

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

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Supplementary information

1 Catalysts

A number of amorphous silicas were purchased from Aldrich; these silicas were high purity powdered materials employed as catalyst supports and stationary phases in chromatography. Aerosil-300 was from Degussa. Also tested were Grace Silica Catalyst Supports (grade 3 to 6) from Grace Catalysts & Carriers. NH₄-ZSM-5 (Si/Al = 180) was obtained from Zeolyst International and converted to HZSM-5 by air calcination at 550°C for 3 h.

Silicalite (MFI structure) was prepared by the literature procedure.¹ The MFI structure of high silica zeolites ZSM-5 and silicalite is a 3-dimensional channel system involving 10-ring straight channels linked by 10-ring sinusoidal channels.² 50 g of tetraethylorthosilicate, 107 g of ethanol, and 112 g of an aqueous solution (10 wt%) of tetrapropylammonium hydroxide were weighed into a Teflon-lined stainless steel autoclave and thoroughly mixed for 2 h. The autoclave was subsequently heated to 105°C, and silicalite crystallisation occurred under autogeneous pressure and vigorous stirring for 96 h. Finally, the zeolite powder was washed with deionised water, filtered, dried at 110°C for 16 h, and ultimately calcined at 550°C for 12 h in air. For the chemical treatment we followed the literature procedure.¹ Silicalite was treated with an aqueous acid (0.01 M or 0.1 M HCl) or base (3.7 M NH₃(aq) or 3.7 M NH₃(aq) + 0.7 M NH₄NO₃) solution in a Teflon-lined autoclave at 90°C for 1 h, then filtered off, washed thoroughly with distilled water and finally oven dried at 110°C for 4 h. Prior to reaction the catalyst was heated in the catalytic reactor at reaction temperature in N₂ flow for 1 h to remove ammonia and nitrate.

The possibility of catalysis by metal impurities in initial and chemically modified amorphous and crystalline silicas had to be considered. ICP analysis showed only traces of metals such as Al, Fe, *etc.* in these materials, and no correlation between catalyst performance and impurities content could be observed. For this reason, we chose the most pure materials, namely the Degussa Aerosil 300 and in-house made silicalite, to demonstrate the ketonisation activity of silicas. It should also be noted that the results did not change when bi-distilled water was used for catalyst preparation and modification. Therefore, we believe that catalysis by metal impurities could be ruled out.

2 Techniques

The BET surface area and porosity of catalysts were determined from nitrogen physisorption measured on a Micromeritics ASAP 2010 instrument at -196°C. Before the measurement, the samples were evacuated at 250°C for 2 h. Powder X-ray diffraction (XRD)

spectra of catalysts were recorded on a PANalytical Xpert diffractometer with a monochromatic CuK α radiation ($\lambda = 0.154$ nm). ICP-AES elemental analysis was carried out on a Spectro Ciros emission spectrometer. Thermo Flash EA 1112 series analyser was used to determine carbon content in spent catalysts. Diffuse reflectance infrared Fourier transform (DRIFT) spectra of catalysts were taken on a Nicolet NEXUS FTIR spectrometer using powdered catalyst mixtures with KBr. The catalysts were pretreated at 300-500°C for 1 h in N₂ flow, as they were pretreated for ketonisation reaction. The DRIFT spectra were recorded at room temperature and ambient pressure under dry N₂.

3 Catalyst characterisation

Table S1 shows the texture of some fresh and spent catalysts that showed best performances in propionic acid ketonisation obtained from the BET method. It can be seen that chemical modification of silicalite practically does not change its BET surface area, average pore size and pore volume. The spent silicalite catalyst, however, shows a small reduction in S_{BET} , pore size and pore volume probably due to catalyst coking.

Table S1 Catalyst characterisation.^a

Catalyst	S_{BET}^b [m ² g ⁻¹]	Pore volume ^c [cm ³ g ⁻¹]	Pore size ^d [Å]
Aerosil-300 ^e	296	1.15	156
Silicalite	379	0.23	24
Silicalite modified by NH ₄ OH/NH ₄ NO ₃	364 (333)	0.23 (0.19)	26 (23)

^a In brackets are the values for spent catalyst after 28 h reaction at 500°C. ^b BET surface area.

^c Single point total pore volume. ^d Average BET pore diameter. ^e Aerosil-300 was wetted to form a gel then oven dried at 110°C and ground to a powder of 45-180 μm particle size.

Figures S1 – S3 display N₂ adsorption/desorption isotherm for fresh and spent silicalite catalysts. The fresh unmodified silicalite exhibits a reversible isotherm typical of microporous materials. The isotherm for the fresh sample modified with NH₃(aq) + NH₄NO₃ (Figure S2) is slightly different from the unmodified silicalite, with a hysteresis at lower P/P₀ of 0.1-0.3. This may be explained by the formation of framework defects (silanol nests) in silicalite. The spent modified catalyst (Figure S3) behaves similarly, with minor differences from the fresh sample probably caused by catalyst coking.

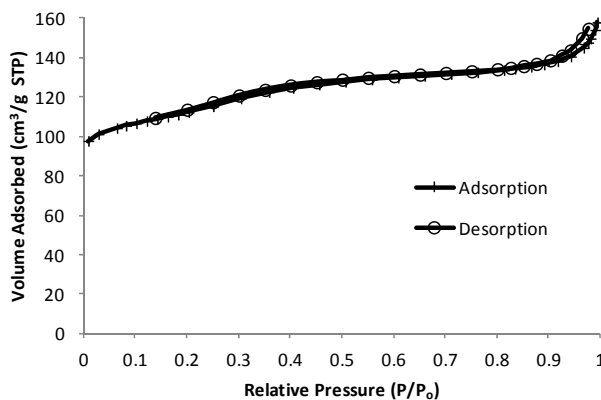


Fig. S1 Nitrogen adsorption and desorption isotherms for fresh unmodified silicalite.

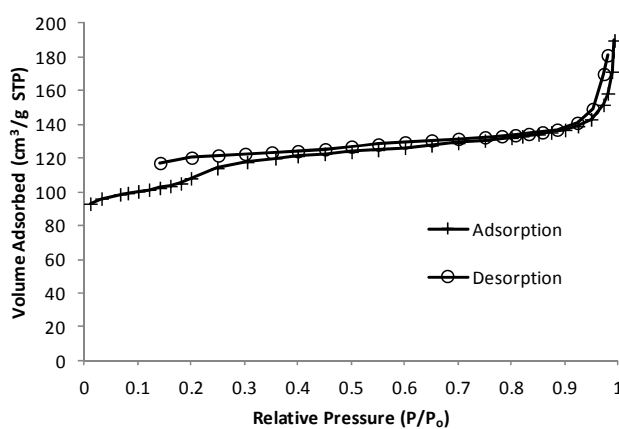


Fig. S2 Nitrogen adsorption and desorption isotherms for fresh silicalite modified with NH₃(aq) + NH₄NO₃.

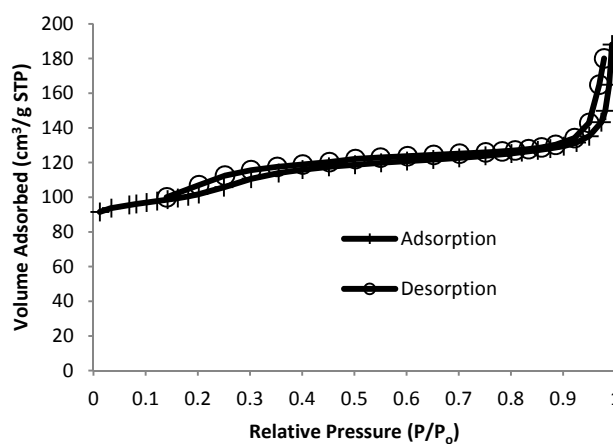


Fig. S3 Nitrogen adsorption and desorption isotherms for spent silicalite catalyst modified with NH₃(aq) + NH₄NO₃ (after reaction at 500°C, 28 h time on stream).

XRD pattern for HZSM-5 zeolite (Si/Al = 180) is shown in Figure S4. It is in perfect agreement with the literature data.³

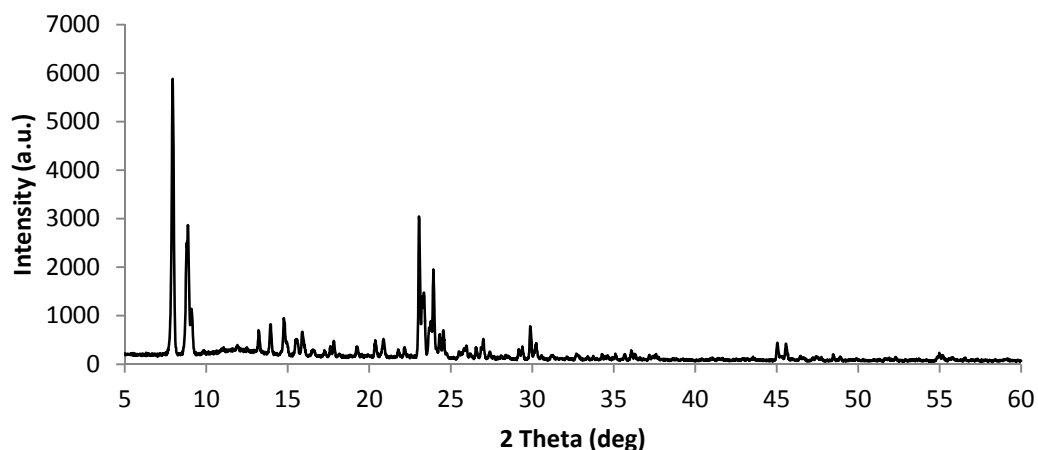


Fig. S4 XRD pattern for HZSM-5 (Si/Al = 180).

4 Catalyst testing

The gas-phase ketonisation of propionic acid was carried in flowing N_2 at 300-550°C under atmospheric pressure in a downflow quartz fixed-bed reactor (9 mm i.d.) with online GC analysis (Varian Star 3400 CX instrument with a 30 m x 0.25 mm ZB-1701 capillary column and a flame ionisation detector). For more accurate analysis of C_1 - C_5 hydrocarbon products, a 60 m x 0.32 mm GSGasPro capillary column was used, which allowed for full separation of these hydrocarbons. The temperature in the reactor was controlled by a Eurotherm controller using a thermocouple placed at the top of the catalyst bed. Propionic acid was fed by passing the carrier gas flow controlled by a Brooks mass flow controller through a stainless steel saturator, which held liquid propionic acid at appropriate temperature to maintain the chosen reactant concentration. The downstream gas lines and valves were heated to 180°C to prevent substrate and product condensation. The reactor was packed with 0.2 g catalyst powder of 45-180 μm particle size. Typically, the reaction was carried out at a propionic acid concentration of 2 vol% and an N_2 flow rate of 20 mL min^{-1} (space time $W/F = 4.0 \text{ h g mol}^{-1}$, where W is the catalyst weight (g) and F the total molar flow rate (mol h^{-1})). The space time W/F is proportional to the residence time τ generally defined as a period of time a volume element of an incoming fluid with the volumetric feed rate V remains in the reactor volume V_R (thus $\tau = V_R/V$). For example, for Aerosil 300 having a density of 0.36 g cm^{-3} , $\tau = (0.2 \text{ g}/0.36 \text{ g cm}^{-3})/20 \text{ mL min}^{-1} = 0.028 \text{ min}$. Prior to reaction, the catalysts were heated at the reaction temperature in N_2 flow for 1 h. Once reaction started, the downstream gas flow was analysed by the on-line GC to obtain reactant conversion and product selectivity. The selectivity was defined as moles of product formed per one mole of propionic acid converted and quoted in mole per cent. CO and CO_2 , which were not quantified and not included in reaction selectivities. The run-to-run deviation of conversion and selectivity was typically within 10% and the carbon balance within 95%.

Figures S5 – S7 show time courses for propionic acid ketonisation over Aerosil 300, demonstrating good catalyst stability over time on stream.

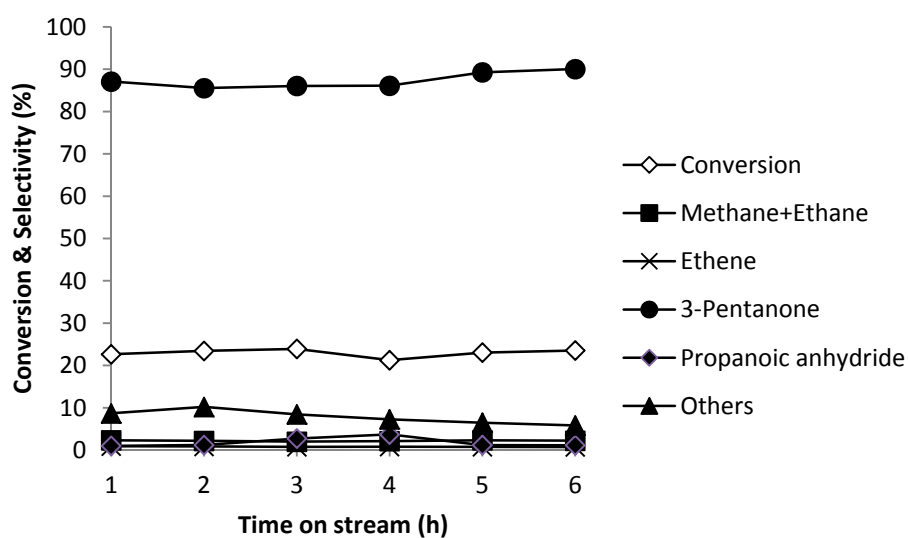


Fig. S5 Time course for propionic acid ketonisation: 0.2 g Aerosil 300, 400°C, 2 vol.% propionic acid, 20 mL min⁻¹ N₂, 4.0 h g mol⁻¹ contact time.

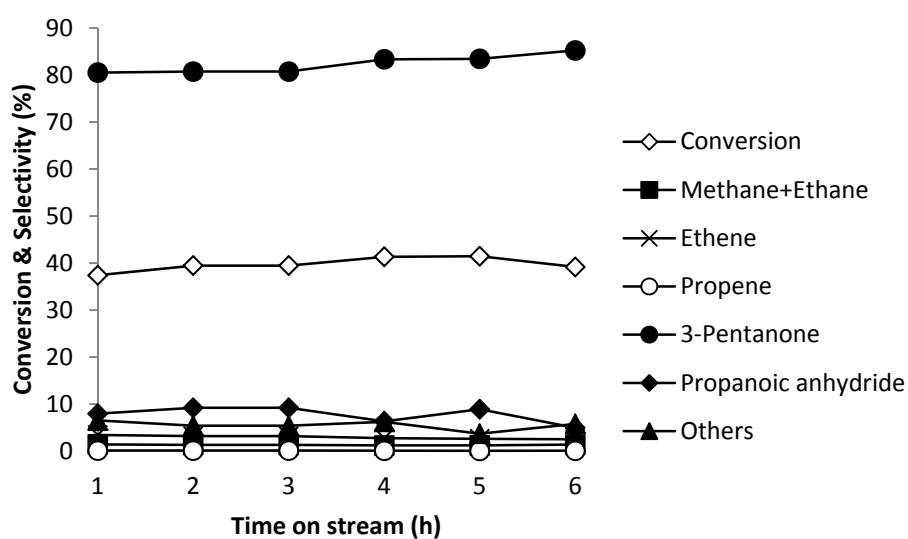


Fig. S6 Time course for propionic acid ketonisation: 0.2 g Aerosil 300, 500°C, 2 vol.% propionic acid, 20 mL min⁻¹ N₂, 4.0 h g mol⁻¹ contact time.

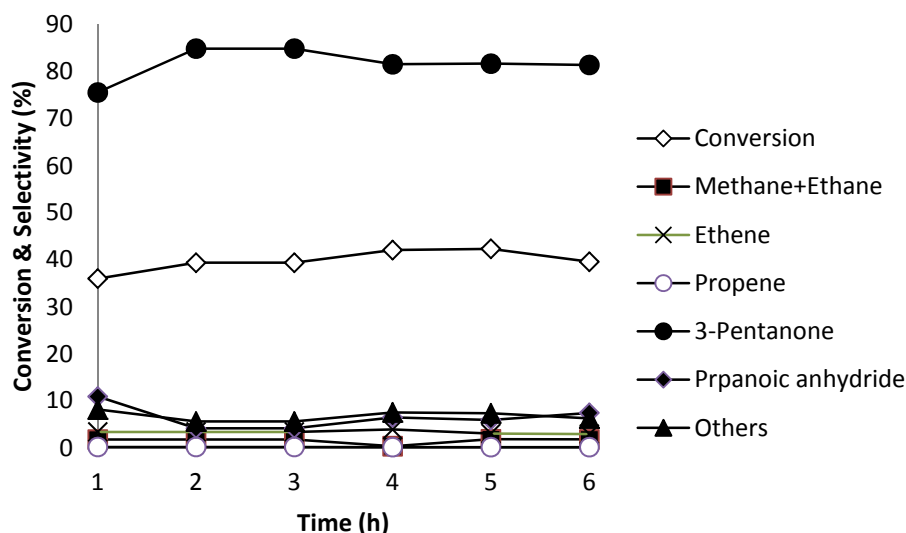


Fig. S7 Time course for propionic acid ketonisation: 0.2 g Aerosil 300 modified with 3.7 M $\text{NH}_3(\text{aq})$ + 0.7 M NH_4NO_3 , 500°C, 2 vol.% propionic acid, 20 mL min^{-1} N_2 , 4.0 h g mol^{-1} contact time.

5 Conversion of 3-pentanone

3-Pentanone, the product of propionic acid ketonisation, was quite stable under reaction conditions (Table S2). It underwent 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.

Table S2 Conversion of 3-pentanone over silicalite modified with 3.7 M $\text{NH}_3(\text{aq})$ + 0.7 M NH_4NO_3 .^a

Temperature [°C]	Conversion [%]	Selectivity ^b [mol%]			
		CH_4	C_2H_6	C_2H_4	Others
450	3	21	17	25	37
500	8	17	23	45	15

^a 0.2 g catalyst, 6 h time on stream, 1 vol.% 3-pentanone concentration in N_2 , 20 mL min^{-1} N_2 flow, 4.0 h g mol^{-1} contact time. ^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 included.

References

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- 3 A. Omega, M. Haouas, A. Kogelbauer and R. Prins, *Micropor. Mesopor. Mater.* 2001, **46**, 177.