High catalytic activity of silicalite in gas-phase ketonisation of propionic acid
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Introduction
Carboxylic acids readily available from natural resources are attractive as renewable raw materials for the production of value-added chemicals and biofuel components[1]. For fuel applications, carboxylic acids require reduction in their oxygen content, i.e., deoxygenation. Ketonisation (eq. 1) allows for partial deoxygenation of carboxylic acids to be achieved accompanied by their carbon backbone upgrade. It is catalysed by many metal oxide and oxide materials, namely amorphous silica and, in particular, crystalline silicalite [3]. PA is chosen as a representative of carboxylic acids with the number of carbon atoms n ≤ 6 derived from carbohydrate feedstocks.

\[ 2 \text{CH}_3\text{CH}_2\text{COOH} \rightarrow (\text{CH}_3\text{CH}_2)\text{CO} + \text{CO}_2 + \text{H}_2\text{O} \quad (1) \]

Experimental/methodology
Silicalite was prepared by the literature procedure [4]. HZSM-5 (Si/Al = 180) was from Zeolyst Int. The catalysts were characterised by BET, FTIR and XRD. The ketonisation of PA was carried out in the gas phase in flowing \( \text{N}_2 \) at 300-550°C under atmospheric pressure and [PA] = 2 vol% in a quartz fixed-bed reactor (9 mm i.d.) with online GC analysis (30 m ZB-1701 capillary column, FID detector) (Alotaibi. et. al., 2013). Prior to reaction, the catalysts were pretreated at the reaction temperature in \( \text{N}_2 \) flow for 1 h.

Results and discussion

![Fig. 1. DRIFT spectra of Aerosil 300 (a), (b) and silicalite (c)-(g)]. Aerosil 300: (a) unmodified and (b) modified with 3.7 M \( \text{NH}_3 \) (aq) + 0.7 M \( \text{NH}_2\text{NO}_3 \), both pre-treated at 500°C in \( \text{N}_2 \) for 1 h. Silicalite unmodified, pre-treated in \( \text{N}_2 \) at: (c) 400°C and (d) 500°C; silicalite modified with 3.7 M \( \text{NH}_3 \) (aq) + 0.7 M \( \text{NH}_2\text{NO}_3 \), pre-treated in \( \text{N}_2 \) for 1 h at: (e) 300°C, (f) 400°C, (g) 500°C.

![Fig. 2. XRD patterns for silicalite: (a) unmodified; (b)-(d) modified by: (b) 3.7 M \( \text{NH}_3 \) (aq) + 0.7 M \( \text{NH}_2\text{NO}_3 \), (c) 3.7 M \( \text{NH}_3 \) \( \text{NO}_3 \) and (d) 0.1 M \( \text{HCl} \).

![Fig. 3. Time course for propionic acid ketonisation: 0.2 g silicalite modified with 3.7 M \( \text{NH}_3 \) (aq) + 0.7 M \( \text{NH}_2\text{NO}_3 \), 500°C, 2 vol.% propionic acid, 20 mL/min \( \text{N}_2 \), 4.0 h g/mol contact time.

Conclusions
Amorphous silica and crystalline silicalite-1 are demonstrated to be active catalysts for PA ketonization at 450-500°C to form 3-pentanone. Silicalite with an MFI structure is particularly efficient, with its ketonization selectivity increasing by basic modification. FTIR data indicates that the surface terminal silanol groups may be responsible for the catalytic activity of silicalite.

References