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Review

Solid acids: Green alternatives for acid catalysis

Princy Gupta*, Satya Paul

Department of Chemistry, University of Jammu, Jammu 180 006, India

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ABSTRACT

This review deals with the general discussion on green chemistry and catalysis; and solid acid catalysts. Various Lewis and Brønsted solid acid catalysts reported in the last few years for various synthetic protocols have been discussed in this review.

Contents

1. Green chemistry and catalysis

It is widely acknowledged that there is a growing need for more environmentally acceptable processes in the chemical industry. This trend towards what has become known as 'Green Chemistry'

* Corresponding author.
E-mail address: guptaprincy2007@gmail.com (P. Gupta).

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[1–9] or 'Sustainable Technology' [10] necessitates a paradigm shift from traditional concepts of process efficiency that focus largely on chemical yield to one that assigns economic value to eliminating waste at source and avoiding the use of toxic and/or hazardous substances. The term 'Green Chemistry' was coined by Prof. Anastas [3] of the US Environmental Protection Agency (EPA). A reasonable working definition of Green chemistry can be formulated as follows [11]: Green Chemistry or environmentally benign chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Green chemistry efficiently utilizes (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products. One of the ways of implementing the principles of Green Chemistry is to use Catalysis.

Catalysis has played a significant role in reducing pollution in our environment. With catalysis, reactions can be more efficient and selective thereby eliminating large amounts of by-products and other waste compounds [8]. Catalysis is of crucial importance for the chemical industry and is used to make an enormous range of products like heavy commodity and fine chemicals. It is one of the fundamental pillars of Green Chemistry [12] and is considered as the most preferred and relevant technology to achieve a reduction in wastes from chemical processes by use of cleaner synthetic methods. Catalysts accelerate reactions by orders of magnitude, enabling them to be carried out under the most favourable thermodynamic regime, and at much lower temperatures and pressures. Thus, catalysts are the key factors in reducing both the investment and operation costs of a chemical process.

Acid catalysis is by far the most important area of catalysis employed by industries in all sectors of chemical manufacturing. A wide range of liquid phase industrial reactions depend on the use of inorganic or mineral acids, while many of these processes are catalytic, some require (e.g. acylation using anhyd. $AlCl_3$) stiochiometric amounts of acids. Some of the major reaction types which are important in this context are Friedel–Crafts alkylations, acylations and sulfonylations, aromatic halogenations, nitrations, isomerisations, and oligomerisations. These reactions are generally catalyzed by mineral acids such as H_2SO_4 and HF; and by Lewis acids such as $AlCl_3$ and BF_3. These reagents are hazardous in handling, damaging the plant through their corrosiveness and add process difficulties through the use of quenching and separation stages, which led to large volume of toxic and corrosive wastes. These acids such as H_2SO_4, HF, $AlCl_3$ and BF_3 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 water quenching stage and require subsequent neutralization; thus, consuming additional (alkaline) resources and producing salt waste. So, in mineral acids,

- volumes of process waste are commonly several times larger than product volumes;
- waste disposal costs exceed the cost of the raw materials;
- are highly toxic;
- leads to separation problems;
- are environmentally undesirable.

2. Solid acid catalysts

Solid acid catalysts are applicable to a plethora of acid-promoted processes in organic synthesis [13–15]. They have served and are serving as an important materials due to their various advantages such as:

- separation of the products from the reaction medium is easy;
- catalyst can be separated easily and re-used several times without loss of activity;
- reactions are generally clean and products are obtained in high purity;
- reactions are generally selective.

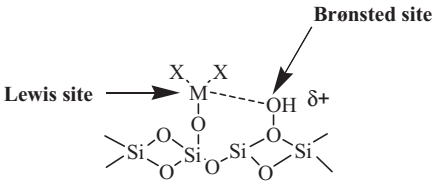

Fig. 1. Brønsted acidity from inductive effect of Lewis acid centre coordinated to a silica support.

Solid acids can be described in terms of their Brønsted/Lewis acidity, the strength and number of these sites, and the morphology of the support (typically in terms of surface area and porosity). High product selectivity can depend on the fine-tuning of these properties. For example, acetal formation and hydrolysis reactions generally require medium acid strength sites, while electrophilic additions of alcohols or water to olefins, skeletal rearrangements, esterification, and alkylation reactions require strong acid sites. Likewise, the importance of the nature of the acid site is demonstrated in Friedel–Crafts alkylation reactions, where Lewis acid sites are required for alkylation of toluene using benzyl chloride, while Brønsted sites are preferred for reactions using benzyl alcohol [16]. The synthesis of pure Brønsted and pure Lewis acid catalysts attracts a great degree of academic interest, although the latter is harder to achieve because Brønsted acidity often arises from Lewis acid-base complexation (Fig. 1).

It has been shown that the type of support material used is a critical factor in the performance of the resulting supported catalyst or reagent in an organic reaction system [17a]. The main factors that should be considered when employing a material as a support are:

- thermal and chemical stability during the reaction process and for batch reactions during the separation stage;
- accessibility and good dispersion of the active sites.

There are numerous inorganic supports which can be used for supporting reagents such as zeolites, silicas, polymers, hydroxyapatite, zirconia, carbons etc. All of these materials have high surface area (100–1000 m^2/g) and are normally porous with average pore diameters ranging from the microporous zeolites to some macroporous silicas [17b]. The particle size of these materials can range from coarse to very fine. However, the choice of support material for the preparation of supported reagents can be the more difficult step [17c].

3. Types of solid acids

3.1. Silica based solid acids

The chemical compound silicon dioxide, also known as silica or silox (from the Latin word "silex"), is the oxide of silicon, chemical formula SiO_2, and has been known for its hardness since the 9th century. Silica is most commonly found in nature as sand or quartz, as well as in the cell walls of diatoms. It is a principal component of most types of glass and substances such as concrete and is usually preferred as a supporting reagent since it is:

- widely available and inexpensive;
- mesoporous and normally possess broad pore size distribution;