Aldol Condensation of Aldehydes and Ketones over Solid Base Catalysts

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Introduction

Industrially condensation reactions are of great importance in the production of a number of key compounds. These include 2-ethyl hexanol, methyl isobutyl ketone (MIBK) and Guerbet alcohols. Over 1.5 million tonnes of these chemicals are produced worldwide every year using homogeneous bases such as NaOH and $Ca(OH)_2$. It has been estimated for these compounds[1] that 30% of the selling price is product purification, recovery and waste treatment. For every 10 tonnes of product formed the current homogeneous catalysts generate about 1 tonne of spent catalyst. High capital costs are also associated with the handling of strong homogeneous bases such as 30% caustic. Although solid base catalysts have a number of advantages over conventional homogeneous (NaOH, KOH) systems, according to a recent review of industrial acid and base catalysis[2] of the 127 processes identified only 10 were solid base catalysed. Solid base catalysis is therefore an area of chemistry that offers an excellent opportunity for exploitation if suitable catalysts and processes can be identified and developed. The mechanistic understanding of the processes taking place on solid base catalysts is also very poor.

Results and Discussion

The mechanism of gas phase aldol condensation reactions over solid base catalysts has been studied using a range of linear and branched aldehydes and ketones as model compounds as follows.

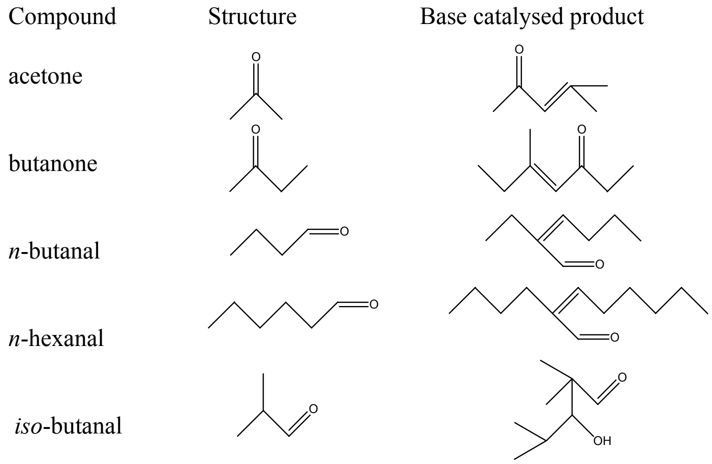

Fig.1 Base catalysed products from Reactions of Model Aldehydes and Ketones

A suitable solid base catalyst must have the appropriate strength for the reaction under investigation. For aldehyde and ketone condensation reactions the base requires to remove protons of pK_a 19.7 –20. There are few available solid base materials, however, in this strong base area (see Fig. 2).

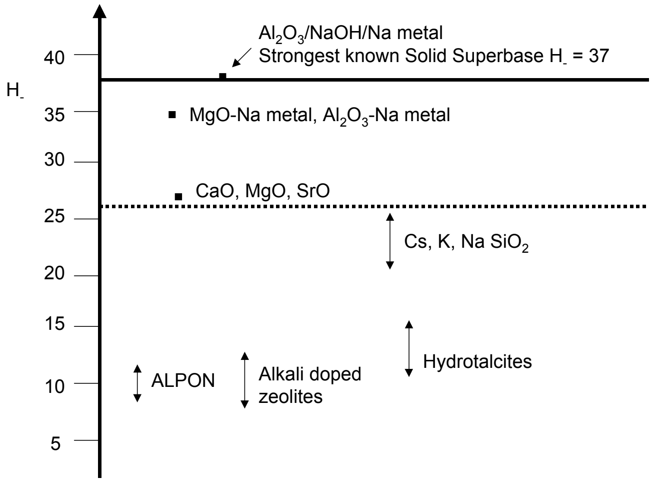

Fig.2 Strength of Solid Base Catalysts (H- Scale)

A series of catalysts based on alkali metals salts (Na, K and Cs) supported on a silica support can be successfully used as strong solid base catalysts under industrial conditions. The reactions of acetone in the gas phase over a K/SiO_2 catalyst leads to the formation of a mixture of the base catalysed product mesityl oxide and trimeric condensation products such as isophorone[3]. This over condensation of acetone makes it a difficult molecule to study for mechanistic information. Clearer information is possible from the reaction of butanone over Na and Cs/SiO_2 catalysts. The reactions of butanone in the gas phase over these catalysts demonstrate a high selectivity for the formation of 5-methylheptan-3-one[1]. This is the kinetically controlled aldol product from the reaction at the terminal position of the butanone. In the presence of acid catalysts the condensation at the internal position would be favoured. Reactions of n-butanal and n-hexanal can be carried out in the gas phase over Na/SiO_2 base catalysts[4]. As the replaceable proton on the aldehyde is more acidic higher conversions are achieved than with the ketones (for *n*-butanal maximum conversion 58%) and with high selectivities (>90%). In contrast, the reaction of *iso*-butanal over a Na/SiO_2 catalyst produces no products at all and leads to carbon laydown on the catalyst and in the reactor. The reaction of a 1:1 molar mixture of *n* and *iso*-butanal produces 2-ethyl hexenal from the n-butanal and a crossed aldol product 2-ethyl-4-methyl–pent-2-enal. Therefore, although a branched aldehyde cannot be reacted in isolation over a solid base catalyst it can be a substrate for a crossed aldol reaction. This gives a strong indication about the probable mechanistic steps in the aldol condensation reaction of aldehydes over solid base catalysts.

References

1. G J Kelly, F King and M Kett, Green Chemistry, 4, 392-399 (2002).
2. K. Tanabe and W. F. Hoelderich, Applied Catalysis A: General 181, 399-434 (1999).
3. G J Kelly, World Pat. Appl. WO 01/87812, Nov 2001
4. G J Kelly, F King, Catalysis Today, 73, 75-81, (2002)