

Solid Acid Catalysts in Green Chemistry

2. Some Practical Examples

Leena Rao

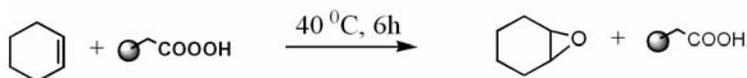


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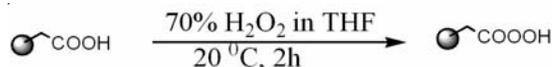
In the first part¹ of this article, the principles of functioning of the solid acid catalysts, their nature and preparation of a few types were described. In this part, some practical examples of such catalysts employed in the synthesis of several organic compounds are presented, which illustrate the extent to which catalysts help reduce pollution, cut costs of production, etc., that are important principles of Green Chemistry.

1. Epoxidation of Cyclohexene [1]

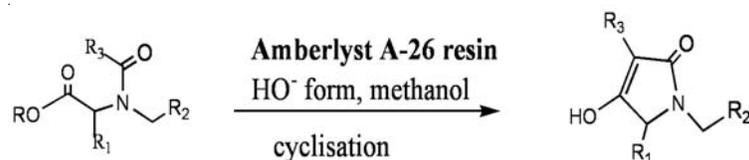
The bead polymers, ---COOH , contain 1 mequiv of perbenzoic acid functional group per gram of polymer. They can be prepared from resins which contain vinylbenzoic acid units.



The polymeric peracids are stable and can be re-generated from the spent ---COOH several times after use, without degradation.



2. Dieckman-like Condensation using Ion-exchange Resin [2]



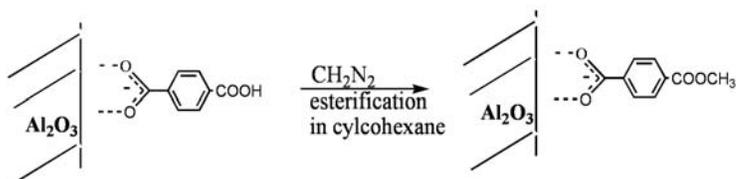
Keywords

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

This is an example illustrating use of a solid base catalyst. The reaction is neat, requires minimal purification and avoids use of corrosive alkali as in conventional processes. Moreover, the resin can be re-used after re-generation, several times.

3. Selective Monomethyl Esterification of a Dicarboxylic Acid [3]

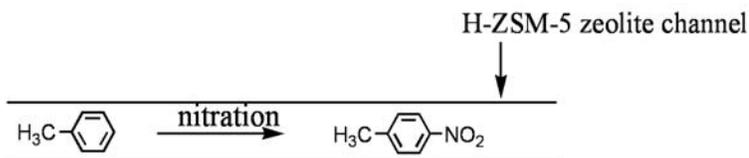
It is difficult to obtain monoesters of dicarboxylic acids by conventional methods. However, selective adsorption of one of the carboxyl groups of the dicarboxylic acid on alumina protects it and blocks its esterification. The free carboxyl group can then be selectively esterified.



4. Regioselective Mononitration of Toluene using H-ZSM5 Zeolite [4]

Nitration of toluene using *n*-propyl nitrate and H-ZSM-5 catalyst gives only the *para*- isomer where as conventional methods of nitration give both *ortho*- and *para*- isomers. This is an example of shape selectivity exercised by the catalyst on the reaction product.

The catalyst H-ZSM-5 is in the form of tubular channels. The internal diameter of the channel is a near-perfect fit for the toluene molecule and allows nitration at only the *para* position.



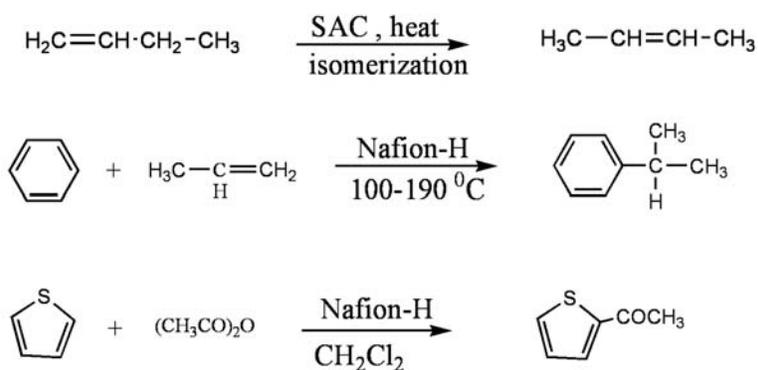
A typical reaction procedure involves refluxing a slurry of

n-propyl nitrate, H-ZSM-5 as the catalyst and toluene in a round-bottomed flask fitted with a water condenser. The reaction mixture is purged and maintained in a nitrogen gas atmosphere. At the end of the reaction the mixture is cooled and filtered to yield the crystals of the nitration product.

Use of the catalyst H-ZSM-5 provides the acidic conditions necessary for formation of nitronium ions from n-propyl nitrate required for nitration reaction. Conventional corrosive liquid acids are done away with. The reagent n-propyl nitrate on H-ZSM-5 is safe to handle, and, the reaction is regioselective.

5. Isomerization of Alkenes (5), Electrophilic Aromatic Alkylations (6a) and Friedel-Crafts Acylations [5,6]

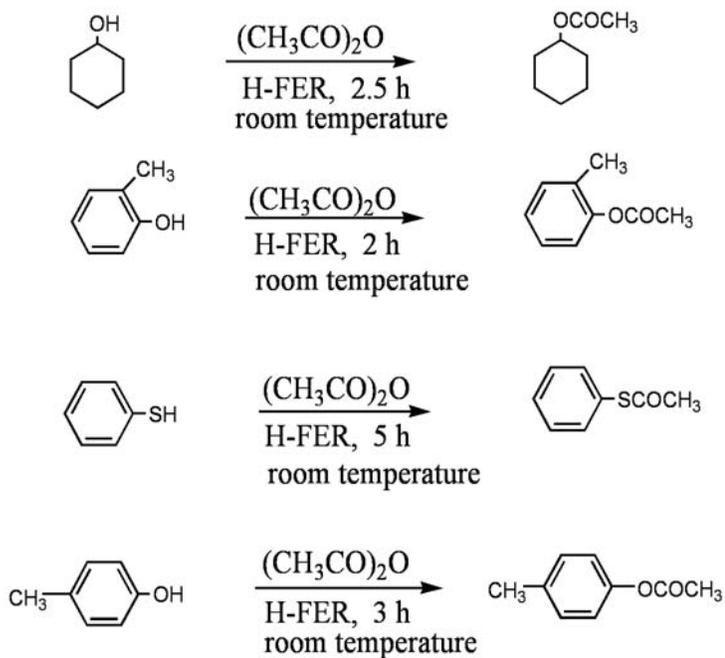
These reactions are important in petroleum refineries and have been traditionally catalyzed by mineral acids like H_2SO_4 and HF or by Lewis acids like AlCl_3 . Environmental concerns associated with their use have encouraged process changes involving solid bed catalysts. H-ZSM-5, perfluorinated resin sulfonic acids (Nafion-H) and others have been developed as alternatives. Constant efforts are being made to enhance their re-cyclability, mechanical robustness and improving operating temperatures.



6. Catalytic Acetylation of Alcohols, Phenols, Thiols and Amines [7]

Acetylation reactions are conventionally carried out using either

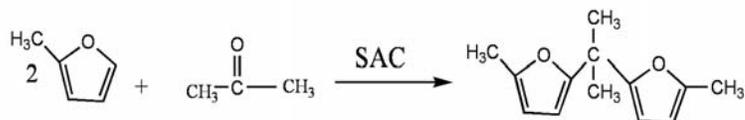
bases such as triethylamine or pyridine or protic acids such as *p*-toluenesulfonic acid or even Lewis acids such as ZnCl_2 .



Solid acid catalysts such as Nafion-H and Zeolite H-FER have been found to be good replacements. They give high yields, are effective under mild conditions and are re-cyclable.

7. Condensation and Esterification Reactions [8]

Mesoporous silica functionalised with sulfonic acid groups constitutes the solid acid catalyst. The synthesis of bisfurylalkane intermediates are important in macromolecular chemistry.

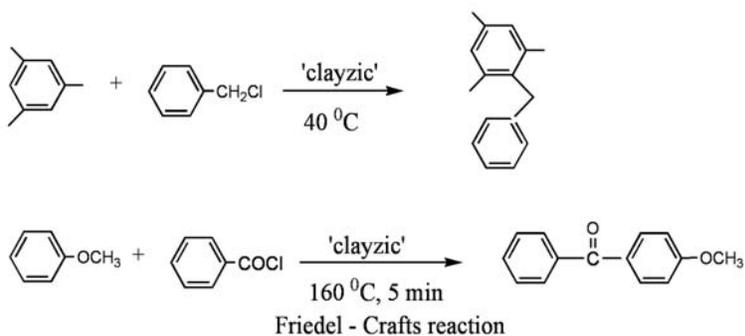


Esterification of polyols can also be done using this catalyst. Polyol esters find applications as emulsifiers, detergents and low-calorific fats. For example, esterification of D-sorbitol with

lauric acid leads to formation of the mono-ester and diester in different time frames.

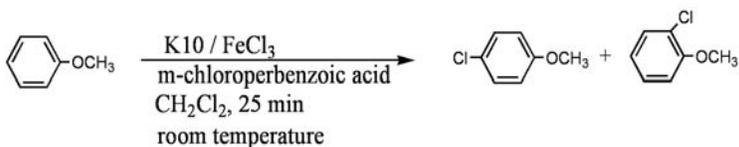
8. Clays as Catalysts [9]

Natural clays can be used as catalysts for organic reactions. They have both Bronsted and Lewis acidic catalytic sites. They have a lamellar structure and provide a large surface area for reaction. They can be easily impregnated with salts used as Lewis acids. And best of all, they are inexpensive.



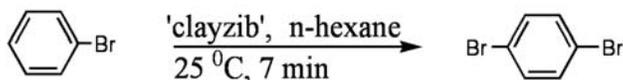
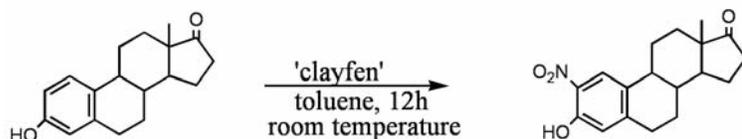
'Clayzic' is zinc chloride impregnated in K10 montmorillonite clay. The short reaction time span gives an indication of the high efficiency of the catalyst.

Lewis acids have also been impregnated in clays such as Kaolinite and montmorillonite clays. Both these clays have surface acidities comparable to concentrated nitric and sulfuric acids and as such are good solid acids on their own. The Bronsted acidity of these clays is boosted when there is ionic exchange with high valent ions such as ferric ions. This is used in performing aromatic chlorinations, an example of which is given below.



Nitration reactions are also facilitated with metal nitrates such as ferric nitrate and copper nitrate, supported on clays. A nitration

reaction which is industrially significant is the nitration of oestrone.



'Clayfen' is ferric nitrate supported on clay. The reaction completely does away with use of the corrosive nitric acid.

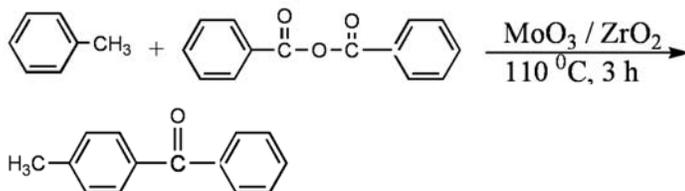
Such catalysts are also called envirocats because they are environmentally benign.

Bromination reactions have also been carried out using clay supports for zinc bromide as brominating agent. This reagent is called 'clayzib'. [10]

This method is an improvement over traditional methods of aromatic bromination which involve the use of non-selective, hazardous and acidic agents leading to toxic and corrosive waste.

9. Solid Superacid Catalyst in Friedel-Crafts Reaction [11]

Along the lines of silica and alumina supports, zirconia can be used as a support for molybdenum oxide. The resultant reagent is a superacid and yielded benzoylation of toluene with benzoic anhydride.



This reaction is known to occur only under the influence of strong acids. In this case the reaction was carried out at the reflux temperature ($\sim 110^\circ\text{C}$) for three hours.

Conclusion

The examples show the important role the solid acid catalysts are playing in implementing eco-friendly manufacturing processes. The chemical industry has been benefited tremendously. Further advances in the development of more efficient, highly selective and cost-effective catalysts that help minimize or eliminate adverse effect on environment are the need of the hour and are bound to draw increasing attention of the concerned scientists.

Suggested Reading

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