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# Catalysed synthesis of 4-heptanone from 1-butanol

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## Abstract

While investigating the reaction of 1-butanol over base catalysts, such as MgO, we observed the formation of small amounts of 4-heptanone. Further studies revealed that a $CeO_2$/MgO catalyst gave good selectivity to this product. To optimise the reaction and determine the reaction mechanism a series of studies were undertaken in which a range of variables were modified viz. cerium loading, temperature, reagent composition and water addition. The optimum conditions for 4-heptanone yield (25.5%) and selectivity (42.5%) were found to be: 450°C, 1:6 oxygen to butanol reagent mixture and a total gas flow rate of 6.74 ml/min. A reaction mechanism in which butanol is oxidised to butanal and then butanoic acid followed by the coupling of two equivalents of butanoic acid to give the symmetrical ketone 4-heptanone and $CO_2$ is proposed. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Heptanone; Butanol; Magnesium oxide; Cerium oxide

## 1. Introduction

Ketones are produced commercially in large volumes, typically in stoichiometric reactions, from alcohols, aldehydes and acids [1]. Generally, if the starting material contains $n$ carbon atoms then the product contains $n$ carbon atoms e.g. oxidation of $CH_3CHOHCH_3$ gives $CH_3COCH_3$ [2]. However, the so-called ketonisation reaction can result in the synthesis of a ketone with $2n-1$ carbon atoms from two starting materials with $n$ carbon atoms each [3–7]. This latter procedure provides for the synthesis of an internal functional group (C=O) in a linear carbon chain.

While investigating the reactions of 1-butanol over base catalysts we observed the formation of small amounts of 4-heptanone. Further studies revealed that a catalyst comprising $CeO_2$/MgO gave good selectivity to this product. Interestingly, there is precedent for the direct synthesis of internal ketones from alcohols over a $Cu/Zn/Al_2O_3$ catalyst [8] and the use of $CeO_2$ for the conversion of aldehydes to internal ketones [9].

Below we discuss our results obtained from the investigation of butanol over $CeO_2$/MgO catalysts.

## 2. Experimental

### 2.1. Reagents

Reagent grade butanol, butanal, butanoic acid from Sigma Chemicals were used without further purification. Magnesium oxide and cerium nitrate from BDH and oxygen from AFROX were used as received.

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### 2.2. Catalyst synthesis

MgO support was pelletised, by pressing the powdered MgO to 20 t using a pneumatic press. The pellets were crushed and screened with the 300–1000 μm fraction collected. The MgO was impregnated with a solution of $Ce(NO_3)_3 \cdot 6H_2O$ dissolved in distilled water, to yield 5–40% loaded catalysts (by mass). The catalysts were then dried in air at 180°C for 16 h followed by air calcination at 550°C for 8 h.

### 2.3. Characterisation studies

Liquid products were condensed in a cold trap attached to the reactor outlet and analysed using gas chromatography, a Brucker AC 400 NMR spectrometer, a VG70 SEQ mass spectrometer with a VG11-250J data system and a Brucker IFS 85 FTIR spectrometer. Gaseous products were analysed with an online GC.

The off-gases were analysed using a gas chromatography. A 2 m Porapak column was used for hydrocarbon analysis (nitrogen carrier gas at a flow rate of 30 ml/min and an FID detector). The products were identified, by correlating residence times with standards injected using identical conditions. CO, $CO_2$, $O_2$ and $N_2$ were analysed using a packed 2 m×1/8 in. Porapak Q column (helium carrier gas at a flow rate of 20 ml/min and a TCD detector).

The liquid fractions were injected off-line into a 30 m megabore capillary column (DB1) manufactured by J&W (nitrogen carrier gas at a flow rate of 10 ml/min and an FID detector).

The BET surface area, pore diameter and pore volume of MgO and 40% Ce/MgO were determined using an ASAP2010 porosimeter (Table 1).

Table 1
The surface area, pore diameter and pore volume of MgO and 40% Ce/MgO

| Catalyst | Surface area ($m^2$/g) | Pore diameter (A) | Pore volume ($cm^3$/g) |
|---|---|---|---|
| MgO | 54.4 | 262.0 | 0.36 |
| 40% Ce/MgO | 29.2 | 424.9 | 0.31 |

### 2.4. Reactor studies

Catalytic reactions were performed in a fixed bed reactor. The reactor was made of quartz glass and was heated by means of an external heating jacket. The temperature was controlled by means of a thermocouple (type J) in contact with the catalyst. 1-Butanol was loaded into a Hamilton series 1010 gas tight syringe and added by means of a syringe pump (Sage instruments, model 355) into the heated oxygen stream prior to the reactor. Both oxygen and 1-butanol were passed through a pre-heated section of the reactor such that the carrier gas was added to the reactor at 110°C. Typically, 5 g of catalyst was placed in the reactor. The catalyst bed was heated to 450°C at 15°C/min and maintained to within 1°C for the duration of the experiment. The oxygen gas flow rate was 24 ml/min and 1-butanol liquid flow rate was 0.1 ml/min. The gaseous product stream from the reaction was passed directly through an on-line column (poropak Q) and the course of the reaction was monitored directly. The macroscopic amounts of the liquid products were isolated, collected at room temperature, and analysed off-line.

Gas flows, temperatures and catalyst loading, were varied in the experiments.

The yield of ketone was calculated as follows:

$$\text{Yield of ketone}\ (\%) = \frac{2 \times \text{moles of ketone produced} \times 100}{\text{moles of alcohol introduced}}.$$

## 3. Results and discussion

Reaction of butanol and oxygen over MgO (350–450°C) gave a wide range of products as determined by gas chromatography. The products included minor amounts of butanal (<1%), butene, butane, ethene and ethane and 97% of the butanol remained unreacted. It appeared that many of the products were derived from aldol condensation reactions (2-ethylhexanal, 2-ethyl-2-hexenal, 2-ethylhexanol). Analysis of the data suggested that insufficient oxygen was available to ensure oxidation of the starting material.

In an attempt to provide an alternative source of oxygen for the reaction 5% $CeO_2$ was added to the MgO. The GC trace of the product from this reaction revealed that one new product dominated the spectrum as indicated in Fig. 1. The identities of the products

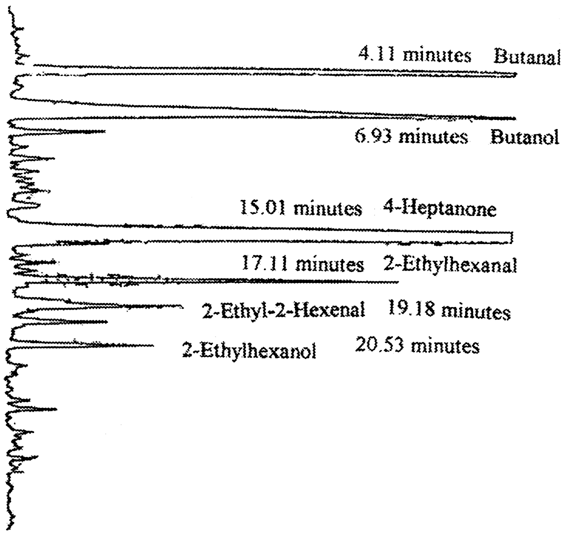

Fig. 1. A GC trace of the products obtained from passage of *n*-butanol and oxygen over 40% $CeO_2/MgO$ (450°C).

from this reaction were determined by a combination of NMR spectroscopy, GC–MS and retention times of standards. In particular, the major component was shown to be 4-heptanone by $^{13}C$ NMR spectroscopy and mass spectroscopy (Table 2).

To optimise the reaction and determine the reaction mechanism a series of studies were undertaken in which reaction variables were modified viz. cerium loading, temperature, reagent composition and water addition. The reactions were repeated at four different flow rates for each variable.

In initial studies the loading of $CeO_2$ on the MgO was increased (5–40%) and this was found to give a maximum selectivity to 4-heptanone with the higher loaded catalysts (see Table 3). Data revealed that the higher *selectivity to butanal* was achieved at the lower $CeO_2$ loading, while the yield of $C_8$ aldol products were low for both reactions. Clearly, the presence of $CeO_2$ inhibits aldol reactions and converts the alcohol to the aldehyde and acid (see below) and eventually to the ketone. Oxidation to $CO_2$ is a competing reaction.

The effect of reaction temperature on the coupling reaction is shown in Fig. 2. The maximum yield of 4-heptanone (16.88%) was achieved at a temperature of 450°C. The yield decreased to 7.51% when the temperature was reduced to 400°C and to 1.03% when the temperature was further reduced to 350°C. This appeared to be consistent with earlier literature reports in which no catalysed ketonisation reaction ($CeO_2$/metal catalyst) was observed below 350°C [9].

Variation of the $O_2$/1-butanol ratio (1:1 to 1:6) also resulted in changes in the product distribution

Table 2
The $^{13}C$ NMR spectral and MS–GC data for 4-heptanone

| $^{13}C$ NMR assignments | | Mass Spectral Data | | |
|---|---|---|---|---|
| Carbon | Shift (ppm) | Mass (amu) | Fragment | Abundance (%) |
| –C=O (ketone) | 211.2 | 15 | $CH_3^+$ | 0.4 |
| $–CH_2–$ | 44.5 | 27 | $CH_3C^+$ | 7.6 |
| $–CH_2–$ | 17.0 | 41 | $CH_3CH_2C^+$ | 11.4 |
| $–CH_3$ | 13.5 | 43 | $CH_3CH_2CH_2C^+$ | 33.6 |
| | | 71 | $CH_3CH_2CH_2C^+{=}O$ | 37.4 |
| | | 114 | $CH_3CH_2CH_2C{=}OCH_2CH_2CH_2^+$ | 7.6 |

Table 3
The effect of cerium loading and reagent composition on the conversion of 1-butanol to 4-heptanone (450°C)

| Cerium loading | Oxygen:butanol | Flow rate (ml/min) | Conversion (%) | Yield of butanal (%) | Yield of heptanone (%) | Yield of $C_8$ aldol (%) |
|---|---|---|---|---|---|---|
| 5% | 1:3 | 1.97 | 97.3 | 0.24 | 2.20 | 0.18 |
| | | 3.93 | 71.8 | 4.41 | 8.56 | 0.40 |
| | | 7.87 | 62.8 | 5.93 | 4.49 | 0.71 |
| | | 15.74 | 42.0 | 10.85 | 2.97 | 1.57 |
| 40% | 1:3 | 3.93 | 99.1 | 0.09 | 0.15 | 0.00 |
| | | 7.87 | 96.3 | 0.33 | 0.48 | 0.00 |
| | | 15.74 | 41.6 | 4.26 | 16.88 | 1.02 |
| | | 31.48 | 36.4 | 5.23 | 10.95 | 1.62 |
| 40% | 1:1 | 6.54 | 97.8 | 0.88 | 0.27 | 0.00 |
| | | 13.08 | 64.5 | 2.85 | 18.47 | 0.38 |
| | | 26.16 | 49.7 | 5.77 | 8.94 | 1.35 |
| | | 52.31 | 48.2 | 7.72 | 6.38 | 1.69 |
| 40% | 1:6 | 3.47 | 63.7 | 4.58 | 5.13 | 1.28 |
| | | 6.74 | 60.0 | 2.96 | 25.53 | 0.66 |
| | | 13.48 | 42.7 | 4.96 | 12.48 | 1.22 |
| | | 27.91 | 54.9 | 5.64 | 7.72 | 1.82 |
| | | 53.91 | 57.0 | 7.37 | 3.78 | 1.71 |

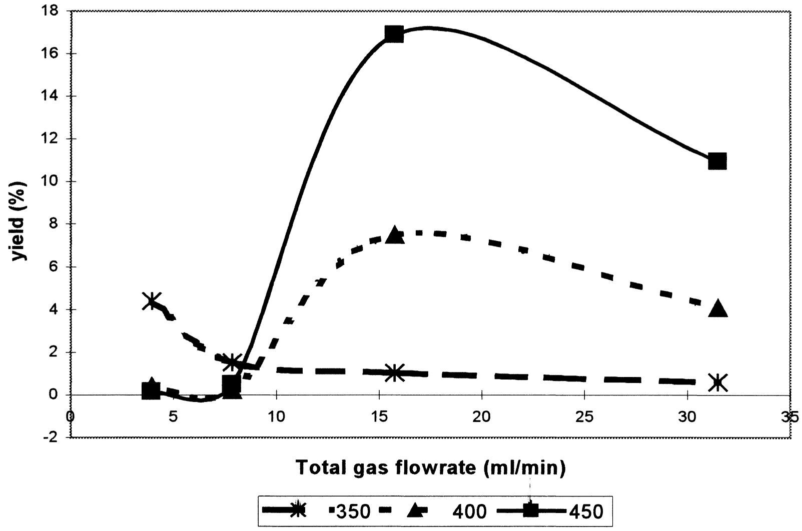

Fig. 2. The effect of temperature and reagent flow rate on the reaction of butanol to 4-heptanone over 40% $CeO_2$/MgO ($O_2$:butanol 1:3).

(Table 2). By reducing the oxygen content from 50% to 25% to 14% the conversion of butanol is generally reduced. However, since the product selectivity varies it is clear that no direct correlation between these variables is possible. The yield of 4-heptanone (25.5%) is maximised with a reagent ratio of 1:6

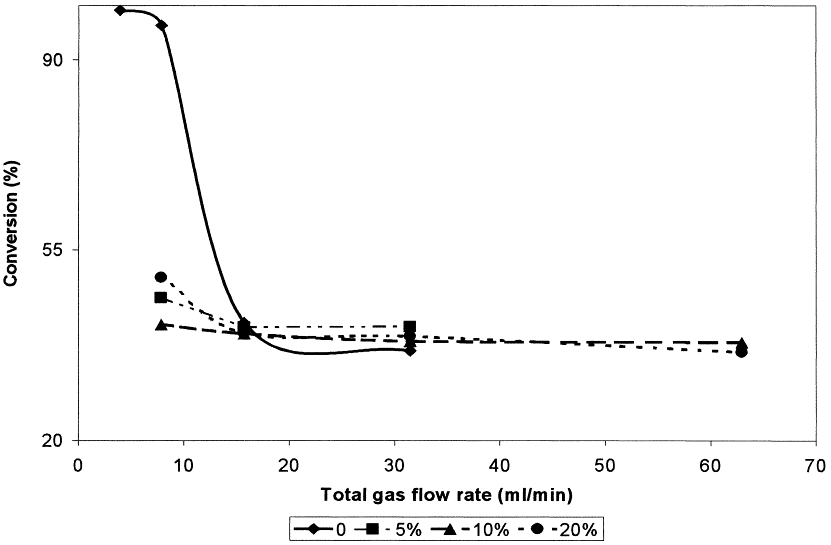

Fig. 3. The effect of water addition on the conversion of butanol over 40% $CeO_2$/MgO.

and a total gas flow rate of 6.74 ml/min. The selectivity to 4-heptanone, neglecting starting material, is 42.55% under these conditions. The selectivity to 4-heptanone in the liquid phase products is greater than 80%. When the gaseous combustion products are included the total selectivity to 4-heptanone is approximately 20%.

The results also indicate that complete oxidation of butanol to $CO_2$ occurs at low flow rates. In an attempt to reduce product combustion, the effect of $H_2O$ on the reaction was studied. The introduction of 5% water to reduce combustion resulted in the conversion being reduced from 96.3% to 46.2% at a total gas flow rate of 7.87 ml/min. At higher flow rates the addition of water had no effect on conversion (Fig. 3). The addition of 5% water resulted in more butanal being produced and an increase in aldol products which is consistent with related literature reports [10]. A total gas flow rate of 7.87 ml/min in the presence of 20% water addition gave the maximum yield of 4-heptanone (18.3%).

The reaction of butanol (20% $H_2O$) over 40% Ce/MgO was monitored for 24 h and the data are shown in Fig. 4. From this figure, it can be seen that the yield of butanal and the aldol products decrease during the first 5 h to a low constant value. During this period the yield of 4-heptanone increases from 18.33% to 20.66%. Thereafter, the yield of 4-heptanone decreases with time on line to 13.22%. The *conversion* increases during the first five hours and then stabilises at ca. 63%. The *selectivity* to 4-heptanone decreases with time on line from 36.76% to 19.98% which suggests the active sites for the ketonisation reaction are lost in the reaction and this leads to a concomitant increase in the total oxidation products ($CO_2$).

### 3.1. Mechanistic studies

From the optimisation experiments it was observed that butanal was a significant product formed in the reaction. Since numerous reports have appeared on the ketonisation reaction, in which aldehydes (or acids) are converted to internal ketones this possibility was tested on these reactions. There are two earlier conflicting reports on the role of $CeO_2$ in the ketonisation reaction. In these reports it was observed that propanol did not give penta-3-one over $CeO_2$ [11] while acetaldehyde gave acetone over metal supported (Co, Pd, Co–Pd) $CeO_2$ [9].

Butanal was passed over 40% $CeO_2$/MgO at three different reaction conditions. The carrier gas used was nitrogen. The liquid products were collected in an air-cooled trap, and analysed using off line GC and $^{13}C$ NMR spectroscopy. The results are presented in Table 4.

The results clearly reveal that butanal is a reagent for the synthesis of 4-hepatanone. Aldol products are

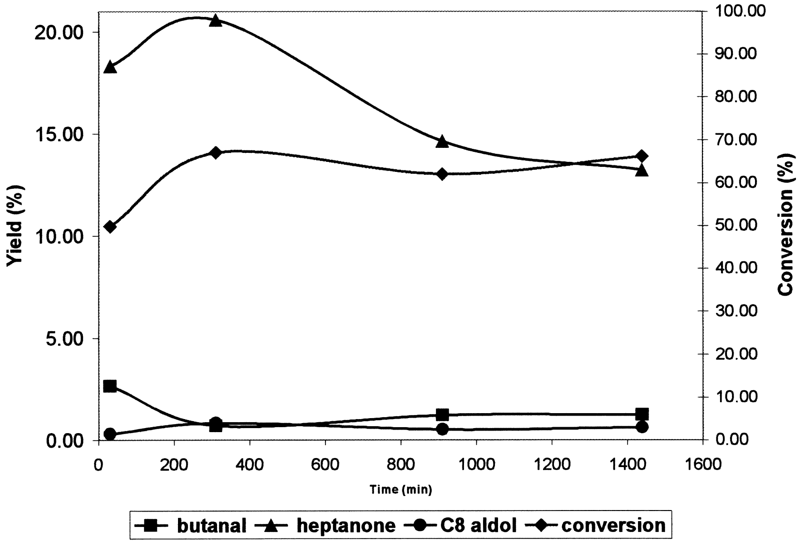

Fig. 4. The effect of time on line on the reaction of butanol (in 20% $H_2O$) to 4-heptanone over 40% $CeO_2$/MgO ($O_2$:butanol, 1:3).

Table 4
GC analysis of products from the reaction of butanal over 40% $CeO_2$/MgO

| Butanal (ml/min) | Nitrogen (ml/min) | Composition of liquid phase | | |
|---|---|---|---|---|
| | | Butanal (%) | 4-Heptanone (%) | Aldol Products (%) |
| 0.003 | 1 | 0 | 61.48 | 9.16 |
| 0.012 | 1 | 51.6 | 24.23 | 10.86 |
| 0.18 | 1 | 85.79 | 6.0 | 3.8 |

also observed and are formed in a coupling reaction. Of significance is the observation that the best selectivities are obtained at low butanal concentrations. Numerous mechanisms have been proposed for the ketonisation reactions, one of which entails the conversion of an aldehyde to an acid with subsequent decarboxylation to give the ketone [3–7].

Passage of butanoic acid over 40% $CeO_2$/MgO gave a clean reaction in which only 4-heptanone and butanoic acid were observed by GC. Butanoic acid was thus passed over MgO to determine whether cerium was necessary for the coupling of butanoic acid to 4-heptanone. The major product was again 4-heptanone with minor amounts of butanoic acid remaining unreacted. Results obtained thus suggest that cerium oxidises butanol to butanal which is further oxidised to butanoic acid. The acid then undergoes a coupling reaction over MgO to form the symmetrical ketone.

A possible mechanism consistent with our results, and the extensive literature data available, is given in Fig. 5.

## 4. Conclusion

The following conclusions were made:

- Butanol can be converted to 4-heptanone over a $CeO_2$/MgO catalyst. The mechanism is proposed to involve the oxidation of the alcohol to the aldehyde to the acid followed by coupling to the ketone.
- The cerium is necessary for the oxidation steps.

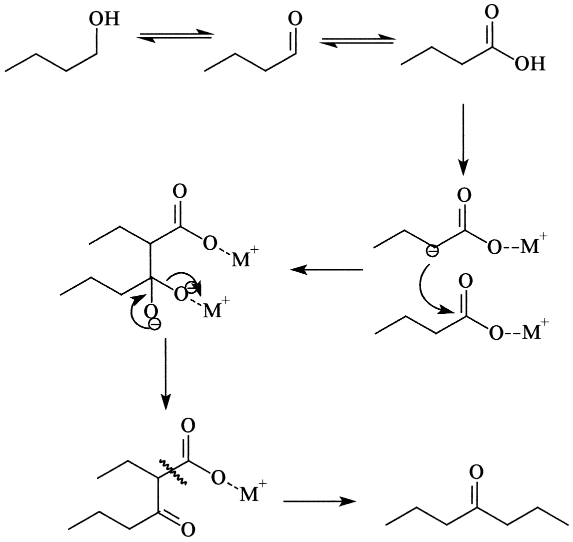

Fig. 5. Proposed mechanism for the coupling of butanol to 4-heptanone.

- The coupling reaction of butanoic acid occurs readily over the MgO catalyst.
- The addition of small amounts of water enhances the aldol condensation reaction.

## Acknowledgements

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