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# High catalytic activity of silicalite in gas-phase ketonisation of propionic acid†

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**Amorphous silica and crystalline silicalite (MFI structure) are demonstrated to be active and environmentally benign catalysts for propionic acid ketonisation at 450–500 °C to form 3-pentanone. The silicalite is particularly efficient, and its ketonisation selectivity is increased by base modification probably through generation of silanol nests.**

Carboxylic acids readily available from natural resources are attractive as renewable raw materials for the production of value-added chemicals and bio-fuel components.[1] For fuel applications, carboxylic acids require reduction in their oxygen content, *i.e.* deoxygenation. Therefore, much current research is focused on deoxygenation of carboxylic acids using heterogeneous catalysis.[2] Ketonisation of carboxylic acids (eqn (1)) is widely used as a clean method for the synthesis of ketones.[3a] It allows for partial deoxygenation of carboxylic acids to be achieved accompanied by their carbon backbone upgrade. Ketonisation is catalysed by many basic and acidic metal oxide and mixed-oxide catalysts in the temperature range of 350–500 °C.[3] But the nature of catalytically active sites is not clear. It is generally thought that basic sites are favourable for ketonisation.[3a] However, heteropoly acid $H_3PW_{12}O_{40}$ possessing very strong proton sites has also been found active in propionic acid ketonisation.[3h] We now report that neutral metal-free silica materials, namely amorphous silica and, in particular, crystalline silicalite (MFI structure[4]), are active and environmentally benign catalysts for the gas-phase ketonisation of propionic acid. Propionic acid is chosen as a representative of carboxylic acids with the number of carbon atoms $n \leq 6$ derived from carbohydrate feedstocks.[3e]

$$2CH_3CH_2COOH \rightarrow (CH_3CH_2)_2CO + CO_2 + H_2O \qquad (1)$$

First we tested a wide range of amorphous silicas for ketonisation of propionic acid (eqn (1)) using a fixed-bed continuous flow reactor (see ESI†). These silicas were high purity powdered materials employed as catalyst supports and stationary phases in chromatography (see ESI†). At 400–500 °C, they exhibited a moderate to good catalytic activity in the formation of 3-pentanone, with some propionic anhydride also being formed. This is really surprising because silica is practically a neutral material. It lacks basicity and possesses a very weak acidity due to its silanol groups, SiOH. Table 1 shows representative results for the commercial Aerosil-300 (Degussa), high-purity amorphous silica consisting of nanosized nonporous spheres fumed in a high-temperature flame (300 $m^2$ $g^{-1}$ specific surface area). Its activity increased with increasing the reaction temperature from 400 to 500 °C. The catalyst showed a respectable 3-pentanone selectivity of 85% at 39% conversion at 500 °C, and no catalyst deactivation was observed for at least 28 h on stream. Blank experiments in the absence of silica showed a small contribution of homogeneous reaction: at 500 °C about 12% of propionic acid underwent pyrolysis, in agreement with the previous report.[5]

**Table 1** Gas-phase ketonisation of propionic acid over amorphous silica Aerosil-300[a]

| Catalyst | Temp. [°C] | Conv. [%] | Selectivity [mol%]<br>3-Pentanone | C1–C3 alkanes | C2–C3 alkenes | Others[b] |
|---|---|---|---|---|---|---|
| None | 500 | 12 | 36 | 14 | 19 | 31 |
| Aerosil-300 | 400 | 23 | 87 | 2 | 1 | 10 |
| Aerosil-300 | 500 | 39 | 85 | 1 | 3 | 11 |
| Aerosil-300[c] | 500 | 40 | 81 | 2 | 3 | 14 |

[a] 0.2 g catalyst, 2 vol% propionic acid in $N_2$ flow, 20 mL $min^{-1}$ flow rate, 4.0 h g $mol^{-1}$ space time, 6 h time-on-stream. [b] Other products included propionic anhydride, isopropanol, acetone together with unidentified organic compounds; CO and $CO_2$ not monitored. [c] Aerosil-300 modified by treatment with 3.7 M $NH_3$(aq) + 0.7 M $NH_4NO_3$.

Next we tested crystalline materials, *i.e.* highly siliceous zeolites. HZSM-5 zeolite (Si/Al = 180) possessing strong proton sites exhibited a low ketonisation activity at 300 °C but no such activity at 400–500 °C, mainly causing cracking of propionic acid to form light hydrocarbons, predominantly ethylene (Table 2). In contrast, purely siliceous silicalite (MFI structure, see ESI†) showed high catalytic activity during ketonisation, which peaked at 500 °C to afford 3-pentanone in 50% yield.

In search for better performance, silicalite was chemically modified with aqueous acidic (0.01 M and 0.1 M HCl) or basic (3.7 M $NH_3$(aq) and 3.7 M $NH_3$(aq) + 0.7 $NH_4NO_3$) solutions.[6] Whereas the acid treatment had little effect, the basic one, with

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**Table 2** Gas-phase ketonisation of propionic acid over silicalite[a]

| | | | Selectivity[b] [mol%] | | | |
|---|---|---|---|---|---|---|
| Catalyst | Temp. [°C] | Conv. [%] | 3-Pentanone | C1–C3 alkanes | C2–C3 alkenes | Others[c] |
| HZSM-5 | 300 | 43 | 30 | 1 | 6 | 64 |
| HZSM-5 | 400 | 98 | 0 | 0 | 39 | 61 |
| HZSM-5 | 500 | 99 | 0 | 0 | 97 | 3 |
| Silicalite | 400 | 23 | 76 | 3 | 0 | 21 |
| Silicalite | 450 | 42 | 72 | 5 | 18 | 5 |
| Silicalite | 500 | 95 | 53 | 15 | 28 | 4 |
| Silicalite[d] | 500 | 57 | 95 | 2 | 2 | 1 |
| Silicalite[e] | 500 | 75 | 75 | 6 | 18 | 1 |
| Silicalite[f] | 400 | 10 | 96 | 2 | 1 | 1 |
| Silicalite[f] | 450 | 46 | 93 | 2 | 1 | 4 |
| Silicalite[f] | 500 | 84 | 92 | 2 | 1 | 5 |
| Silicalite[f] | 550 | 92 | 65 | 3 | 5 | 27 |

[a] 0.2 g catalyst, 2 vol% propionic acid in $N_2$ flow, 20 mL min$^{-1}$ flow rate, 4.0 h g mol$^{-1}$ space time, 6 h time-on-stream. Silicalite was prepared by the literature procedure[7] and calcined at 550 °C in air for 12 h. [b] The selectivity defined as moles of product formed per 1 mole of propionic acid converted and quoted in mole%; CO and $CO_2$ not monitored. [c] Other products included propionic anhydride, isopropanol, acetone together with unidentified compounds. [d] Silicalite modified by 0.1 M HCl. [e] Modified by 3.7 M $NH_3$(aq). [f] Modified by 3.7 M $NH_3$(aq) + 0.7 M $NH_4NO_3$.

$NH_3$(aq) + $NH_4NO_3$, significantly improved ketonisation selectivity (Table 2). A similar effect has been found for the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam over silicalite, which has been attributed to the formation of framework defects (silanol nests) in silicalite, acting as catalytically active sites.[7] In contrast, the base treatment had practically no effect on the performance of amorphous Aerosil-300 (Table 1). The conversion of propionic acid over silicalite increased with the reaction temperature, although, predictably, with some loss in 3-pentanone selectivity. At 500 °C and a space time of 4.0 h g mol$^{-1}$ the base-modified silicalite gave a very good 3-pentanone yield of 77% with 92% selectivity at 84% conversion (average for 6 h time-on-stream). Increasing the space time to 10 h g mol$^{-1}$ (*i.e.* a 2.5-fold residence time increase) increased the yield to 87% which matches the performance of the best metal oxide catalysts.[3a] The silicalite catalyst showed a stable performance at this temperature for at least 28 h with 84–92% 3-pentanone selectivity at 93–80% propionic acid conversion (Fig. 1). A small decrease in catalyst activity over time-on-stream was probably caused by coke deposition on the catalyst, which amounted to 6.6 wt%. Coke could be removed by aerobic gasification at 450–500 °C, allowing full recovery of catalyst activity. The 3-pentanone product was quite stable under the reaction conditions, undergoing 3 and 8% conversion over base-treated silicalite at 450 and 500 °C, respectively, to form a mixture of C1–C3 alkanes and alkenes as well as some heavier products (see ESI†). Although silicalite works at a higher temperature than the best metal oxide catalysts, *e.g.* $CeO_2$–$Mn_2O_3$[3c] and $CeO_2$–$ZrO_2$,[3e] it has the important advantage of being an easy available non-toxic metal-free material, having perfect performance stability in the ketonisation reaction and allowing easy regeneration.

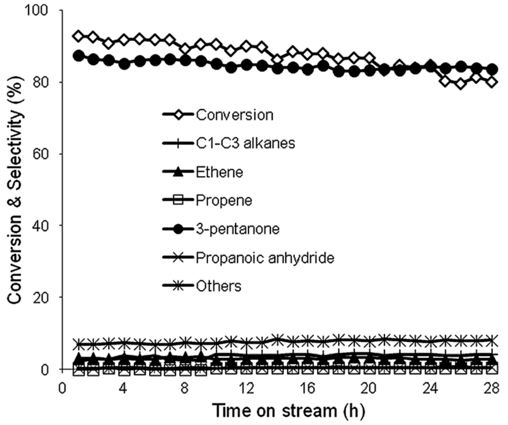


**Fig. 1** Time course for propionic acid ketonisation: 0.2 g silicalite modified with 3.7 M $NH_3$(aq) + 0.7 M $NH_4NO_3$, 500 °C, 2 vol% propionic acid, 20 mL min$^{-1}$ $N_2$, 4.0 h g mol$^{-1}$ space time.

The possibility of catalysis by metal impurities in silicalite and Aerosil-300 can be ruled out because ICP analysis showed only traces of metals such as Al, Fe, *etc.* in these materials. Also the results did not change when bi-distilled water was used for catalyst preparation and modification (see ESI†).

Characterisation of the silicalite catalysts using DRIFT spectroscopy[8] revealed significant differences and gave important information regarding the active sites in the ketonisation reaction. Fig. 2 shows the DRIFT spectra of our Aerosil-300 {(a) and (b)} and silicalite {(c)–(g)} samples in the region of OH stretching modes of silanol groups SiOH. These spectra are in agreement with those reported in the literature.[7,9] The sharp peak at 3744 cm$^{-1}$ is attributed to the free terminal silanol groups located on external and internal surfaces. The broader band around 3680 cm$^{-1}$ is attributed to the hydrogen-bonded vicinal silanols. The very broad band in the 3600–3100 cm$^{-1}$ region is generally ascribed to silanol nests that consist of a number of silanol groups interacting through extended hydrogen bonding. Such nests occur at silicon vacancies (defects) created by removing a tetrahedral Si atom from the framework and termination of the four loose O atoms by H atoms (Scheme 1).[9] DFT analysis shows[10] that the OH groups in silanol nests, due to the extended H-bonding, possess enhanced acidity

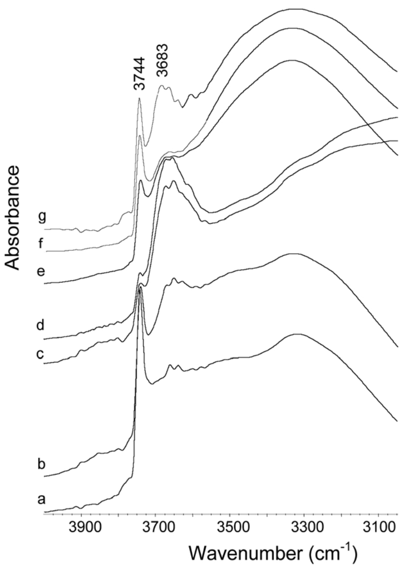
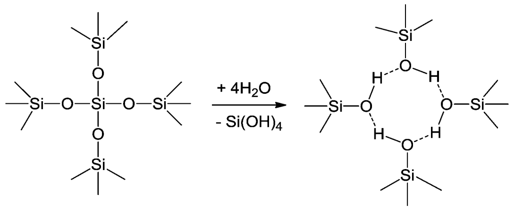


**Fig. 2** DRIFT spectra of Aerosil-300 {(a) and (b)} and silicalite {(c)–(g)}. Aerosil-300: (a) unmodified and (b) modified with 3.7 M $NH_3$(aq) + 0.7 M $NH_4NO_3$, both pretreated at 500 °C in $N_2$ for 1 h. Silicalite unmodified, pretreated in $N_2$ for 1 h at: (c) 400 °C and (d) 500 °C; silicalite modified with 3.7 M $NH_3$(aq) + 0.7 M $NH_4NO_3$, pretreated in $N_2$ for 1 h at: (e) 300 °C, (f) 400 °C, (g) 500 °C.



**Scheme 1** Formation of silanol nest.

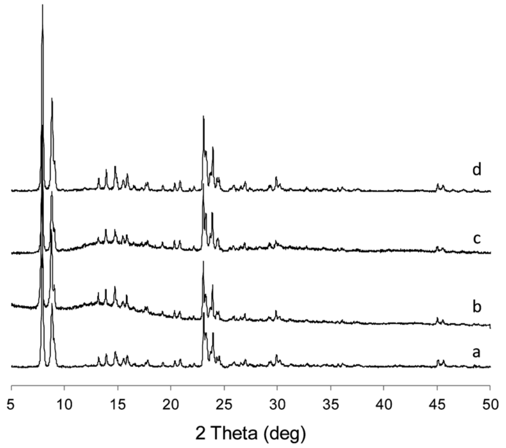


**Fig. 3** XRD patterns for silicalite: (a) unmodified; (b)–(d) modified by: (b) 3.7 M $NH_3$(aq) + 0.7 M $NH_4NO_3$, (c) 3.7 M $NH_3$(aq) and (d) 0.1 M HCl.

compared to that of an isolated silanol group. This effect leads to increased reactivity of silanol nests, as documented for the Beckmann rearrangement of cyclohexanone oxime over defective silicalite.[7] As can be seen from the band in the 3600–3100 $cm^{-1}$ region, our base-modified silicalite samples {(e)–(g)} have a much higher density of silanol nests compared to that of the unmodified silicalite {(c) and (d)} (Fig. 2). This is in agreement with the previous report,[7] which has demonstrated the formation of silanol nests in silicalite upon base treatment. By contrast, the base treatment did not create new silanol nests in amorphous Aerosil-300, *cf.* (a) and (b), and the amount of silanol nests in it was significantly smaller than in the base-treated silicalite. Therefore, our DRIFTS data indicate that the silanol nests may be the active sites responsible for the high selectivity of the base-modified silicalite in propionic acid ketonisation. It should be noted that the density of silanol nests decreases upon heating above 500 °C due to dehydration of silanol groups.[9a] This may be the reason for the lower efficiency of the unmodified silicalite (Table 2), which had been calcined at 550 °C for 12 h in the final step of its preparation (see ESI†).

The XRD pattern of our silicalite samples (Fig. 3) matched the one of the authentic material.[7] It did not change upon treatment with base or acid, which indicates that the crystal structure of silicalite was not affected by the chemical modification. Base-treated samples (b) and (c), however, show small broad humps centred at a $2\theta$ of 15°, which may be attributed to amorphous silica formed upon generating silanol nests by base treatment (Scheme 1). Therefore the XRD is in agreement with the formation of silanol nests upon base treatment of silicalite. The texture of zeolite was not affected by the chemical treatment, as its surface area, pore diameter and pore volume practically did not change (see ESI†).

Ketonisation occurs with carboxylic acids possessing α-hydrogen atoms.[3a] Several mechanisms have been proposed for this reaction.[3] These include (i) decomposition of metal carboxylate, (ii) *via* an acid anhydride intermediate route, (iii) *via* a β-keto acid intermediate route and (iv) *via* a ketene intermediate route. The mechanism may depend on many factors, especially the type of catalyst used. Pestman *et al.*[11] suggested ketene intermediacy for the ketonisation of acetic acid over metal oxides (eqn (2)). Ketonisation of propionic acid over heteropoly acid $H_3PW_{12}O_{40}$ may also occur *via* the ketene intermediate route.[3h] Silica has been patented as a catalyst for the gas-phase production of ketenes from carboxylic acids.[12] This suggests that ketonisation of propionic acid over amorphous silica and silicalite may occur *via* ketene intermediacy as well.

$$\begin{aligned} &CH_3CH_2COOH \xrightarrow[-H_2O]{} CH_3CH{=}C{=}O \\ &\xrightarrow{+CH_3CH_2COOH} (CH_3CH_2)_2CO + CO_2 \end{aligned} \quad (2)$$

In conclusion, we have demonstrated that neutral materials – amorphous silica and crystalline silicalite – are active and environmentally benign catalysts for propionic acid ketonisation. Silicalite is particularly efficient, and its ketonisation selectivity is increased by base modification. DRIFT spectroscopy indicates that silanol nests generated by base modification in silicalite are responsible for its enhanced catalytic activity.

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