Strong base catalysts for fine chemical synthesis: relating reaction energetics to base strength.

S. David Jackson*, Arran S. Canning, Eilidh McLeod and Gemma M. Parker.
WestCHEM, Department of Chemistry, The University, Glasgow G12 8QQ, Scotland.
sdj@chem.gla.ac.uk

Introduction
The aldol condensation reactions of aldehydes and ketones are commonly used in organic synthesis reactions for preparing chemicals containing a double bond conjugated with a carbonyl group. Industrially this process is carried out in the liquid phase with homogeneous alkaline bases. However, solid base catalysts are becoming more interesting due to several advantages that they offer. The aldol condensation of acetone to diacetone alcohol (DAA) is the first step in a three-step process in the traditional method for the production of MIBK via MO [1]. This paper investigates the acetone condensation reaction in the vapour phase over NaOH/SiO\textsubscript{2}, KOH/SiO\textsubscript{2} and CsOH/SiO\textsubscript{2} solid base catalyst over a range of reaction temperatures using hydrogen as carrier gas.

Materials and Methods
The solid base catalysts were prepared by dissolving NaOH, KNO\textsubscript{3} and CsNO\textsubscript{3} in the minimum amount of distilled water before addition to the silica support. The amount of each precursor added was calculated in order to give a 10% loading of metal on each catalyst. The catalyst was dried in an oven overnight at 373 K, calcined \textit{in situ} in a flow of N\textsubscript{2} for 2 hours at 723 K. Carbon dioxide chemisorption was carried out on a pulse-flow microreactor system with on-line GC-MS. After the catalyst was saturated with carbon dioxide, a temperature programmed desorption (TPD) was carried out by heating the sample in helium from room temperature to 873 K. The condensation reaction was carried out in a continuous flow microreactor. Acetone was pumped at 5 ml hr\textsuperscript{-1} into the carrier gas stream of H\textsubscript{2} (50 cm\textsuperscript{3} min\textsuperscript{-1}). The carrier gas and reactant then entered the reactor containing the catalyst (0.50g). The reactor was run at 5 bar pressure and at reaction temperatures between 373 and 673 K. Samples were collected and analysed by GC-MS.

Results and Discussion
The amount of carbon dioxide adsorbed over each of the three catalysts was \(~17 \mu mol.g\textsuperscript{-1}. However the TPD gave a unique spectrum for each catalyst. Rather surprisingly the NaOH/SiO\textsubscript{2} catalyst appeared to have both the weakest and strongest base sites, with desorption peaks at 373 K and 525 K.

The catalysts were tested over a range of temperatures and activity/selectivity data generated. From this activation energies for MO and MIBK were calculated. The \(E_a\) for MO production over the NaOH/SiO\textsubscript{2} catalyst (33±1 kJ.mol\textsuperscript{-1}) is higher than that obtained for the other alkali hydroxides (25±4 and 23±4 kJ.mol\textsuperscript{-1} for KOH/SiO\textsubscript{2} and CsOH/SiO\textsubscript{2} respectively) but the differences are at the limit of statistical significance. The hydrogenation reaction is, as may be expected, a higher energy pathway than the aldol condensation. Indeed the \(E_a\) for MIBK correlates well with the CO\textsubscript{2} desorption peak temperature (Figure 1.) showing a direct link between reaction energetics and base strength. When the CO\textsubscript{2} desorption temperature is compared with the decomposition temperature of the alkali metal hydrogen carbonate it is observed that there is a one to one correspondence suggesting that the CO\textsubscript{2} evolution in the TPD is due to decomposition of the alkali metal hydrogen carbonate that is formed during the CO\textsubscript{2} adsorption. Therefore the CO\textsubscript{2} TPD is not a measure base strength and the relationship with MIBK activation energy is due to the decomposition temperature being an inverse measure of the ionisation potential of the alkali metal. The relationship between MIBK activation energy and ionisation potential confirms that as the base strength increases the activation barrier to hydrogenation is reduced.

Significance
Carbon dioxide adsorption and desorption is often taken as a measure of base strength, however here we show that this can be misleading as it is possible to form the metal hydrogen carbonate which will release carbon dioxide when it decomposes. We have also shown that there is a direct link between basicity as measured by ionization potential and activation energy.

References