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 forthe 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-like catalysts. We now report on gas-phase ketonisation of propionic acid (PA) catalysed by weakly acidic silica 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 $n \leq 6$ derived from carbohydrate feedstocks.

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

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 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 N_2 flow for 1 h.

Results and discussion

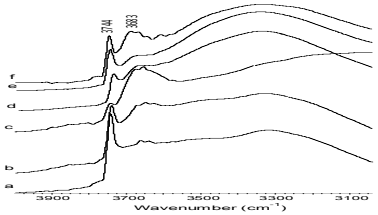

Fig. 1. DRIFT spectra of Aerosil 300 {(a), (b)} and silicalite {(c)-(g)}. Aerosil 300: (a) unmodified and (b) modified with 3.7 M NH_3 (aq) + 0.7 M NH_4NO_3, both pre-treated at 500°C in N_2 for 1h. Silicalite unmodified, pre-treated in N_2 for 1 h at: (c) 400°C and (d) 500°C; silicalite modified with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

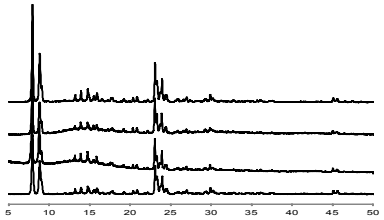

Fig. 2. XRD patterns for silicalite: (a) unmodified; (b)-(d) modified by: (b) 3.7 M NH_4OH + 0.7 M NH_4NO_3, (c) 3.7 M NH_4OH and (d) 0.1 M HCl.

Table 3 Gas-phase ketonisation of PA over HZSM-5 (Si/Al = 180) and silicalite.

Catalyst	Temp. [°C]	Conv. [%]	Selectivity[b] [mol%]			
			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

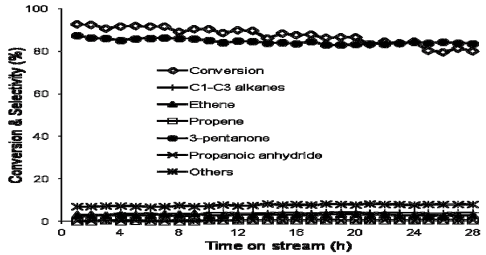

Fig. 3 Time course for propionic acid ketonisation: 0.2 g silicalite modified with 3.7 M NH (aq) + 0.7 M NHNO, 500C, 2 vol.% propionic acid, 20 mL/ min N, 4.0 h g/ mol contact time.

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

[1] A. Corma, S. Iborra and A. Velty, *Chem. Rev.* **107**(2007) 2411.
[3] H. Bayahia, E. Kozhevnikova, I. Kozhevnikov, *Chem.Comm.* **49** (2013) 3842.
[4] G.P. Heitmann, G. Dahlhoff, W.F. Hoelderich, *J. Catal.* **186** (1999) 12.