Novel alkaline earth supported catalysts for thiophene synthesis

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3-Methylthiophene can be synthesised in yields >95 mol% from the reaction of 2-methylbutanol and CS_2 over MgO-supported potassium-promoted '$Fe_{0.95}Cr_{0.05}OOK$'; catalysts using γ-Al_2O_3 or other alkaline earth oxides as supports are less effective.

The derivatives of the sulfur-containing heterocycle thiophene have been widely used for many years as raw materials in the production of agrochemicals, dyes and pharmaceuticals.[1] As a consequence the synthesis of such compounds on an industrial scale (1000 tonnes per annum) is of significant economic importance and provides considerable incentive for research. Currently market demand is met by two heterogeneous catalytic processes involving the reaction of organic oxygenates (alcohols, carbonyls, α,β-unsaturated aldehydes) with a suitable sulfur source (CS_2 or H_2S) over γ-Al_2O_3-based catalysts at high temperatures (>450 °C).[2,3] However, the synthesis of substituted thiophenes by standard high temperature vapour phase methods has been found to be far less efficient than the synthesis of the unsubstituted parent molecule, with yields decreasing from $>90\%$ for thiophene to *ca.* 40–50% for 3-methylthiophene.[2,3] Here we address this problem and present initial results for catalysts based upon alkaline earth oxide-supported $Fe_{0.95}Cr_{0.05}OOK$ catalysts which give yields of 3-methylthiophene (3MT) >95 mol% from the reaction of 2-methylbutanol and CS_2.

Catalysts were prepared by dissolution of 95 : 5 wt% Fe_2SO_4 : Cr_2SO_4 in distilled water (80 °C), with constant stirring. K_2CO_3 solution (2 : 1 K : Me^{3+}) was added, followed by the weight balance of support (85%). The mixture was evaporated to a paste, dried (120 °C, 24 h) and calcined (air, 24 h, 700 °C). Samples were then pelleted and sieved (0.6–1.0 mm), prior to testing for 3-methylthiophene synthesis in a fixed bed microreactor.[4] All reactions involved passing a reagent stream of 2-methylbutanol (2MB), CS_2 and N_2 (1 : 1.5 : 80 molar ratio) at a GHSV of 12 000 h^{-1} over 1.0 g of catalyst. Product analysis was performed by on-line GC FID analysis with a carbon balance of 98–100% for all data quoted, based upon conversion of 2MB.

Previously we have demonstrated that a mixed α-$Fe_{0.95}Cr_{0.05}OOH$ material is a highly efficient low temperature 3MT synthesis catalyst.[5,6] Further data have shown that the activity, selectivity and thermal stability of this material may be enhanced by addition of 7.5% K_2CO_3. This is postulated as being linked to the formation of mixed MOOK species (M = Fe or Cr).[6a] In addition, Stobbe *et al.*[4] have shown MgO-supported FeoOK to be an active and selective dehydrogenation catalyst. Hence we have examined the activity of MgO-supported $Fe_{0.95}Cr_{0.05}OOK$ for 3MT synthesis.

The effect of temperature on the performance of $Fe_{0.95}Cr_{0.05}OOK/MgO$ for 3MT synthesis is illustrated in Fig. 1 and Table 1. Initially there is negligible 2MB conversion, however, for $T > 325$ °C there are dramatic increases in conversion and 3MT yield. This is initially coupled with a significant production of thiophene arising from β-methyl scission, as reflected in the concomitant increases in light fractions. However, at temperatures >425 °C there is a plateau of activity with 3MT yields >95 mol%, at 100 mol% conversion of 2MB. This contrasts with the data obtained for the current commercially utilised catalyst (7.5% K_2CO_3-promoted Cr_2O_3/γ-Al_2O_3), which gave a peak yield of *ca.* 78 mol% 3MT at 475 °C. In this case the selectivity of the catalyst is limited by extensive side reactions such as cracking and β-methyl fission which not only limit 3MT selectivity but are also known to have a deleterious effect on catalyst lifetime due to coke build-up.[6a]

In a further set of experiments the effect of support on the activity of the FeCrOOK phase was examined (Table 1). It is apparent that the choice of support has a marked effect on catalyst performance, with optimum activity being obtained for the MgO case. The use of alternative alkaline earth oxide supports resulted in significant decreases in overall activity and 3MT selectivity down the group. Moreover, the selectivity towards 2-methylbutene also increased with the increasing basicity of the support. Conversely, while there is minimal production of the alkene on the acidic FeCrOOK/γ-Al_2O_3, more cracking of the alcohol is observed and the peak of 3MT synthesis activity (*ca.* 95 mol%) is observed at 500 °C. Furthermore, the 3MT production increases linearly with temperature for the γ-Al_2O_3 variant with no observed plateau temperature, further hindering its industrial application.

The high activity of these materials is consistent with previous findings[5–7] and is ascribed to the presence of $Fe_{0.95}Cr_{0.05}OOK$. Attempts to characterise this phase *via* X-ray

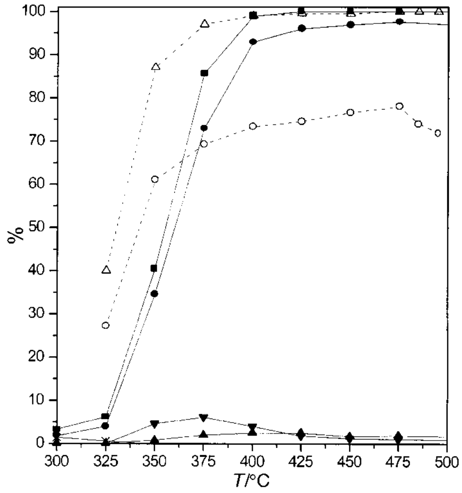

Fig. 1 3MT synthesis performance comparison of $Fe_{0.95}Cr_{0.05}OOK/MgO$ and the current industrial catalyst (7.5 K_2CO_3/11% Cr_2O_3/γ-Al_2O_3). Gas hourly space velocity (GHSV) = 12 000 h^{-1}, all samples taken after 15 min equilibration at temperature. (△) indcat conversion of 2MB, (○) indcat 3MT mol% yield, (■) 2MB conversion FeCrOOK, (●) 3MT yield FeCrOOK, (▼) thiophene yield FeCrOOK, (▲) cracked fractions FeCrOOK, (x) 2-methylbutene FeCrOOK.

Table 1 The activity of supported ‘FeCrOOK’ for 3MT synthesis

Catalyst	Activity/ mol%	T/°C 300	325	350	375	400	425	450	475	500
FeCrOOK/MgO	3MT yield	1.8	4.0	34.5	72.9	92.9	96.0	96.9	97.6	97.0
	2MB conv	3.3	6.2	40.3	85.6	98.9	100	100	100	100
	Thiophene	0.0	0.1	4.6	9.0	5.2	0.8	0.4	0.6	0.7
	Cracked	1.4	0.1	0.8	3.6	0.8	3.2	2.6	1.8	2.3
	2MeButene	0.1	2.1	0.4	0.0	0.0	0.0	0.0	0.0	0.0
FeCrOOK/CaO	3MT	1.5	1.2	1.5	3.3	13.3	35.3	49.6	67.0	52.5
	2MB conv	3.1	3.3	4.8	11.3	30.2	51.3	63.5	79.4	68.4
	2MeButene	1.4	2.0	3.3	7.8	16.1	14.5	12.1	10.9	14.8
FeCrOOK/SrO	3MT	0.7	0.4	1.1	1.1	2.3	4.4	8.6	12.3	11.2
	2MB conv	1.6	1.4	2.7	3.6	7.5	12.0	19.9	24.3	24.8
	2MeButene	0.6	0.6	1.3	2.2	4.8	7.1	10.6	11.4	13.1
FeCrOOK/BaO	3MT	0.4	0.9	1.2	1.4	3.1	3.9	4.9	6.7	7.4
	2MB conv	1.6	2.2	3.2	4.1	6.9	9.4	12.8	17.5	17.0
	2MeButene	0.9	1.1	1.8	2.5	3.6	5.3	7.7	10.5	9.3
Ind. Cat$^+$	3MT	—	27.2	60.9	69.8	73.3	74.6	78.0	74.1	72.1
	2MB conv	—	40.1	87.0	97.2	99.0	99.5	100	100	100
7.5% K/11% Cr_2O_3/MgO	3MT	0.0	5.4	14.6	19.2	29.1	40.1	82.9	90.9	94.1
	2MB Conv	4.2	12.4	26.9	33.4	45.7	61.3	95.9	97.2	99.0

Table 2 Normalised activities of catalysts for 3MT synthesis

Catalyst	Surface area/ $m^2\ g^{-1}$	NA[a]	CrUV[b]
FeCrOOK/MgO	30	15.12	919200
Industrial catalyst[c]	125	2.90	4000
FeCrOOK/γ-Al_2O_3	220	1.60[d]	97300
Cr_2O_3/MgO	30	9.87	1200
7.5% K Cr_2O_3/MgO	30	14.58[d]	20100

[a] Normalised activity (moles of 3MT per hour per square metre surface area of catalyst). [b] Cr_2O_3. Utilisation value (normalised activity per mole of Cr_2O_3) (nominal values reflecting the effective use of Cr). [c] 7.5 K_2CO_3/11% Cr_2O_3/γ-Al_2O_3. [d] Based upon yield at 500 °C, *cf.* 475 °C for all other samples.

diffraction were unsuccessful, with only support oxide and K_2SO_4 being detected. Similarly, whilst X-ray photon spectroscopy analysis indicated the presence of Fe^{3+} as oxide/oxide hydroxide,[8] no Cr^{3+} (present at 0.3 wt%) was detected. Thus we ascribe the high selectivity to a synergistic phase formation. This premise is suggested by the lower activity of K-promoted Cr_2O_3/MgO (Tables 1, 2) and further supported by the lower intrinsic activity of Fe, *cf.* Cr for heterocycle synthesis.[6a] A comparison of normalised activities and Cr utilisation values (Table 2) supports the claim that activity is not merely due to mixed supported oxides. These findings are also consistent with the work of Stobbe *et al.*[6] who have shown FeOOK to be a specific phase of high dehydrogenation function, a feature which has been found to be of specific importance in the thiophene synthesis mechanism.[5–7]

These data briefly summarise initially findings regarding the activity of this highly promising new class of catalysts.[7] Ongoing trials are assessing their lifetime performance, regeneration characteristics and suitability for industrial application.

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