Novel catalysts for thiophene synthesis at lower temperatures

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Thiophenes can be synthesised in high yields from the reaction of C_{4+} oxygenates and CS_2 at temperatures 140 °C lower than current industrial catalysts, using novel materials based upon chromium substituted iron oxide hydroxide.

Thiophene derivatives are widely used as raw materials in the production of dyes, agrochemicals and pharmaceuticals.[1] However, in recent years much research has been devoted to their catalytic destruction *via* HDS for obvious environmental reasons.[2] Conversely, the catalytic synthesis of thiophenic systems has received scant attention. Thiophene and alkylthiophenes are currently synthesised on an industrial scale (*ca.* 1000 tonnes p.a.) *via* two processes. The first involves the reaction of C_{4+} alcohols or carbonyls with CS_2 over alkali-promoted chromia alumina.[3] The second is based upon the reaction of an α,β-unsaturated aldehyde with H_2S over alkali/alkaline earth-promoted γ-Al_2O_3.[4] However, the use of alumina-based catalysts results in some disadvantages, chiefly that at the temperatures required to achieve economic yields of product (450–500 °C), cracking reactions occur with resultant losses in yields and premature catalyst deactivation through coke deposition. Hence it is desirable to design a catalyst that can operate at lower temperatures and/or give lower by-product formation. Here we address this problem and present initial data for Cr^{III}-substituted FeOOH, which has been found to be an effective thiophene synthesis catalyst at comparatively low temperatures.

Catalyst synthesis was based upon the method developed by Flanigen *et al.*[5] for the synthesis of Jarosites. This involved dissolving the required molar ratios of Fe^{III} and Cr^{III} sulfates in distilled water at 80 °C. The pH of the resulting solution was adjusted to 4 using aq. NaOH. The slurry formed was then refluxed for 20 h and the solid recovered by vacuum filtration, washed with distilled water and dried (110 °C, 12 h). Samples were then pelleted and sieved (0.6–1.0 mm), prior to testing for thiophene synthesis in a fixed bed microreactor.[6] A typical reaction involved passing a mixed vapour/gas stream of 2-methylbutanol (2MB), CS_2 and N_2 (1:1.5:80 molar ratio) at a total flow rate of 12000 h^{-1} over 1.0 g of catalyst. Product analysis was performed on-line by GC FID analysis with a carbon balance of 98–100% for all data quoted, based upon conversion of the alcohol.

A series of catalysts with increasing Cr content were prepared and tested for their efficacy in the synthesis of 3-methylthiophene (3MT), giving the results shown in Fig. 1 and Table 1. As the Cr concentration increased the yield of 3MT and conversion of alcohol were seen to increase to a maximum at *ca.* 5% Cr (57 mol% 3MT, conversion of 78 mol%), before declining to very low yields at higher Cr levels. The optimum temperature for reaction was found to be 330–350 °C, with typical temperature profile data for the reaction being shown in Table 1. Another obvious advantage of these materials was their very low by-product formation, with only minor levels of alkene formation, presumably *via* dehydration, being observed. Moreover, the proportion of cracked fractions was low and mirrored

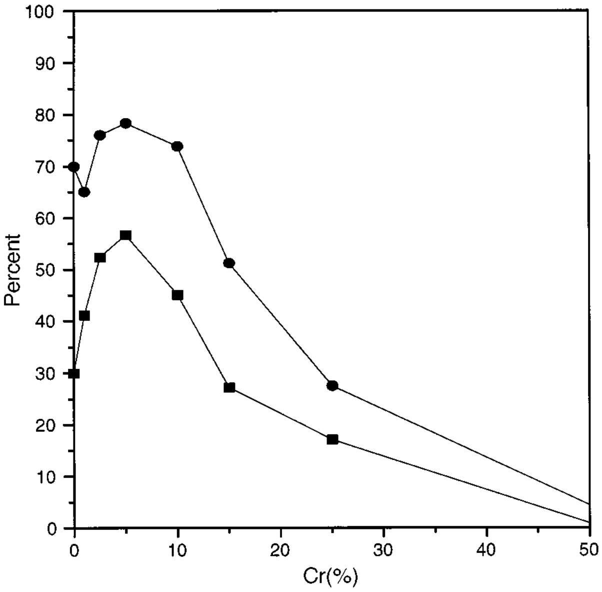

Fig. 1 The effect of Cr loading on the activity and selectivity of catalysts for the synthesis of 3-methylthiophene: (■) 3MT (mol% yield) and (●) 2MB (% conversion). Reaction conditions: 2MB:CS_2:N_2 (1:1.5:80), GHSV = 12000 h^{-1}, all samples taken at optimum temperature of activity (340–360 °C).

Table 1 The effect of Cr content and temperature on catalyst activity.

Cr (%)[a]	Fraction	*T*/°C 300	320	340	360	380	400	420
1	3MT/mol%	22.5	22.0	30.4	35.6	41.2	39.7	29.0
	2MB (% conversion)	44.9	46.8	56.9	61.1	65.1	63.7	49.7
2.5	3MT/mol%	23.1	31.3	52.4	49.1	43.8	35.4	30.2
	2MB (% conversion)	46.7	59.3	76.0	72.7	68.0	58.0	51.7
5	3MT/mol%	36.6	43.8	56.7	43.2	31.6	24.0	23.7
	2MB (% conversion)	55.4	66.4	78.4	64.4	53.8	44.8	45.4
	Thiophene (% conversion)	4.4	5.1	4.4	3.7	3.0	5.3	5.7
	2-Methylbutene (% conversion)	10.2	13.0	15.0	13.6	15.6	13.4	13.6
	Cracked (% conversion)	4.3	4.5	4.4	4.1	3.6	6.2	7.5
10	3MT/mol%	22.0	23.0	31.8	45.1	39.2	31.9	22.8
	2MB (% conversion)	46.6	45.5	58.5	73.9	69.6	60.8	49.6
15	3MT/mol%	24.2	23.6	27.5	27.2	31.1	48.5	66.1
	2MB (% conversion)	40.0	45.9	51.2	50.5	54.5	64.4	79.4
25	3MT/mol%	21.2	16.0	15.6	17.1	28.9	38.0	50.1
	2MB (% conversion)	31.1	26.7	26.5	27.5	40.5	50.2	63.3
50	3MT/mol%	0.4	0.3	0.4	0.6	0.9	1.4	1.9
	2MB (% conversion)	2.0	2.0	2.4	3.1	4.4	6.5	8.6

[a] Nominal Cr loading.

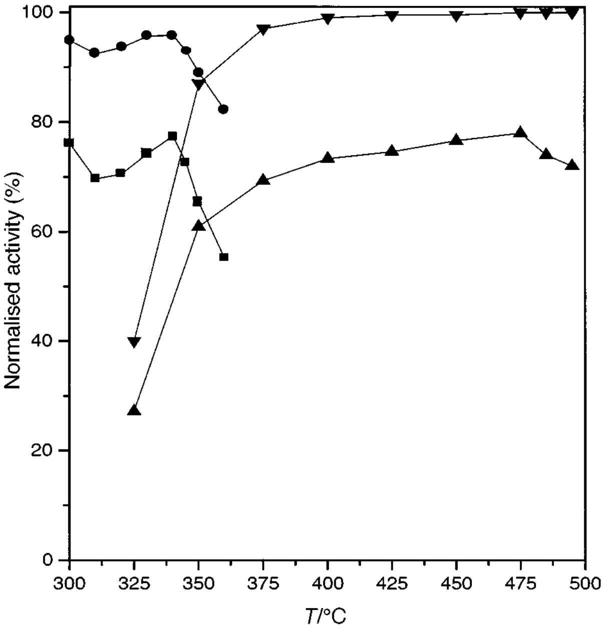

Fig. 2 Comparison of the normalised activities of α-Fe$_{0.95}$Cr$_{0.05}$OOH and the current commercial catalyst for the synthesis of 3-methylthiophene: (■) 3MT (FeCrOOH, mol% yield), (●) 2MB (FeCrOOH, % conversion), (▲) 3MT, (▼) 2MB (commercial catalyst, conversion). Reaction conditions: 2MB:CS$_2$:N$_2$ (1:1.5:80), GHSV = 12000 h^{-1}, all samples taken after 15 min equilibration at each temperature.

the yield of thiophene, hence this was ascribed to β-methyl cleavage of the alcohol, rather than skeletal cracking as observed with Al$_2$O$_3$ based catalysts.

In a further set of experiments the activity of the 5% Cr catalyst (SA 103 m^{2}g^{-1}) was compared to that of a commercial catalyst (7.5% K$_2$CO$_3$ promoted 11% Cr$_2$O$_3$ on γ Al$_2$O$_3$, SA = 125 m^2 g^{-1}). The results, normalised to surface area, are given in Fig. 2. It is apparent that the commercial catalyst is only active at temperatures > 360 °C, and that temperatures as high as 475 °C are required to attain yields of 75 mol% 3MT, *cf.* 340 °C for the novel 5% Cr catalyst. Moreover, the commercial catalyst gave this optimum yield at a 2-methylbutanol conversion of 99 mol%, *cf.* 95 mol% for the 5% Cr catalyst, reflecting a lower selectivity and a higher formation of potentially deleterious reaction by-products for the commercial catalyst.

The changes in catalytic activity with increasing Cr content (Fig. 1) is not considered to be merely due to variation in surface area. This is confirmed by the similar BET SAs of samples with 0–10% Cr, which were all in the range 100–120 m^2 g^{-1}. However, at higher loadings of Cr, decreases in SA were recorded (15 m^2 g^{-1} for the 49% Cr sample). Hence it is clear that the intrinsic activity of the 5% Cr sample is significantly higher than that of catalysts with higher Cr loadings. Moreover, detailed powder XRD of the samples was performed which indicated that phase changes occurred as a function of Cr concentration. Thus, at $0 < \mathrm{Cr} < 2.5\%$ the catalyst was found to comprise of natrojarosite, with traces of α-FeOOH (Goethite) and α-CrOOH (Bracewellite).[7] However, for $3 < \mathrm{Cr} < 10\%$, samples contained only a mixed α-FeOOH/α-CrOOH phase, whilst at $\mathrm{Cr} > 10\%$ only the presence of a mixed FeCr phase supported on sodium sulfate (Thenardite) was recorded. This latter observation is consistent with the activity displayed by the intermediate Cr (15–25%) loaded samples, which exhibited performance profiles typical of supported oxides.[6] We therefore conclude that the high activities of the low Cr catalysts are related to the presence of a mixed FeOOH/CrOOH phase.

In these initial studies no attempt has been made to optimise catalyst performance by increasing the concentrations or relative proportions of the active phases. However, the data obtained demonstrate the discovery of a new class of catalysts for a lower temperature vapour phase synthesis of thiophenes[8] and may prove to be a starting point for the development of a new generation of industrial catalysts.

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