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Synthesis of methyl mercaptan and thiophene from $CO/H_2/H_2S$ using α-Al_2O_3

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Methyl mercaptan and by-product thiophene can be obtained from the reaction of $CO/H_2/H_2S$ mixtures over α-Al_2O_3 at 340 °C, and selectivities of methyl mercaptan of $\geq 98\%$ can be readily obtained in a sustained reaction. γ-Al_2O_3 and Cr_2O_3 were also found to be active catalysts and gave high selectivities to methyl mercaptan, although these catalysts gave $(CH_3)_2S$ as by-product rather than thiophene. In the absence of H_2S, all the catalysts displayed virtually no catalytic activity.

KEY WORDS:

1. Introduction

Synthesis gas $(CO + H_2)$ reactions are used to prepare a wide range of commodity chemicals [1], e.g., methanol, ammonia, as well as fuels using the Fischer–Tropsch reaction [2], and recently there has been a resurgence of interest worldwide in gas-to-liquids technology, which is based on synthesis gas production and utilization. These reactions and catalysts have been extensively studied and optimized. In contrast, the co-reaction of synthesis gas with other molecules has received scant attention, yet there is the possibility of synthesizing useful materials using such an approach. This is particularly true for S-containing molecules, since methyl mercaptan and thiophene are both useful intermediates in the chemical, agrochemical and pharmaceutical industries. At present, methyl mercaptan is produced by the reaction of methanol with H_2S [3], and thiophenes are produced by reaction of a sulfur source (COS, CS_2 or H_2S) with either C_{4+} alcohols [4] or α,β unsaturated aldehydes [5] using chromia alumina or alkali/alkaline earth-promoted γ-alumina catalysts [4–7]. Since methanol and C_{4+} alcohols are well-known products from the reaction of synthesis gas [2], it seems feasible that the introduction of a sulfur source could lead to the synthesis of S-containing molecules. Of course, this approach is counterintuitive since sulfur is known to be a potent poison of most catalysts utilized for synthesis gas reactions [1], although there are reports of sulfur acting as a catalyst promoter [8,9]. Relatively few previous studies [10–13] have attempted to simultaneously react $CO/H_2/H_2S$ mixtures and most report the formation of methyl mercaptan but, usually, with significant amounts of by-product methane and carbon dioxide. Recently, Mul *et al.* [14] have investigated a route to methyl mercaptan based on the reaction of CO and H_2S, in the absence of co-fed H_2, using V_2O_5 supported on TiO_2 or Al_2O_3. However, this route gives low selectivities of methane mercaptan and it is concluded to have a theoretical limit of 33%. Hence, the approach using the reaction of CO and H_2S alone is not expected to give high selectivities (>90%). To date, there have been no reports of thiophene synthesis, which is surprising given the thermodynamic stability of this molecule. In this communication, we successfully address this problem and report our preliminary results showing, for the first time, that small but significant amounts of thiophene can be formed as a by-product, together with the highly selective formation of methyl mercaptan, when a low-area α-Al_2O_3 $(1\,m^2g^{-1})$ is used as a catalyst.

2. Experimental

A number of catalysts were investigated for the reaction of $CO/H_2/H_2S$. α-Al_2O_3 (Aldrich, $1\,m^2\,g^{-1}$), γ-Al_2O_3 (Synetix, $300\,m^2\,g^{-1}$) and Cr_2O_3 (Aldrich, $3\,m^2\,g^{-1}$) were calcined at 550 °C for 6 h prior to use. Cu/α-Al_2O_3 (7.8% Cu), Cu/γ-Al_2O_3 (7.8% Cu) and Cu/Cr_2O_3 (14.4% Cu) were prepared by impregnation of Al_2O_3 or Cr_2O_3 with an aqueous solution of $Cu(NO_3)_3 \cdot 2.5H_2O$ using the incipient wetness method, dried and calcined (550 °C, 6 h). K/α-Al_2O_3 (5.0% K_2O) was prepared by impregnating α-Al_2O_3 with aqueous K_2CO_3 using the incipient wetness technique, followed by drying and calcination (550 °C, 6 h). K_2MoO_4/SiO_2 (50.3% K_2MoO_4) was prepared according to the method of Yang *et al.* [13]. In addition, composites of Cr_2O_3 with α- or γ-Al_2O_3 were produced by grinding these together (Cr_2O_3, 10%) followed by calcination (550 °C,

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6 h). CO/H_2 and $CO/H_2/H_2S$ reactions were carried out using a stainless steel tubular fixed-bed micro-reactor, previously described [15]. In a typical reaction, either $CO : H_2 = 1 : 1$ or $CO : H_2 : H_2S = 4 : 5 : 1$ were passed over the heated catalyst (2 mL) at 340 °C at a gas hourly space velocity (GHSV) of $200\,h^{-1}$ at a total pressure of 2.0 MPa.

3. Results and discussion

In the absence of co-fed H_2S, the catalysts showed very little activity for the reaction of $CO + H_2$. For example, α-Al_2O_3 at 340 °C, $200\,h^{-1}$ and 2.0 MPa gave CO conversions of 1–3%, producing products comprising 20.0 mol% CH_4, 19.3 mol% C_2–C_5 hydrocarbons, 28.5 mol% CH_3OH and 21.1 mol% CH_3CHO. Interestingly, on the introduction of H_2S to the synthesis gas, the CO conversion increases markedly to 6.0% and the product distribution switches almost exclusively to the formation of S-containing products (table 1). In addition, variation of the reactor pressure from 0.1 to 2.0 MPa at 340 °C increased the CO conversion from 2.1 to 6.0% but had no effect on the product selectivity. In these initial experiments, we have not been able to investigate higher pressures, but it is possible that further improvement in catalytic performance could be expected at higher pressures. Variation of temperature did affect the selectivity to thiophene and the highest selectivity was observed at 340 °C (0.6 mol%). Control experiments using BN, SiC or glass wool, without the addition of a catalyst, gave low CO conversion, mainly to methane and methyl mercaptan, confirming that the formation of thiophene was due to the presence of α-Al_2O_3. These results represent the first time that thiophene has been observed as a product in the reaction of $CO/H_2/H_2S$ mixtures.

Other oxide catalysts were also found to be active for this reaction but gave lower thiophene and methyl mercaptan selectivities (table 1), although traces of thiophene were still observed together with methyl mercaptan using γ-Al_2O_3, Cr_2O_3 and Cr_2O_3/α-Al_2O_3. Addition of copper to α-Al_2O_3, γ-Al_2O_3 or Cr_2O_3 led to increased methane formation at the expense of thiophene and methyl mercaptan. Addition of K^+ decreased the catalyst activity and the thiophene selectivity, but had virtually no effect on the selectivity to methyl mercaptan. Interestingly, K_2MoO_4/SiO_2, a catalyst that had previously been shown to give very high selectivities to methyl mercaptan [13], gives no thiophene and gives a higher selectivity to methane under these reaction conditions, although these results were obtained at a markedly higher conversion.

The results of this study show that α-Al_2O_3 acts as an efficient catalyst for the synthesis of methyl mercaptan with the by-product thiophene. As noted previously, the current commercial process for the synthesis of methyl mercaptan is from the reaction of methanol over H_2S, possibly via the reaction of CH_3O- and HS-fragments arising from chemisorption on the catalyst surface, and this probably is the mechanism operating with our catalysts [16]. From the data in table 1, a relationship between CH_4, CH_3SH and $(CH_3)_2S$ is apparent, in that a decrease in CH_3SH selectivity leads to an increase in $(CH_3)_2S$ and CH_4. This may be attributed to the Lewis acidity of the catalysts and the stronger Lewis acidity suppresses the formation of CH_3SH. The formation of thiophene probably results from the reaction of higher hydrocarbon or oxygenate species with surface –SH groups [7]. This is consistent with the loss of these

Table 1
Reaction of $CO/H_2/H_2S$ over various catalysts[a]

Catalyst	Product selectivity (mol%)							
	CO conversion (%)	CH_4	C_2–C_5 hydrocarbon	C_2–C_3 aldehydes	CH_3SH	$(CH_3)_2S$	C_4H_4S	C_3H_7SH
α-Al_2O_3	6.0	0.6	0.3	0.5	98.0	–	0.6	–
γ-Al_2O_3	4.5	0.4	0.9	0.2	92.1	6.0	t	0.3
Cr_2O_3	7.0	13.5	0.1	t	82.5	3.9	t	–
K-α-Al_2O_3	2.1	0.7	0.4	–	97.9	0.9	0.1	–
Cu-α-Al_2O_3	6.0	2.8	1.2	–	84.6	11.4	–	–
Cu-γ-Al_2O_3	5.1	60.4	0.9	t	12.5	25.9	–	0.2
Cu-Cr_2O_3	7.3	26.8	1.4	–	67.3	4.2	–	0.2
Cr_2O_3/α-Al_2O_3	6.8	12.1	0.2	t	86.0	1.6	t	–
Cr_2O_3/γ-Al_2O_3	4.5	3.4	0.1	t	95.7	0.5	–	0.3
K_2MoO_4/SiO_2	20.8	5.0	0.1	–	93.9	0.8	–	t
SiO_2	0.8	4.6	–	–	95.4	–	–	–
BN	0.4	15.5	–	–	84.5	–	–	–
SiC	0.4	12.0	–	–	88.0	–	–	–
glass wool	0.4	100	–	–	–	–	–	–

[a] Reaction conditions: 340 °C, $CO : H_2 : H_2S = 4 : 5 : 1$, GHSV = $200\,h^{-1}$, 2.0 MPa, 24 h time onstream, t = trace < 0.1%.

products when H_2S is introduced into the reactant gases. However, it was somewhat unexpected that the conventional catalyst for thiophene synthesis, i.e., Cr_2O_3/γ-Al_2O_3, did not show any activity for thiophene formation under the reaction conditions used in this study, although it did show some Fischer–Tropsch activity in the absence of H_2S. This may indicate that a different reaction pathway exists for thiophene formation from that of $CO/H_2/H_2S$ mixtures. At present, no attempt has been made to optimize the formation of the by-product thiophene, and it is expected that, with further catalyst design, improved results can be obtained. However, we consider that the cosynthesis of methyl mercaptan and thiophene by a modified Fischer–Tropsch route could, with further development, replace the current two-step process for the synthesis of methyl mercaptan [16].

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