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Combined solid base/hydrogenation catalysts for industrial condensation reactions

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Abstract

Solid base catalysts of the type Na/SiO_2 have been developed for the fixed-bed vapour-phase aldol condensation of aldehydes (*n*-butanal and *n*-hexanal) which can run continuously at high activity (*n*-butanal maximum conversion 58%) and selectivity. These industrially significant reactions can be also be combined with hydrogenation steps using either a single bed or dual bed system. Using a $Pd/Na/SiO_2$ catalyst the saturated aldehyde product can be selectively produced over a single bed without hydrogenating the original feedstream. The $Pd/Na/SiO_2$ catalyst has a higher initial conversion (82%) than the Na/SiO_2 catalyst but deactivates more rapidly. A dual bed system using a conventional CuO/ZnO hydrogenation catalyst can be used to produce a mixed stream of alcohols. © 2002 Elsevier Science B.V. All rights reserved.

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1. 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 $Ca(OH)_2$ [1]. 2-Ethyl hexanol is predominately converted to di-ethylhexyphthalate, which is used as a plasticiser for PVC, MIBK is an excellent solvent for cellulose and resin based coatings, Guerbet alcohols are used in cosmetics, textiles, lubricants and surfactants. It has been estimated for these compounds [2] that 30% of the selling price is product purification, recovery and waste treatment. For every 10 t of product formed the current homogeneous catalysts generate about 1 t of spent catalyst [2]. High capital costs are also associated with the handling of strong homogeneous bases such as 30% caustic.

Solid base catalysts have a number of advantages over conventional homogeneous (NaOH, KOH) systems as follows [3,4]:

- High catalytic activity and selectivity are often observed.
- Solid base catalysts do not corrode reaction vessels or reactors.
- Repeated use is possible.
- Easier separation from the products.
- Less waste than produced from stoichiometric reagents.
- Lower operation and maintenance costs.
- No acid or base containing waste streams.
- Lower energy synthesis.
- Solid base catalysts do not catalyse cracking reactions.

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- In the presence of solid base catalysts there are no strong adsorption complexes as found between acid sites and N- and O-containing, i.e functionalised organic compounds. Desorption energy is lower allowing reactions at lower temperatures.

Most industrial condensation products also pass through a fixed-bed hydrogenation step after the homogeneous condensation step [1]. The use of solid base catalysts also allows the easier integration of the condensation step with any subsequent hydrogenation steps. This hydrogenation step may use either a selective hydrogenation catalyst using a Pd based catalyst or an unselective hydrogenation over a Cu or Ni based catalyst.

Despite the many possible advantages of using solid base catalysts there are in fact very few solid base catalysts currently in use commercially. According to a recent review of industrial acid and base catalysis [5] of the 127 processes identified only 10 were solid base catalysed. Solid base catalysis is therefore an area of chemistry that offers an opportunity for exploitation if suitable catalysts and processes can be identified and developed.

The aim of this work was to identify solid base catalyst, suitable for the industrial aldol condensation of aldehydes (*n*-butanal and *n*-hexanal) [6]. A suitable solid base must have the appropriate base strength for the reaction under investigation. If the initial reaction step is the removal of a proton from a reactant of the form R_1–CH_2–R_2 then the acidity of the proton to be removed depends on the identity of the R_1 and R_2 groups [7] (Table 1). The solid base selected should have sufficient base strength to carry out the reaction but should not have excessive base strength as this may lead to rapid catalyst deactivation (due to carbon laydown for instance) or to side-product formation. For aldehyde condensation therefore with a pK_a of ∼19.7 a strong base is required but not a superbase material [8]. Caustic can be used to carry out reactions with reactants with the removable proton having a pK_a of up to around 20. For less acidic protons stronger base materials are usually required to give sufficient rate of reaction [9].

The strength of surface base sites on solids can be measured by the use of Hammett indicators [10] and expressed in terms of the acidity function (H_-) proposed by Paul and Long [11]. There are a number of mild base materials (H_- 10–15) such as hydrotalcites, alkali doped zeolites and aluminophosphates oxynitrides (ALPON) available [12] and at the other extreme a number of super basic materials (H_->26) such as alkaline earth oxides (CaO, MgO) and alkaline metal based catalysts (Na/NaOH/Al_2O_3, Na/MgO, etc.) [8]. There are few available solid base materials, however, in the strong solid base area (H_- 20–25) that would be suitable for the aldol condensation of aldehydes (Fig. 1). One example of a recently developed strong basic catalyst is a Cs/SiO_2 material developed for a new route for producing methyl methacrylate from the reaction of methyl propionate ester with formaldehyde [13].

Table 1
Base strength required to remove proton from a R_1–CH_2–R_2 reactant molecule

R_1	R_2	pK_a	Base required
–CH_3	–CH_3	42	Super base
–CH_3	CH=CH_2	35.5	
–C_6H_5	H	35	
–C_6H_5	–C_6H_5	33	
–CH_3	–CN	25	Strong base (NaOH)
–CH_3	–COOR	24.5	
–CH_3	–$COCH_3$	20	
–CH_3	–COH	19.7	
–COOR	–COOR	11.5	Medium base (NaOH)
–CN	–CN	11.2	
–CH_3	–NO_2	10.6	
–COR	–COR	9	
	–COOR	5.8	Mild base (NaOH)
–COH	–COH	5	
–NO_2	–NO_2	3.6	

This work also aims to identify suitable combined solid base/hydrogenation systems using either a single catalyst bed or a dual bed system [6]. The product from the aldol condensation of aldehydes is usually an α,β-unsaturated aldehyde (Fig. 2) from the dehydration of the aldol product. The choice of product formed on the hydrogenation of this α,β-unsaturated aldehyde depends largely on the metal function used. A Pd catalyst could be used to selectively hydrogenate the –C=C as it is often inactive with regard to the carbonyl group [14]. Promoted Pt or Ru catalysts can be used to selectively hydrogenate the carbonyl to produce α,β-unsaturated alcohols [14]. Cu or Ni catalysts are the conventional catalysts for fully hydrogenating

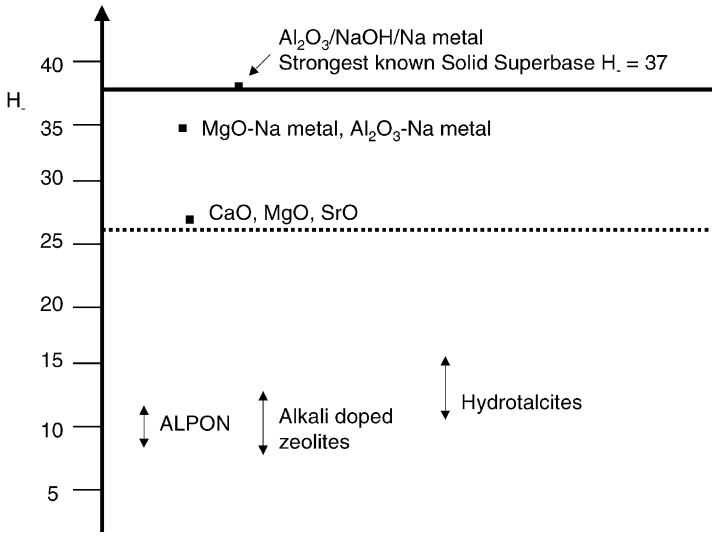

Fig. 1. Strengths of solid base catalysts (H_- scale).

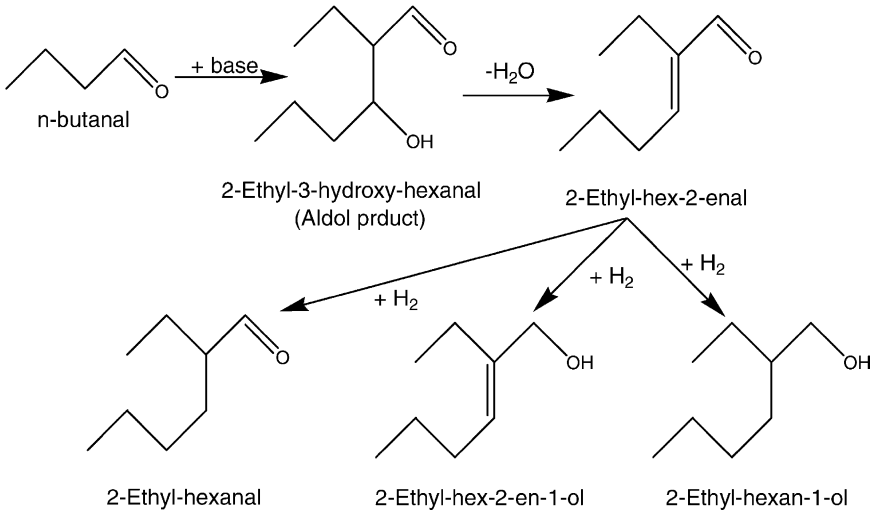

Fig. 2. *n*-Butanal condensation/hydrogenation reaction scheme.

the α,β-unsaturated aldehyde through to the saturated alcohol [1].

2. Experimental

2.1. Catalyst preparation

A 4 wt.%Na/SiO_2 catalyst was prepared by an impregnation method using nitrate salts. Fuji Q10 silica spheres (2–3 mm) were used which have a surface area of 359 $m^2\,g^{-1}$ and a pore volume 1.01 $cm^3\,g^{-1}$. A Pd doped version of this catalyst was also prepared by co-impregnating the Fuji Q10 silica with a mixture of Na and Pd nitrates to produce a catalyst of the following formulation 0.1 wt.%Pd/4 wt.%Na/SiO_2. Both catalysts were dried overnight at 100 °C after impregnation and calcined at 450 °C for 3 h. A CuO/ZnO hydrogenation catalyst

was prepared by co-precipitation and contained 35 wt.% CuO.

2.2. Catalyst testing

Reaction testing was carried out in a stainless steel fixed-bed microreactor system that allowed testing at a range of pressures and aldehyde and carrier flow rates. The catalysts were crushed to a particle size of 0.6–1 mm before testing. H_2 was used as a carrier gas for all of the experiments. To carry out the experiments the catalysts were brought up to reaction temperature in a flow of H_2 (50 ml min^{-1}) before initiating the aldehyde flow. Before commencing testing, the CuO/ZnO hydrogenation catalyst, where used, was reduced in a 10% H_2/N_2 flow at 160 °C over a period of 24 h. The aldehyde flow was controlled using a HPLC pump. Reaction products were analysed off-line using a combination of GC and GC–MS. Catalyst temperature was recorded from a thermocouple in the catalyst bed. Where two beds were in place a thermocouple was inserted into each of the beds. In the single bed experiments a single bed of 3 ml of catalyst was used. In the dual bed experiments two 3 ml beds of catalyst separated with space were used. After purging and discharge the spent catalyst samples were analysed for carbon content using a Leco analyser.

2.3. Treatment of results

The following treatment of the raw data was used to derive the product selectivities and activities for the single bed experiments

$$\text{conversion} = \left(\frac{\text{moles aldehyde reacted}}{\text{moles aldehyde fed}}\right) \times 100\%$$

$$\text{selectivity} = \left(\frac{2 \times \text{moles of aldol products formed}}{\text{moles aldehyde reacted}}\right) \times 100\%$$

Product distribution

$$\%\text{2-ethyl hexenal} = \left(\frac{\text{moles 2-ethyl hexenal}}{\text{total moles aldol products}}\right) \times 100$$

$$\%\text{2-ethyl hexanal} = \left(\frac{\text{moles 2-ethyl hexanal}}{\text{total moles aldol products}}\right) \times 100$$

$$\%\text{2-ethyl hexanol} = \left(\frac{\text{moles 2-ethyl hexanol}}{\text{total moles aldol products}}\right) \times 100$$

For the dual bed experiments the following treatment of results was used

$$\frac{\%\text{2-ethyl hexanol}}{n\text{-butanol}} = \frac{\text{moles of 2-ethyl hexanol}}{\text{moles } n\text{-butanol}} \times 100\%$$

$$\frac{\%\text{2-butyl octanol}}{n\text{-hexanol}} = \frac{\text{moles of 2-butyl octanol}}{\text{moles } n\text{-butanol}} \times 100\%$$

$$\%\ \text{conversion } n\text{-hexanal} = \frac{(2 \times \text{moles 2-butyl octanol})}{(2 \times \text{moles2-butyl octanol} + \text{moles } n\text{-hexanol})} \times 100$$

3. Results and discussion

3.1. Single bed reactions

The aldol condensation reaction of *n*-butanal was carried out over the 4 wt.%Na/SiO_2 and the 0.1 wt.%Pd/4 wt.%Na/SiO_2 catalysts under near identical conditions (Tables 2 and 3). The *n*-butanal liquid feed rate was in both cases 0.05 ml min^{-1}. Although the 0.1 wt.% Pd containing catalyst initially has a higher conversion of *n*-butanal it undergoes a more rapid deactivation than the Na/SiO_2 catalyst (Fig. 3). The other major difference between the two catalysts is in the product spectrum achieved. The Na/SiO_2 catalyst produces almost exclusively (>99%) the α,β-unsaturated aldehyde despite carrying out the reaction in a hydrogen carrier stream. Less than 0.5% of the *n*-butanal feed was hydrogenated to *n*-butanol. The 0.1 wt.% Pd containing catalyst produces a high selectivity towards the saturated aldehyde product 2-ethyl hexanal (maximum 94.9%) with less than 2% of the butanal feed hydrogenated to either *n*-butanol or 2-ethyl hexanol [6]. This demonstrates the selective hydrogenation activity that can be achieved with Pd. No lights were produced over either of these catalysts. The reason for the more rapid deactivation of

Table 2
Reaction of *n*-butanal over Na/SiO_2 catalyst

Time (h)	Temperature (°C)	H_2 flow rate ($ml\,min^{-1}$)	Conversion (%)	Selectivity (%)	Product spectrum		
					2-Ethyl hexenal (%)	2-Ethyl hexanal (%)	2-Ethyl hexanol (%)
2	350	42	45	72	99.0	0.5	0.5
4	350	42	58	86	98.4	1.3	0.3
6	350	42	50	89	99.5	0.2	0.3
22	350	42	38	99	99.2	0.6	0.2
30	350	21	40	91	100	0.0	0.0
46	350	21	41	92	99.5	0.5	0.0
53	400	21	43	100	99.8	0.2	0.0
70	400	21	40	89	99.6	0.2	0.2
72	450	21	47	79	99.7	0.3	0.0

Table 3
Reaction of *n*-butanal over $Pd/Na/SiO_2$ catalyst

Time (h)	Temperature (°C)	H_2 flow rate ($ml\,min^{-1}$)	Conversion (%)	Selectivity (%)	Product spectrum		
					2-Ethyl hexenal (%)	2-Ethyl hexanal (%)	2-Ethyl hexanol (%)
4	350	50	82	81	30.2	69.2	0.6
6	350	50	58	92	13.6	86.0	0.4
8	350	50	49	94	7.0	92.5	0.5
24	350	50	42	100	4.5	94.9	0.6
31	350	25	39	96	6.6	92.6	0.8
48	350	25	34	100	10.6	88.6	0.8
55	400	25	40	86	12.2	87.0	0.8
72	400	25	32	92	16.2	83.1	0.7
77	450	25	38	75	25.4	73.9	0.7

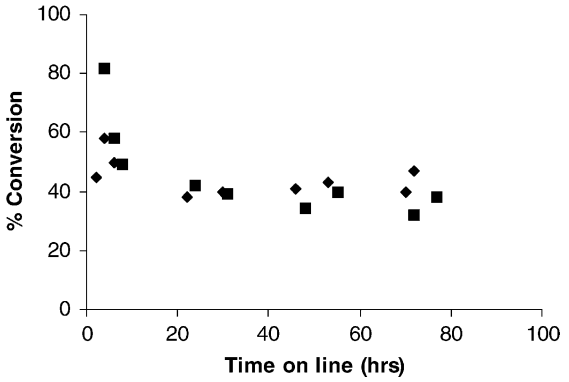

Fig. 3. Reaction on *n*-butanal over 4 wt.%Na/SiO_2 catalyst (◆) and 0.1 wt.%Pd/4 wt.%Na/SiO_2 catalyst (■).

the $Pd/Na/SiO_2$ catalyst are not clear but may be due to catalyst poisoning by the branched saturated aldehyde product itself. The 2-ethyl hexanal product has a replaceable proton of a similar acidity to the *n*-butanal feed. The adsorption of the 2-ethyl hexanal onto the solid base surface and removal of this proton may form an unreactive intermediate that leads to catalyst deactivation. This theory will require further investigation. Aldol condensation is an equilibrium-limited reaction. The position of the equilibrium for the Na/SiO_2 reaction is hard to calculate, as there is very little thermochemical data available for 2-ethyl hexenal. Swift et al. [15] estimated that the vapour-phase condensation of *n*-butanal equilibrium conversion was 75% at 250 °C. The basis of this estimation is not however clear. The reaction of *n*-butanal over the $Pd/Na/SiO_2$ catalyst to form 2-ethyl hexanal is not equilibrium limited under these reaction conditions.

Table 4
Reaction of *n*-butanal over Na/SiO_2 catalyst followed by CuO/ZnO catalyst

Pressure (bar g)	H_2 flow rate (ml/min)	*n*-Butanal flow rate (ml liquid/min)	2-Ethyl hexanol/ *n*-butanol (%)	Conversion of *n*-butanal to aldol products (%)
3	80	0.05	14.9	22.9
5	80	0.05	19.9	28.4
7	80	0.05	23.3	31.7
5	80	0.025	17.3	25.7
5	40	0.025	21.5	30.0
5	100	0.025	9.8	16.3

3.2. Dual bed reactions

Reactions of both *n*-butanal and *n*-hexanal were carried out over dual bed reactor systems with 4 wt.%Na/SiO_2 catalysts followed by a bed of a CuO/ZnO hydrogenation catalyst loaded into a single reaction tube. The reaction with *n*-butanal is shown in Table 4. The Na/SiO_2 bed was held at 350 °C and the CuO/ZnO bed at 130 °C. The reaction products in this case were only 2-ethyl hexanol and *n*-butanol. It can be seen that the proportion of 2-ethyl hexanol increases as the pressure increases and as the hydrogen feed is decreased. At a constant hydrogen to butanal ratio, the proportion of 2-ethyl hexanol increases as the *n*-butanal feed decreases, i.e. as the space velocity decreases.

The reaction of *n*-hexanal is shown in Table 5. The Na/SiO_2 top bed was held at 350 °C and the CuO/ZnO bed was held at 259 °C. In this case the only products detected were *n*-hexanol and 2-butyl octanol. 2-Butyl octanol is a member of the branched alcohol series often termed Guerbet alcohols. With the reaction of *n*-hexanal there is a higher initial conversion of the aldehyde to the aldol product (maximum 59.3%) compared to the *n*-butanal example. The more rapid deactivation with *n*-hexanal does not appear to be associated with carbon laydown (Section 3.3). With the *n*-hexanal, however, there is a more rapid catalyst deactivation than for the *n*-butanal example. Due to this rapid deactivation it is not clear if there is any conversion benefit from increasing the pressure. At 7 bar g decreasing the H_2 carrier flow rate flow from 85–22 ml min^{-1} produces an increase in *n*-hexanal conversion from 23.3 to 42.7%.

3.3. Carbon laydown

The carbon laydown figures for three of the reaction runs are shown in Table 6. These results show that for a similar time on-line the $Pd/Na/SiO_2$ catalyst has a

Table 5
Reaction of *n*-hexanal over Na/SiO_2 catalyst followed by CuO/ZnO catalyst

Time on-line (h)	Pressure (bar g)	H_2 flow rate (ml/min)	*n*-Hexanal flow rate (ml liquid/min)	2-Butyl octanol/ *n*-hexanol (%)	Conversion of *n*-hexanal to aldol products (%)
6	3	85	0.05	72.7	59.3
24	3	85	0.05	50.0	50.0
30	3	85	0.05	37.7	43.0
47	5	85	0.05	36.5	42.2
52	5	85	0.05	24.5	32.9
76	7	85	0.05	15.2	23.3
107	7	55	0.05	17.8	26.3
155	7	55	0.05	12.7	20.3
162	7	42	0.05	14.6	22.6
179	7	42	0.05	15.0	23.1
186	7	22	0.05	29.0	36.7
203	7	22	0.05	37.3	42.7

Table 6
Carbon laydown levels on spent catalysts

Catalyst	Reaction run	Time on-line (h)	Carbon level (wt.%)
4 wt.%Na/SiO_2	Single bed *n*-butanal	72	10.6
0.1%Pd/4 wt.%Na/SiO_2	Single bed *n*-butanal	77	8.2
4 wt.%Na/SiO_2	Dual bed *n*-hexanal	203	4.2

slightly lower carbon laydown figure than the Na/SiO_2 catalyst. The lowest carbon laydown figure is shown for the Na/SiO_2 catalyst, which made up part of the dual bed system for the reaction of *n*-hexanal. In this case even after 203 h on-line the carbon laydown level is still less than half of that of the other catalysts even though it has been on-line over twice as long. Carbon laydown figures were not measured for the Na/SiO_2 catalyst for the dual bed system reaction of *n*-butanal. From the information available, however, the carbon laydown figure on the solid base catalyst appears to be dependent on the feedstock used with greater carbon laydown with *n*-butanal than with *n*-hexanal.

4. Conclusions

The viability has been demonstrated for a solid fixed-bed basic material Na/SiO_2 to carry out the industrially important aldol condensation of aldehydes. This gives the opportunity to eliminate the use of 30% caustic solution normally used for condensation reactions and dramatically reduce the amount of waste produced. These catalysts can be run continuously on-line for hundreds on hours at high conversions and selectivities. The Na/SiO_2 catalyst can be doped with small amounts of Pd to selectively hydrogenate the α,β-unsaturated aldehyde intermediate to the saturated aldehyde without hydrogenating to any extent the aldehyde feed. This selectivity would allow the use of a recycle system to return the unreacted aldehyde to the reactor. The use of a combined bed system following the Na/SiO_2 catalyst with a conventional CuO/ZnO hydrogenation catalyst allows the co-production of easily separable alcohols. This combination of aldol condensation and hydrogenation offers the possibility of the removal of a process step and consequent capital saving.

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