The effect of pre-sulfiding of catalysts for the vapour phase catalytic synthesis of thiophenes

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A study of catalyst pre-sulfiding for the synthesis of 3-methylthiophene from 2-methylbutanol and carbon disulfide over potassium-promoted chromia–alumina has been performed. Pretreatment with CS_2 results in enhancements in 3MT yield and catalyst lifetime. The benefits observed are ascribed to a combination of enhanced Cr_2S_3 formation and poisoning of sites responsible for side reactions which limit selectivity and result in the formation of deactivating by-products.

Keywords: thiophene synthesis, heterogeneous catalyst, vapour phase, chromia–alumina, pre-sulfiding

1. Introduction

Thiophene is a widely used feedstock and intermediate within the chemical industry [1]. It is produced on the kilotonne p.a. scale by two heterogeneous catalytic processes [2,3]. These are based upon the vapour phase reactions of C_{4+} oxygenates with CS_2 [2] or H_2S [3] over Al_2O_3-based catalysts. Previously we have examined the mechanism of thiophene synthesis from the reaction of butanol and CS_2 over alkali-promoted chromia–alumina [4]. This study demonstrated that thiophene is formed via reaction of organic intermediates and multiple surface sulfur species and that a pre-sulfided catalyst can convert butanol into thiophene in the absence of co-fed CS_2.

This idea of pre-sulfiding is well known within the field of HDS where there have been many attempts to understand and enhance the benefits of pre-sulfiding [5,6]. However, while it is accepted that pre-sulfiding converts the oxide into the active sulfide, there is still debate regarding the sites formed and optimal conditions [5,6].

In order to explain previous data we have examined the phenomenon of pre-sulfiding for the butanol/CS_2 reaction. This letter presents our initial findings and attempts to account for the data obtained.

2. Experimental

All reactions were performed in a fixed-bed microreactor described elsewhere [7]. The standard reaction entailed passing a vaporised stream of feed (2-methylbutanol : CS_2 : N_2 molar ratio 1 : 1.5 : 80) over 1.0 g of 7.5% K_2CO_3-promoted 11% Cr_2O_3–Al_2O_3 at a total STP GHSV of 12000 h^{-1}. The reaction stream was scrubbed to remove H_2S and other sulfur residues and the products analysed by on-line GC-FID analysis using a Perkin–Elmer sigma 4B GC equipped with a diatomite CLQ 80–100 mesh on 5% PEG column. Carbon mass balances of 98–100% were recorded for all data, based upon conversion of the alcohol. Catalyst pre-sulfiding was performed by treatment of the catalyst with 1 ml of CS_2 in N_2 (1.5 : 80 molar ratio), corresponding to 0.01659 moles of CS_2 : 0.00072 moles of Cr_2O_3 over 1 h at 475 °C.

XPS analysis was performed using an ESCAIII spectrometer [8] equipped with an Al Kα source ($h\nu = 1486.6$ eV). Binding energy values were normalised to the C $1s_{1/2}$ signal at 284.7 eV. Narrow scan data was accumulated to 0.1 eV resolution by co-addition of 64 scans across a 30 eV window. Assignments of oxidation and chemical state were made by reference to standards recorded in the NIST database [9].

3. Results and discussion

Figure 1 (a)–(c) shows the lifetime activity profiles of untreated and pre-sulfided catalysts for 3-methylthiophene synthesis. These data reflect clear improvements in performance post-sulfidation. Indeed, the untreated sample displayed a marked induction period, accompanied by significant levels of thiophene and methane production (the latter grouped as a component of light fractions trace (▼), figure 1(b)) from β-methyl fission of the feed. Moreover, even as this induction period ceased the onset of deactivation was apparent. In marked contrast the pre-sulfided catalyst exhibited no induction period and displayed high and near constant 3MT yields exceeding 80% for the dura-

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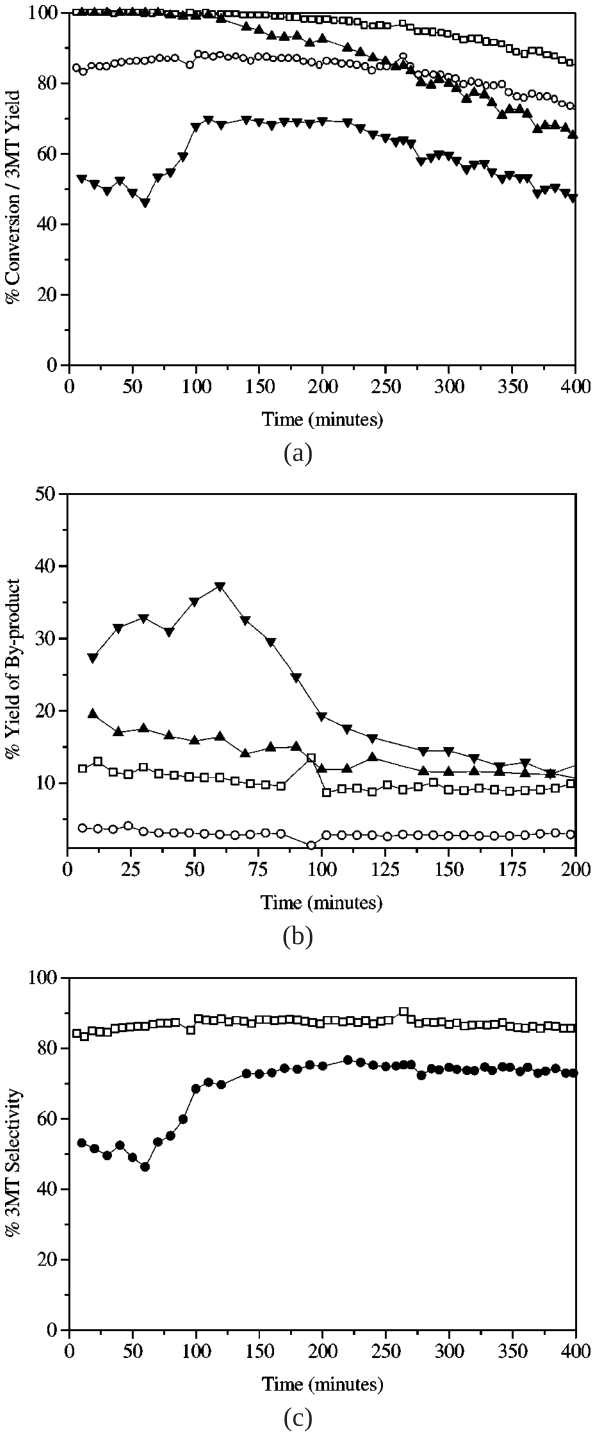

Figure 1. (a) 2-methylbutanol conversion 3-methylthiophene yield profiles: (▲) 2-methylbutanol conversion standard, (▼) 3-methylthiophene yield standard, (☐) 2-methylbutanol conversion ex-PS, (○) 3-methylthiophene yield ex-PS. (b) 2-methylbutanol/CS_2 reaction by-product profiles: (▲) thiophene yield standard, (▼) "lights" standard, (○) thiophene yield ex-PS, (☐) "lights" ex-PS. (c) 2-methylbutanol/CS_2 reaction 3MT selectivity: (☐) ex-pre-sulfided, (●) standard. Conditions of reactions (a)–(c): organic : CS_2 : N_2 = 1 : 1.5 : 80, GHSV = 12000 h^{-1}.

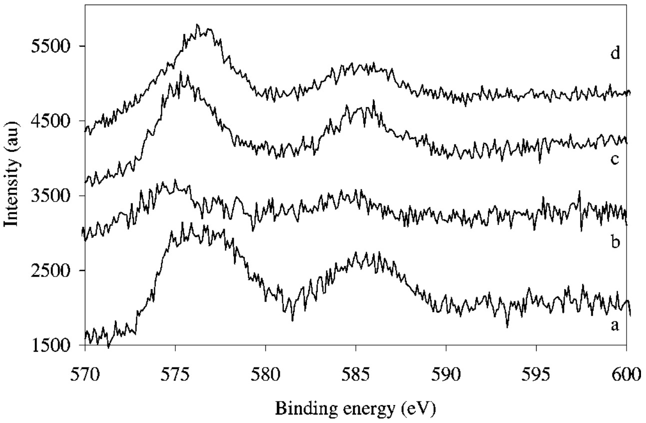

Figure 2. Cr $2p_{1/2}$ and $2p_{3/2}$ XP spectra: (a) fresh sample, (b) post-reaction, (c) post-pre-sulfided reaction and (d) post-regeneration.

tion of the active lifetime of the catalyst (defined as >98% conversion). Hence the ex-pre-sulfided catalyst yielded correspondingly lower levels of thiophene or light fractions, presumably due to a decrease in acidic sites responsible for these side-reactions. This is consistent with the significantly longer active lifetime of the pre-sulfided catalyst which was ca. twice that of the untreated sample. The lower degradation of feedstock is also reflected in the XPS of the ex-reactor catalysts. These show a larger intensity increase for the C $1s_{1/2}$ and greater attenuation of the Al and Cr signals for the untreated catalyst despite the longer catalyst lifetime and higher exposure of the ex-pre-sulfided catalyst to CS_2 and alcohol (figure 2, traces (b) and (c), respectively). These trends are further reflected in the comparison of the 3MT selectivities obtained for the two samples. The enhancement of catalyst selectivity from pre-sulfiding is clear, as is the significant contribution of the side reactions occurring in the standard reaction "induction" period which result in a far lower initial 3MT selectivity. Moreover, a comparison of the steady state 3MT selectivities (ca. 75%; cf. 88% for the ex-pre-sulfided case) reflected the superior performance of the pre-sulfided sample. It should also be noted that in both cases selectivity is unaffected by the loss of activity, suggesting a loss or blockage of active sites rather than a change in the nature of sites present is responsible for deactivation.

XPS of the two catalysts also revealed shifts in the Cr 2p peaks (figure 2) and the presence of multiple sulfur species post-reaction (figure 3). For both samples twin S 2s and 2p peaks were recorded, consistent with the presence of sulfate (for S 2p ca. 169 eV) and sulfide (162 eV) phases [9], the former arising from the re-oxidation of the latter upon exposure to air. However, the proportions of the two phases differed for the samples. The ex-pre-sulfided catalyst was found to have ca. 1.4 times more S-containing surface species based upon relative intensities. Additionally, the ratio of sulfide to sulfate was larger for this sample. This increase is not considered to be due to the higher absolute exposure of the ex-pre-sulfided to CS_2 during reaction since without pre-treatment, deactivation is observed. Moreover, there is no corresponding increase in the C $1s_{1/2}$ peak, but in fact a lower signal, reflecting the lower concentration of surface carbon.

Figure 3. S $2p_{1/2}+2p_{3/2}$ XP spectra: (a) ex-standard reaction and (b) post CS_2 reaction.

The higher sulfur content of the ex-pre-sulfided catalyst is ascribed to the formation of a specific Cr_2S_3 phase (figure 2, compare traces (a) and (c)) during the pre-treatment. The presence of this optimally active phase is consistent with previous data where residual O_2^- or sulfide depletion have been found to limit heterocycle selectivity [4,10]. In addition it has been claimed that conversion of the oxide to the sulfide results in the formation of highly dispersed Cr_2S_3 [10,11], which would also have performance benefits. The data also suggests an optimal "steady state" concentration of metal sulfide, which is established during pre-treatment and maintained during reaction, or alternatively slowly depleted in the absence of co-fed CS_2 [4]. Clearly, such a phase can form during a standard reaction, as is reflected in the similar shifts of the Cr 2p peaks (Cr $2p_{3/2} = 576.9$ eV for Cr_2O_3 vs. 574.8 eV for Cr_2S_3 [9]). However, in a standard reaction there is competition for the surface between the CS_2 and the alcohol, with the side-reactions of the alcohol resulting in the formation of deactivating residues in addition to inhibition of sulfidation. Hence, these data suggest that, in common with HDS, the formation of a bulk sulfide is necessary for activity and the presence of the oxide precursor is detrimental [5,6].

Additional benefits regarding 3MT selectivity may arise from the poisoning of trace Cr II sites. These sites are known to be highly active for dehydrogenation and polymerisation, as in the ubiquitous Phillips catalyst [12]. However by their nature, the strong interactions between organic and active site would lead to product retention and poisoning as a consequence of surface nucleation and oligomerisation. In addition the process of pre-sulfiding alters the Al_2O_3 support [13], a factor which cannot be overlooked given the significant contribution of the support within thiophene synthesis [4,7]. Indeed exposure of pure Al_2O_3 to CS_2 also leads to the formation of a sulfide phase, presumably at co-ordinated unsaturated sites [7,13], which have previously been found to play a part in the reaction mechanism. This is corroborated by previous data and the work of Barrault et al. [3,7], who have shown that alumina itself can catalyse the conversion of alcohol to heterocycle, albeit with a lower selectivity [3,4,7]. In addition co-ordination and reaction of CS_2 on alumina has been also demonstrated to reduce the concentration of Brønsted acid sites [13], again consistent with the data presented.

4. Conclusions

Catalyst pre-sulfiding using CS_2 results in significant improvements in selectivity and lifetime for the synthesis of 3-methylthiophene. These improvements are ascribed to a combination of enhanced Cr_2S_3 formation and poisoning of sites present on the support and chromia responsible for reactions which limit selectivity and result in the formation of deactivating by-products.

Acknowledgement

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