## 1. Emerging Eco-Friendly Practices in Chemical Industry

*Leena Rao*

**This article deals with various ‘supported’ acid catalysts developed as alternatives for the conventional ones in organic synthesis. They have advantages such as producing less toxic waste and using less energy.**

Acid catalysts are widely used in chemical industry. They are either ‘Bronsted acids’ or ‘Lewis acids’. All these acids generate significant amounts of toxic wastes. This article attempts to address this problem.

Bronsted acids owe their acidic character to protons. If spent Bronsted acids are discharged into the environment, the pH of the soil and the water body into which they are discharged, decreases – sometimes to a harmful extent, thereby making them toxic to plant and animal life. Also, microorganisms in the soil get destroyed. The consequence is a lowering of soil quality for agricultural use, and loss in marine produce.

Even if the spent acid effluent is chemically treated to restore its pH, it still results in the release of deleterious chemical wastes into the environment, as other chemicals would be present. For example, if slaked lime is used to neutralise the spent acid, it will result in the generation of calcium-saturated effluents. Calcium ions are responsible for hardness in water. The chemical dye manufacturing industry and the petroleum industry, which utilise Bronsted acid-consuming reactions like nitration, sulfonation and isomerisation, are responsible for producing huge quantities of acid effluents.

Lewis acids are usually metal salts like aluminium chloride, ferric chloride, antimony fluoride, titanium chloride and tin chloride. The chemical industry uses them for a variety of electrophilic



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### Keywords

Solid acid, Lewis site, Bronsted site, zeolites, resins, clays, Green chemistry.

In SPOS reactions, the reactants are usually in the liquid phase and the catalyst is in the solid phase. On completion of the reaction the solid catalyst is filtered off and can be regenerated for re-use. The process ensures acid-free effluents and decrease in operational costs since the acid catalyst can be recovered.

substitution reactions in aromatics. Lewis acids need to be hydrolyzed during the work-up process after which the spent Lewis acids cannot be recovered. When discarded into the environment they release toxic cations.

The rising environmental awareness has compelled the chemical industry to take up measures to overcome the effects of polluting effluents, including those which are termed as 'Green Chemistry' processes.

Solid Acid Catalysis (SAC) is a part of the broader realm of Solid Phase Organic Synthesis (SPOS) and constitutes an important facet of Green Chemistry.

### SPOS and SAC

In SPOS reactions, the reactants are usually in the liquid phase and the catalyst is in the solid phase. On completion of the reaction the solid catalyst is filtered off and can be regenerated for re-use. The process ensures acid-free effluents and decrease in operational costs since the acid catalyst can be recovered. Novel SAC compounds are developed following this principle.

### Preparation of Solid Acid Catalysts

SAC compounds are made by grafting acid catalytic sites on polymer surfaces. The polymers should be insoluble in the solvent medium, and should have a large surface area in order to accommodate as many catalytic sites as possible.

The mechanical strength of a given polymer matrix (also called the 'support') limits the temperature at which a given reaction can be carried out. If the polymeric matrix starts disintegrating at, say, 135 °C, the reaction obviously has to be carried out below this temperature.

Initially, the polymeric surfaces used were of natural origin (e.g. the 'clay minerals'), but in recent times, they are tailor-made for specific reactions. For example, chemically modified alumina,



silica, zeolites and synthetic resins are used as supports.

### Clay Minerals

Clays were the first solid acid catalysts used in organic synthesis. However, due to their wide variety they lack perfect reproducibility in yields with different samples. Otherwise, they have considerable potential as environmental friendly solid acid catalysts. Some of the types of clays frequently used are *Bentonite*, *Montmorillonite K<sub>10</sub>* and *Montmorillonite-KSF* [1].

### Amorphous Silicas and Aluminas

Silica and alumina constitute a group of polymeric oxides of silicon and aluminium respectively. They can also be obtained in mixed polymeric forms.

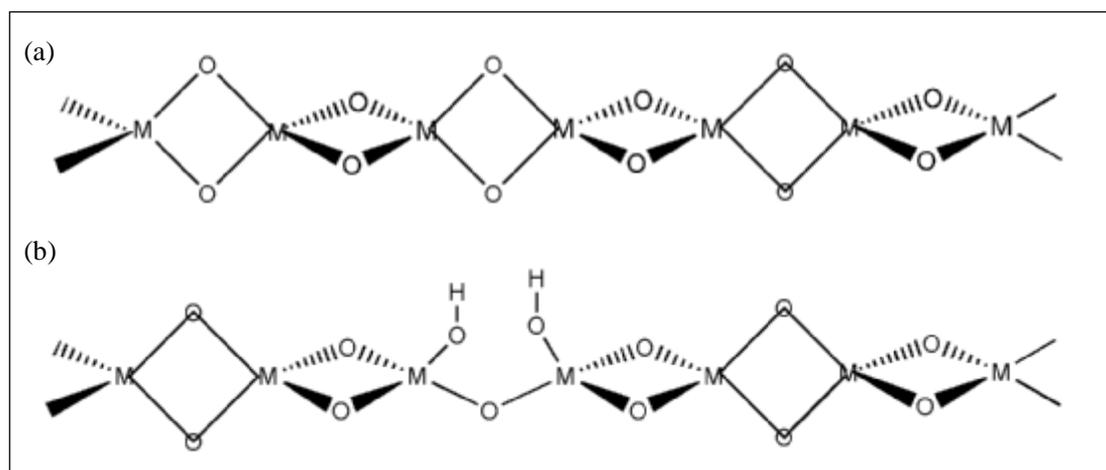
Their anhydrous forms have a general structure as shown in *Figure 1a*, where  $M = \text{Si}$  or  $\text{Al}$ .

On hydration, some divalent oxide linkages are replaced by  $M\text{-O-H}$  bonds in the matrix. The protons released on ionization of these  $\text{O-H}$  bonds are the source of Bronsted acidity (*Figure 1b*).

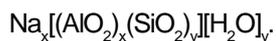
Oxides like titania, zirconia, magnesia as well as mixed oxides are also used. The physical structures of all these oxides consist of random pores in which adsorption and catalysis takes place.

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**Figure 1. (a) Representative structure of silica and alumina. (b) Representative structure of hydrated silica and alumina.**



Zeolites are also known as molecular sieves. They are aluminosilicates with the general formula



They have a tetrahedral structure with each atom of silicon and aluminium surrounded by oxygen atoms

Hence the surface is very irregular. The extent of their usefulness is dependent on particle size, surface area, pore structure and acidity. For instance, the surface area of silicas should be in the range of 50 – 400 m<sup>2</sup>/g and that of aluminas should be in the range of 120 – 300 m<sup>2</sup>/g.

### Zeolites

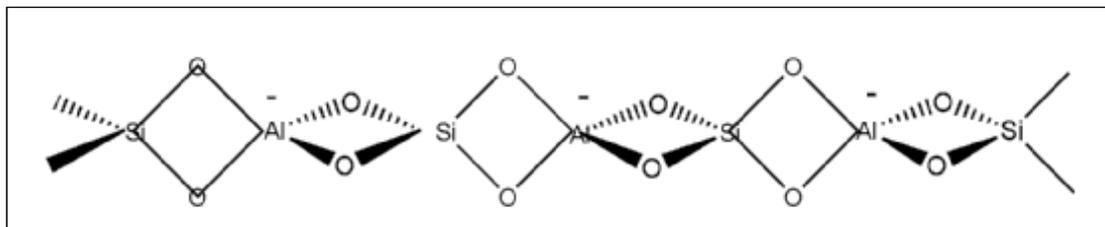
Zeolites are also known as molecular sieves. They are aluminosilicates with the general formula  $\text{Na}_x[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot y\text{H}_2\text{O}$ . They have a tetrahedral structure with each atom of silicon and aluminium surrounded by oxygen atoms (*Figure 2*). In natural samples, they have three-dimensional crystalline microporous channels in which molecules of appropriate size can diffuse and react. The pore size in zeolites can be controlled using synthetic methods.

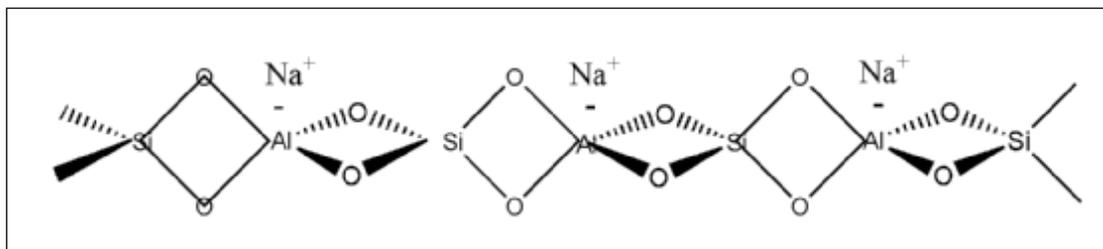
In the three-dimensional structure illustrated in *Figure 2*, it can be seen that the four-bonded tetravalent silicon site is neutral whereas the four-bonded trivalent aluminium site is negative. This requires positively charged counter-ions such as Na<sup>+</sup>, as indicated in the general formula for zeolites.

In order to make the zeolite acidic, sodium counter-ions are replaced with protons. This is done by first exchanging the sodium ions with ammonium ions (*Figure 4*) and then heating the zeolite sample. On heating, NH<sub>3</sub> is released and protons are left behind as the counter-ions, in place of sodium ions (*Figure 5*).

**Figure 2. Representative structure of the zeolite skeleton.**

So each aluminium ion will have a proton counter-ion in the zeolite network and this is the cause of its Bronsted acidity. In other words, the ratio Si/Al determines the polarity, the acidity





**Figure 3. Representative structure of zeolite.**

and the exchange capacity of the zeolites. These parameters also control the catalytic properties of zeolites.

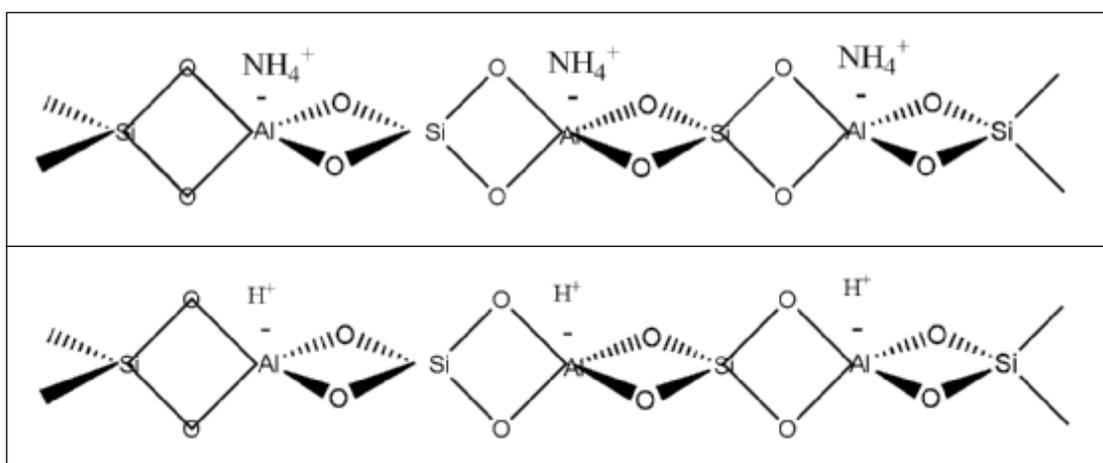
Such a zeolite network was first used by A J Houdry in the 1920s for isomerisation of straight-chain petroleum hydrocarbons to branched hydrocarbons. This conversion process increased the octane number or the anti-knock property of gasoline.

In zeolites, the active sites are protons and they are inside the pores (pore size  $< 8 \text{ \AA}$ ), and so the pore size places restriction on the shape and size of the molecule that can enter it. Bulky molecules cannot enter them. Therefore zeolites are useful in reactions involving either only small molecules or a mixture of different-sized molecules with the same functional group, where only the reaction of the smaller sized molecules is desired.

Zeolites also form excellent drying agents as their pores can absorb and hold a large quantity of water ( $\text{H}_2\text{O}$ : size  $< 8 \text{ \AA}$ ).

**Figure 4 (top). Representative structure of zeolite after ion exchange.**

**Figure 5 (bottom). Representative structure of zeolite with proton (Bronsted) catalytic sites.**



Resins are supports made of synthetic polymers like polystyrene or co-polymers of polystyrene and divinylbenzene. They are used very often in the form of beads of various sizes. The beads may be micro-porous (pore size  $< 20 \text{ \AA}$ ), meso-porous (pore size  $20\text{--}100 \text{ \AA}$ ) or macro-porous (pore size  $> 100 \text{ \AA}$ ) or non-porous.

### Synthetic Resins

Resins are supports made of synthetic polymers like polystyrene or co-polymers of polystyrene and divinylbenzene. They are used very often in the form of beads of various sizes. The beads may be micro-porous (pore size  $< 20 \text{ \AA}$ ), meso-porous (pore size  $20\text{--}100 \text{ \AA}$ ) or macro-porous (pore size  $> 100 \text{ \AA}$ ) or non-porous. The diameters of the spherical beads decide the surface area. If the bead is also porous then this contributes to enhancement of surface area.

The amount of cross-linking of the polymer decides the mechanical strength of the bead and other properties such as the extent of solvation possible in the bead. If the extent of cross-linking of the polymer is less, then the bead is soft. If the bead has polar groups grafted on it, then it will have a tendency to swell as polar solvent molecules will penetrate its pores. When the bead swells, more active sites are exposed and that is good for the chemical reaction.

However, if the bead has a very large number of polar groups on its surface but is not of very high molecular weight then it will dissolve in polar solvents. Sometimes, this is a desirable character as one can perform reactions in a polar medium under homogeneous condition. At the conclusion of the reaction, the support can be precipitated out by adding a suitable non-polar solvent.

### Representative Illustrations of SAC Surfaces

#### *I. Spherical Beads with Acidic Sites on the Surface*

The acidic sites are very often sulfonic acid groups as these are strong acids. Carboxyl groups are not used for catalytic purposes.

#### *II. Spherical Beads with Acidic Sites in the Pore*

#### *III. Spherical Beads with Acidic Sites both within the Pore and on the Surface*

Such beads do not offer shape and size selectivity in reactions.



They however offer a larger number of active sites per unit weight of the beads.

### Synthesis of SAC Surfaces

Modern organic polymeric resins are made by addition polymerization or vinyl polymerization. Sulfonic groups are introduced onto the surface by way of sulfonation reactions. A silica surface can also be sulfonated.

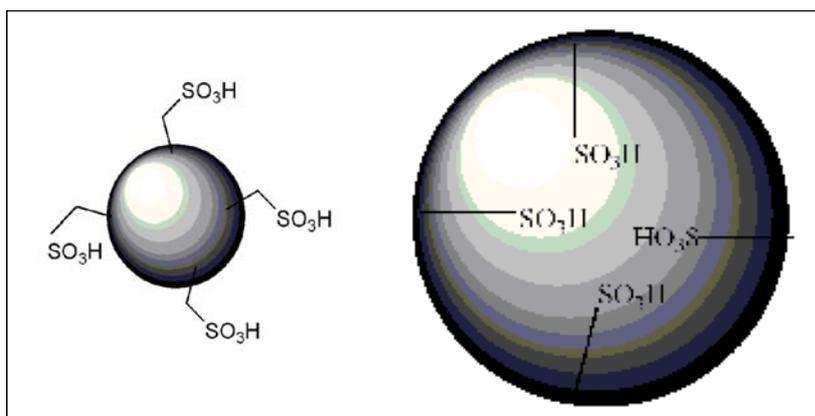
Catalyst structure may be made up of a two-dimensional polymer sheet with the 'pendant' catalytic centres (in this case the  $-\text{SO}_3\text{H}$  groups) either on one side of the polymeric sheet or on both sides of the sheet. The polymeric sheet can then be rolled and joined at the ends with the pendant catalytic centers outward, as in *Figure 6* or inward as in *Figure 7*, or on both sides as in *Figure 8*. *Figure 8c* gives a schematic representation of the preparation of a copolymer of styrene-divinyl benzene and introduction of  $\text{SO}_3\text{H}$  groups by sulphonation.

An advantage with the form shown in *Figure 7* is that the presence of the catalyst inside the pore enables only molecules that fit into the pore volume to access the catalyst, and molecules of larger dimensions cannot react. For example, in a mixture of phenolic molecules of unequal size, only the smaller molecule can enter the pore and get acetylated. That is, there is size and shape selectivity for reactions.

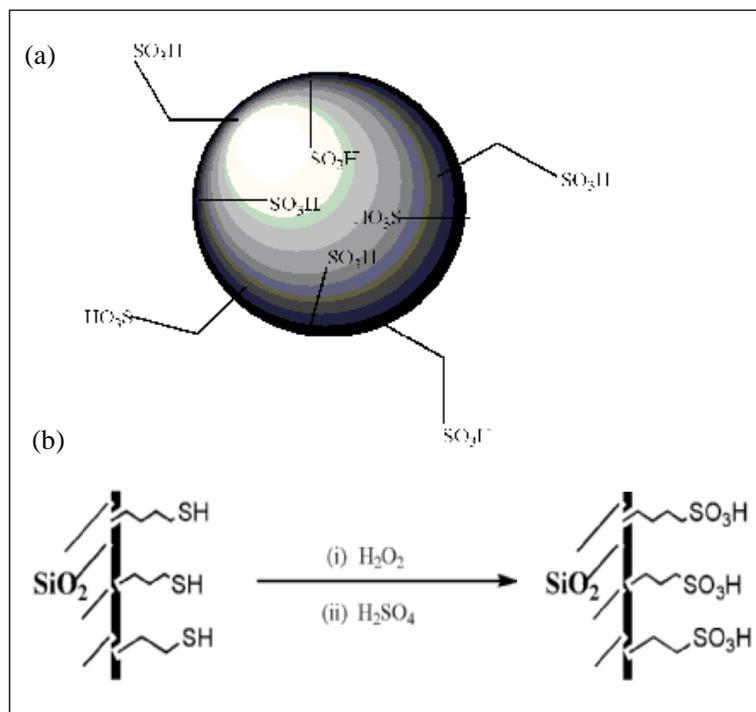
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**Figure 6 (left).** Polymeric bead without pore and with Bronsted sites on its surface.

**Figure 7 (right).** Polymeric bead with pore and acid catalyst embedded within it.



**Figure 8.** (a) Polymeric bead with acid catalyst sites on surface as well as inside pore. (b) Introduction of sulfonic groups on -SH functionalised silica.



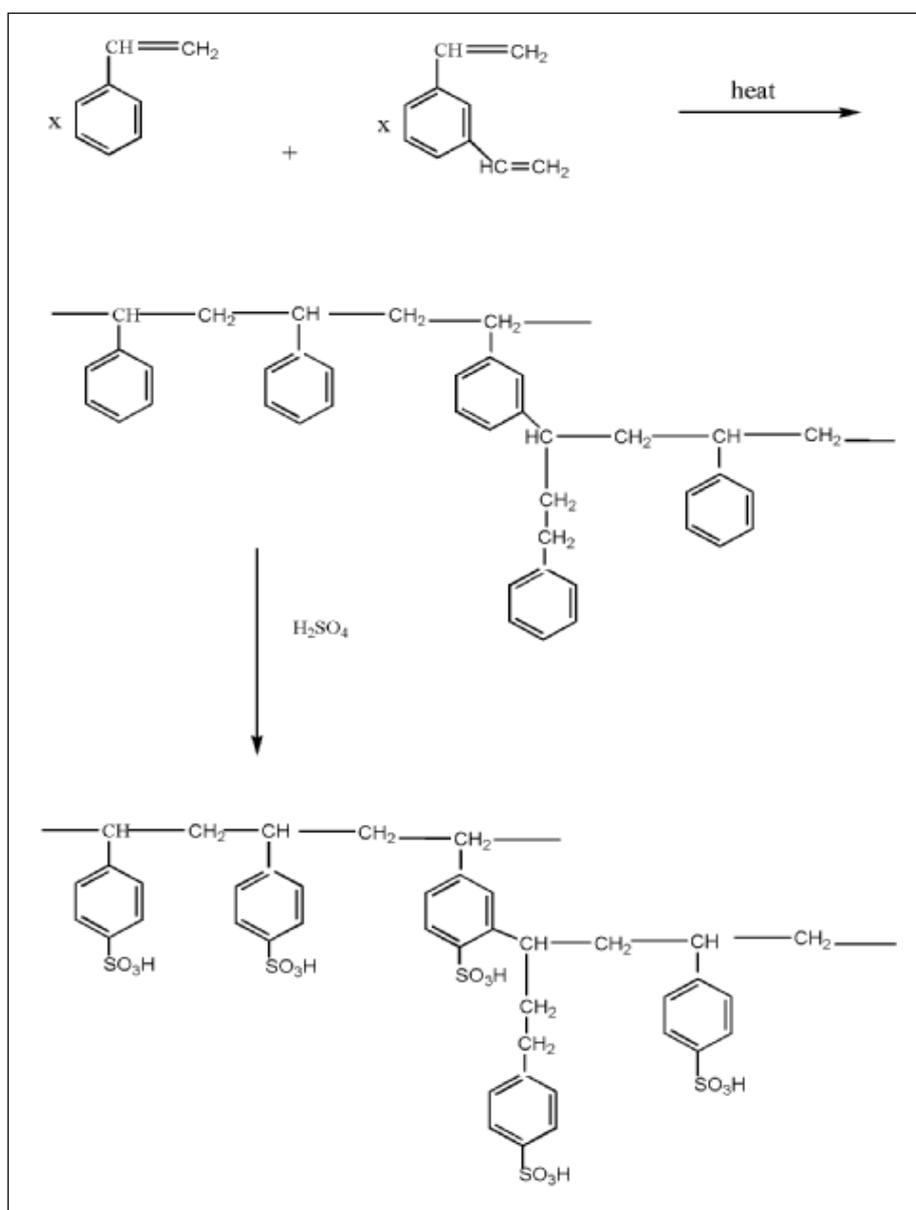
### Capacity of the Bead

It is important to estimate the capacity of the polymeric surface before the start of a reaction. If the beads are used as catalyst then their surface should bear the required catalytic centers like  $\text{SO}_3\text{H}$  groups, and if the beads are used as support then all of the substrate or reagent molecules must get loaded onto them.

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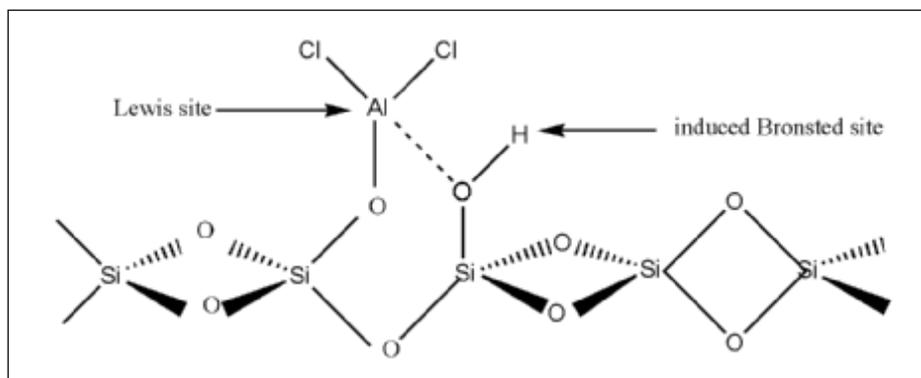
The capacity of the beads can be determined by simple analytical techniques such as titrimetry using a standard base for SAC analysis and the capacity is expressed as the number of milli equivalents of the reactive centers per gram of the polymeric bead sample. It is common to use beads of capacity ranging from 2 to  $10 \text{ meq g}^{-1}$ .

A typical reaction using a sulfonic acid resin as SAC in an acetylation reaction takes place as follows:



Take 1 equivalent of a phenol and 1 equivalent of the SAC resin in a conical flask and add 1.2 equivalents of acetic anhydride to it. The conical flask warms up on mixing the reaction components. Keep it aside for 20 minutes. Pour the liquid contents over iced water carefully, leaving the polymeric beads behind. Filter off the precipitated solid, wash and dry.

**Figure 8c. Sulfonation of styrene-divinylbenzene copolymer.**



**Figure 9.** Anhydrous aluminium chloride on silica.

The polymeric beads are washed with water jets till all the solid attached to it is removed; they can then be re-used for further reactions.

#### IV. Silica and Anhydrous Aluminium Chloride on heating (refluxing) in Toluene Solvent Yield $\text{AlCl}_3$ Grafted on Silica

It is possible to carry out a supported reaction in a homogenous medium instead of heterogenous media as suggested above. In this case the catalyst, the reagent on support and the substrate will be in one single phase. For example, dendrimers are water-soluble polymers with a large number of polar groups branching out extensively from a central core, and the acid catalytic sites on the surface. After the reaction the dendrimer can be recovered by precipitation with a non-polar solvent or by membrane filtration. However, this is still a developing field and has still to be adapted to industrial use.

The discussion presented above gives a brief picture about how the solid acid catalysts function and their environmentally benevolent role in many organic synthetic routes. To appreciate the usefulness of these catalysts, a number of examples of reaction that employ them are provided in the second part of the article.

#### Suggested Reading

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