

# Strong solid base reagents and catalysts based on carbonaceous supports

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Porous carbons are shown to have very high affinities for basic hydroxides, fluorides and oxides. The resulting materials are demonstrated to be strong base catalysts for solution and gas phase reactions. They can also be used as stoichiometric reagents to generate carbanions in solution. When the solid is filtered off and the solution temperature raised to initiate the reaction, very selective Michael addition reactions occur.

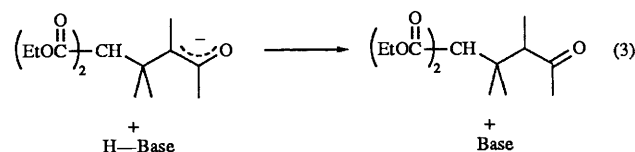
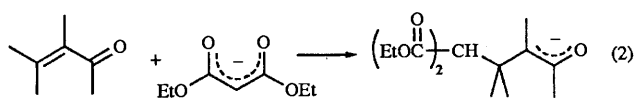
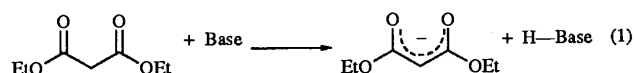
## Introduction

In contrast to the extensive research in the area of solid acid catalysts, relatively little has been reported on solid base catalysts. Solid base catalysts are desirable for several reasons. They permit base catalysed reactions in the vapour phase. In reactions involving liquids, solid catalysts can be used in a liquid flow system to vary the contact time of a solution with the solid catalyst. Removal of product from the basic component prevents further reaction of the product and permits optimization of product selectivity and conversion. Furthermore, base catalysed reactions could be carried out without having to expose equipment to large concentrations of caustic chemicals in solution. The catalyst can be separated from the reaction, washed, dried and reused, solving the problem of disposing of concentrated basic solutions. If acid is generated in a reaction, insoluble solid supported bases can function in a non-catalytic manner as buffers.

One of the most thoroughly investigated solid base catalysts is KF on alumina,<sup>1-15</sup> first reported by Ando *et al.*<sup>12</sup> The best catalysts are prepared by adding 0.5 to 2 mmol of KF per gram of alumina. The catalyst is activated by heating at 150 °C for 24 h under reduced pressure. Although there is uncertainty concerning the composition of the basic species in solution, KF-alumina has been successfully used in a wide variety of carbon-carbon bond forming reactions. Typical base-catalysed organic reactions that are reported include the Michael,<sup>1-3</sup> Wittig, Wittig-Horner and Knoevenagel reactions,<sup>7</sup> the synthesis of phosphoric esters,<sup>8</sup>  $\alpha$ -nitro alcohols,<sup>9</sup> 1,4-diketones<sup>3</sup> and pseudoionones.<sup>10</sup> In some cases, the reactions were carried out in the absence of solvent, but most often by percolating the substrate or substrates dissolved in methylene dichloride through a bed of KF-alumina.<sup>11</sup> These 'chromatographic reactions' give good yields of generally very pure products. For the catalytic C-C bond forming condensations, the KF-alumina was reusable after washing and thermal activation. Flash chromatography was found to be especially effective for larger scale reactions.<sup>11</sup>

Due to the amphoteric nature of the alumina support, the inherent basicity of the supported species is levelled to that of aluminate by reaction with alumina. This reactivity has led to questions concerning the catalytic species in KF-Al<sub>2</sub>O<sub>3</sub>. This question motivated the synthesis of supported solid bases utilizing solid carbon supports that would not react with hydroxide or fluoride.

The Michael reaction<sup>1-3</sup> is a typical base-catalysed class of reactions that are widely used<sup>12</sup> in organic syntheses as a method for forming a new C-C bond between a carbanionic nucleophile and an acceptor. The latter, an activated olefin, is typically an  $\alpha,\beta$ -unsaturated ketone. The most common carbanionic nucleophiles used in these alkylation reactions are



enolate anions. The Michael addition is believed to proceed by reactions 1-3 (shown for diethyl malonate).

The function of the base is to abstract a hydrogen ion from the diethyl malonate ester and thus generate a carbanion [reaction (1)], which, acting as a nucleophilic reagent, attacks the conjugated system (the  $\alpha,\beta$ -unsaturated carbonyl compound) [reaction (2)]. The process regenerates the base and the reaction is catalytic in base [reaction (3)].

The above reaction mechanism is typical of the base-catalysed reactions reported in this work. The compound from which the carbanion is generated is a weakly acidic substance which contains a -CH<sub>2</sub>- or -CH- group flanked by electron-withdrawing groups to stabilize the negative charge of the anion, generated by removal of the CH<sub>2</sub> or CH proton [e.g. reaction (1)].

## Results and discussion

### KOH affinity studies

The experiments were designed to investigate the affinity of carbonaceous adsorbents for potassium hydroxide. In order to function as base catalysts, the hydroxide must be held in the pores of the substrate and still be accessible to the reactants. These experiments were designed to test the former property. The carbon samples selected for this study were the commercially available (Rohm and Haas Co.) Amborsorb adsorbents (AMB).<sup>16</sup>

Two separate carbons were investigated; a hydrophobic 572I sample and a hydrophilic 572 sample. The solids were pore filled using solutions of KOH in water or ethanol. Pore filling consists of adding just enough solution to yield a moist solid. The pore filled samples were allowed to equilibrate overnight

**Table 1** Affinity of amborsorb adsorbents for KOH in aqueous solution

Amborsorb	Solvent	KOH pore filled/mmol	KOH remaining/ mmol g <sup>-1</sup> carbon <sup>a</sup>	
			I	II
572	H <sub>2</sub> O	0.50	0.474 (0.485)	0.472
572	H <sub>2</sub> O	2.00	1.920 (1.94)	1.909
572	EtOH	0.50	0.479 (0.485)	0.479
572I	H <sub>2</sub> O	0.50	0.479 (0.487)	0.479
572I	H <sub>2</sub> O	2.00	1.944 (1.95)	1.943
572I	EtOH	0.50	0.473 (0.483)	0.472
572I	EtOH	2.00	1.993 (2.00)	1.993

<sup>a</sup> The amount of KOH remaining in the solid is calculated from the pH of the solution. The numeral I corresponds to exposure of the first sample to 40 cm<sup>3</sup> of water and II to the second exposure of the same sample to a second 40 cm<sup>3</sup> of water. The values in parentheses were obtained on sieves that were stored for one week and then analysed.

and then dried at 140 °C *in vacuo*. The resulting solids were added to water and the mixture allowed to stand until a constant pH value was obtained. The amount of KOH remaining in the solid was calculated from the pH and is indicated in Table 1 under column I. The solid was filtered off and dried overnight at 140 °C. These samples were added to water again and stirred until a constant pH resulted. The amount (mmol) of KOH remaining in the Amborsorb adsorbent after this second exposure is indicated under column II. The larger values found in the first wash are in part due to KOH remaining on the surface of the solid after pore filling. It is clear that the majority of the 0.5 and 2.0 mmol added per gram of solid goes into and remains in the pores of the solid.

In order to show that the KOH was remaining inside the Amborsorb adsorbent, two of the samples in Table 1 were titrated with hydrochloric acid. The undoped 572 and 572I when added to water gave a pH of 6.8 and 6.7, respectively. The doped samples were titrated to this pH as the equivalence point. After each addition of HCl, the solution was allowed to stand until the pH became constant. The results confirm that the KOH represented as remaining in the carbon is indeed contained unreacted in the pores of the carbon. The titration further shows that the KOH is available for reaction with acid. When 1.0 g of 572 was added to a solution of 2 mmol of KOH in 40 cm<sup>3</sup> of water, the pH did not change over a period of 8 h. This suggests that kinetic factors determine the results in Table 1.

### Michael reaction

The Michael reaction is a base-catalysed class of reactions involving carbon-carbon bond formation. The reaction of acetylacetone (pentane-2,4-dione) and acrolein (acrylaldehyde) was selected for study to avoid any problems of mixed products and selectivity.

In many Michael reactions the initial condensation product is readily deprotonated, forming a carbanion that attacks the  $\alpha,\beta$ -unsaturated ketone, leading to higher molecular weight products. The reaction was carried out in the neat liquids as solvents at room temperature. All of the catalysts prepared by pore filling and vacuum drying were very active in this reaction, leading to a mixture of products of high molecular weight. GC-MS analysis revealed the presence of products formed through the addition of one molecule of acrolein (formula mass = 156), two molecules of acrolein (FM = 212) and four molecules of acrolein (FM = 324) to the acetylacetone. Results for various catalyst preparations are shown in Table 2. Product yield distributions varied from 12–19% FM 156, 9–16% FM 212 and 6–12% FM 324.

Comparison of the results for KOH- and KF-doped Amborsorb adsorbents is of interest in view of questions about

**Table 2** The reaction of acrolein with pentane-2,4-dione

Catalyst	Yield (%) <sup>a</sup>		
	FM 156	FM 212	FM 324
572I + 2 mmol KOH (EtOH)	17.9	12.0	8.0
572 + 2 mmol KOH (H <sub>2</sub> O)	11.2	16.2	12.5
572I + 2 mmol KF (EtOH)	18.0	12.1	7.9
572 + 2 mmol KF (H <sub>2</sub> O)	12.2	16.0	12.1
572I + 0.5 mmol KOH (EtOH)	18.4	9.5	6.6
572 + 0.5 mmol KOH (H <sub>2</sub> O)	12.0	17.9	9.4

<sup>a</sup> Yields are based on the moles of product divided by the moles of acetylacetone taken for the reaction. The difference in the acetylacetone peak in the products and reactants corresponds to the moles of product formed providing a mass balance.

the role of KF-alumina in its reactions.<sup>13</sup> Uncertainty exists over the nature of the species present and the cause of the strong basicity.<sup>14,15</sup> The Amborsorb adsorbents modified with 2 mmol of KOH per gram, KOH (2 mm)/AMB, were very active catalysts and the majority of the substrates reacted completely after a few hours. The products obtained were mainly of higher molecular weight (FM = 212 and 324) and the viscosity of the product mixture noticeably increased as the reaction proceeded. The samples of KF (2 mm)/AMB 572 (H<sub>2</sub>O) and KF (2 mm)/AMB 572I (EtOH) showed comparable activity to the KOH doped materials. Since KF is not reactive with the carbon support, these results support the position of Clark *et al.*<sup>1</sup> that dispersion and increased surface area of the KF are the critical features that lead to the strong base catalytic property of KF-alumina. Interaction of the potassium ion with carbon and oxygen surface sites on the carbon support can decrease ion pairing of the cation to F<sup>-</sup> and increase its basicity.

### Selective Michael reactions

The results in Table 2 suggest that, like HCl, acetylacetone (Hacac) reacts with KOH-AMB to generate K<sup>+</sup> acac<sup>-</sup> in solution or on the solid. Reaction proceeds as in reactions (2) and (3) to regenerate KOH. The product of the condensation reaction is also deprotonated by reaction with KOH-AMB and reacts with acrolein to form higher molecular mass products. In attempting to determine if K<sup>+</sup> acac<sup>-</sup> is formed on the solid or in solution, a procedure for a very selective Michael reaction was discovered. The KOH (2 mmol)/AMB 572 was washed with water and dried, producing a material comparable to II in Table 1. Acrolein (8.4 cm<sup>3</sup>) and acetylacetone (13.0 cm<sup>3</sup>) were stirred with 0.5 g of catalyst for 5 h at room temperature to produce the equilibrium concentration of carbanion in solution. The solid catalyst was filtered off and the solution heated to 50 °C for 40 h to bring about the Michael reaction. A single product (FM = 156) was obtained in 70% yield.

The above reaction was repeated except that catalyst was stirred in acetylacetone (13.0 cm<sup>3</sup>) for 5 h and then filtered off. Addition of acrolein (8.4 cm<sup>3</sup>), heating to 50 °C and stirring for 40 h led to one product (FM = 156) in 42% yield.

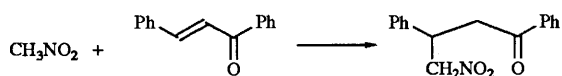
These experiments show that acetylacetone reacts with the base in the Amborsorb adsorbent pores just as HCl does, leading to a solution containing enough K<sup>+</sup> acac<sup>-</sup> to catalyse a homogeneous reaction with very high selectivity. These solid materials provide the requisite amount of base for a highly selective reaction in the neat liquid reactants at mild temperatures. The high selectivity of the reaction carried out after removal of the catalyst contrasts to the formation of higher molecular mass products when the reaction is carried out with the solid present.

### Carbanions from weaker acids

In order to assess the base strength of KF-AMB, a series of reactions were carried out in which the carbanion is not as easily generated as in the case of acetylacetone. The reaction

Table 3 Vapour phase aldol reactions

Catalyst	Starting material	Formaldehyde source	Product (yield/%)	Selectivity (%)
AMB 563 + 2 mmol MgO	Acetaldehyde	37% Solution in water	Acrolein (58)	93
AMB 572 + 2 mmol MgO	Acetaldehyde	37% Solution in water	Acrolein (41)	81
AMB 563 + 2 mmol MgO	Acetaldehyde	Paraformaldehyde	Acrolein (80)	90
AMB 563 + 2 mmol MgO	Propionaldehyde	37% Solution in water	Methacrolein (60)	94
AMB 563 + 2 mmol MgO	Propionaldehyde	Paraformaldehyde	Methacrolein (83)	92



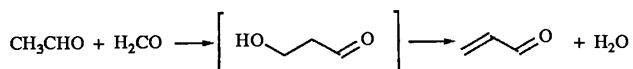
of nitromethane with chalcone ( $\text{C}_6\text{H}_5\text{CH}=\text{CHCOC}_6\text{H}_5$ ) was carried out in benzene solvent at 70 °C for 24 h with KF (2 mm)/572 and KF (2 mm)/572I as catalysts. Both catalysts were active giving 40% conversion and high (>99%) selectivity to the indicated product. When diphenylmethane or toluene was substituted for nitromethane, no reaction was observed.

Base catalysts were prepared by doping the Amborsorb adsorbents with enough  $\text{Mg}(\text{NO}_3)_2$  and  $\text{Ba}(\text{NO}_3)_2$  to produce a catalyst containing 2 mmol  $\text{g}^{-1}$  of MgO and BaO by thermally decomposing the nitrates. Using 1 g of the catalyst, a 1:1 molar ratio of chalcone (20 g) and nitromethane (5.2  $\text{cm}^3$ ) were allowed to react at 100 °C for 24 h. Conversion to a single product occurred with a conversion of ~100%. When the above reaction was carried out at 50 °C, no product was observed.

The base catalysed reaction of ethylene oxide and diethylene glycol was examined. A 0.5 g sample of AMB 563 doped with 0.5 mmol of BaO was added to a 1:1 molar ratio of diethylene glycol (1.9  $\text{cm}^3$ ) and ethylene oxide (1  $\text{cm}^3$ ) in a pressure bottle. The reaction was carried out at 275 °C for 70 h and produced triethylene glycol as the sole product with ~6% conversion.

#### Vapour phase aldol condensations

Acrolein is produced by the partial oxidation of propene or by the base catalysed aldol condensation of formaldehyde with acetaldehyde. Yields of 42–62% are reported when this reaction



is carried out over alkali and alkaline earth hydroxides.<sup>17</sup> A yield of 41% is reported<sup>18,19</sup> for a reaction between an equimolar amount of acetaldehyde and 30% aqueous formaldehyde on silica gel impregnated with 10% sodium silicate at 305 °C.

Two catalysts, 2 mm MgO-AMB 563 and 2 mm MgO-AMB 572, were used in gas phase reactions of acetaldehyde and propionaldehyde with formaldehyde at temperatures of 280–320 °C. Good conversions and high selectivity to acrolein (from acetaldehyde) and methacrolein (2-methylacrylaldehyde) (from propionaldehyde) were obtained as shown in Table 3. The reaction is very sensitive to contact time with optimum values being less than 10 s. At longer times no product is observed. Yields of 80% with 90% selectivity were obtained when paraformaldehyde was used as the formaldehyde source instead of 37% aqueous formaldehyde.

With aqueous formaldehyde, the activity of the catalyst decreases to about 20% conversion with time over a 20 h period. This catalyst can be regenerated by passing a stream of dry nitrogen over it at the reaction temperature. The 563 material recovers fully to the original level of activity but the regenerated 572 catalyst only produced a 41 mol % conversion to acrolein. When paraformaldehyde is used as the formaldehyde source, the 80% conversion and 90% selectivity remain constant for the entire period of the 100 h used to study the reaction.

## Experimental

The Amborsorb adsorbents 572, 572I and 563 taken for these studies were obtained from the Rohm and Haas Company. The term 'KF (2 mm)/AMB 572', for example, indicates the 572 resin was pore filled with 2 mmol  $\text{g}^{-1}$  of KF.

The affinity of the solid for KOH compared to water was measured by adding 0.5 g of catalyst to 40  $\text{cm}^3$  of distilled water. The whole mixture was stirred and the pH determined at frequent intervals until a constant pH value was reached (~4 h). From the pH value, the amount of KOH that dissolved in water was calculated. Then, the doped carbon was separated from the solution by filtration, dried *in vacuo* at 160 °C for 9 h and the above procedure repeated. The amount of KOH that dissolved in water in the second step was also determined from the pH. In order to demonstrate that unreacted KOH remained in the pores of the solid, the amount of KOH left inside the catalyst after the second exposure to water was determined by titration of the solid sample with 0.1 mol  $\text{dm}^{-3}$  solution of HCl. The titration was carried out until the pH value of the solution was equal to that of the undoped Amborsorb in water.

Amborsorb adsorbents, doped as described above, were used in the Michael reaction with pentane-2,4-dione and acrolein. A volume ratio of 1:1 or a molar ratio of 1:2 was employed and the reactions were carried out for 24 h in a 100  $\text{cm}^3$  round bottom flask, in the neat substrates at room temperature.

The products were analysed chromatographically using a 2 m column packed with 15 wt % of DEGS on Chrom WAW, 80–100 mesh and flame ionization detection at 180 °C. Calibration curves were made to quantify the GC areas. GC-MS was also used to identify the reaction products.

The Michael reaction of chalcone with nitromethane was carried out using KF (2 mm)/AMB. Directly before the reaction, the catalyst (1.0 g) was placed in a round bottom reaction flask (100  $\text{cm}^3$  volume) and dried *in vacuo* at 180 °C overnight. The reagents were added to the reaction under a nitrogen atmosphere in a molar ratio of 1:1 (0.05 mol of chalcone + 0.05 mol of nitromethane) with 30  $\text{cm}^3$  of distilled benzene as a solvent. The reaction was carried out at 70 °C for 24 h with stirring. The products were separated from the catalyst by filtration and benzene was distilled off *in vacuo*. The products were analysed by NMR.

The MgO- and BaO-doped Amborsorb adsorbents were prepared by pore filling with aqueous  $\text{Mg}(\text{NO}_3)_2$  or  $\text{Ba}(\text{NO}_3)_2$ . The solids were dried at 160 °C *in vacuo* for 6 h and then decomposed to the oxides by heating at 350 °C under a  $\text{N}_2$  flow (5  $\text{cm}^3 \text{min}^{-1}$ ) overnight.

The product of the reaction of ethylene oxide and diethylene glycol was analysed by gas chromatography at 275 °C using FID and a 30 m capillary column.

The vapour phase aldol condensation reaction was carried out with a continuous flow system at atmospheric pressure at 300 °C. Nitrogen, the carrier gas, was fed in from the top of the reactor at a rate of 10–20  $\text{cm}^3 \text{min}^{-1}$ . The mixture of reactants was fed in two different ways: In the first few experiments the liquid mixture of acetaldehyde, 37% solution of HCHO in water, and methanol in a volume ratio of 3.2:8.8:1 was fed at a rate of 0.5  $\text{cm}^3 \text{h}^{-1}$ . This corresponds to acetaldehyde,

formaldehyde, methanol, water and N<sub>2</sub> feed rates of 2.2/4.5/0.9/12.8/26.8–53.6 mmol/h<sup>-1</sup>. In experiments with propionaldehyde this material was fed as a liquid using a syringe (0.1 cm<sup>3</sup> h<sup>-1</sup>) and formaldehyde was added by thermal decomposition of paraformaldehyde at temperatures in the range of 393–415 K. In this case, all tubing was heated to ~400 K to prevent formaldehyde condensation. In one experiment with acetaldehyde, paraformaldehyde was also used as a source of formaldehyde. The products were analysed by gas chromatography using FID and a 30 m capillary column at 100 °C. The product yields in Table 3 (mol%) are based on the acetaldehyde or propionaldehyde content in the gas stream.

### Acknowledgements

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