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Catalytic synthesis of methanethiol from CO/H_2/H_2S mixtures using α-Al_2O_3

Baojian Zhang, Stuart H. Taylor and Graham J. Hutchings*

Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff CF10 3TB, UK.
E-mail: hutch@cardiff.ac.uk

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Sustained synthesis of methanethiol from the reaction of CO/H_2/H_2S mixtures is reported and discussed. Surprisingly, unmodified α-Al_2O_3 gives the best results for this reaction and methanethiol selectivities of $>98\%$ at CO conversions of *ca.* 6% can be readily obtained (CO:H_2:H_2S = 4:5:1, 340 °C, total pressure = 20 bar, 200 h^{-1}). Reaction of CO + H_2 (CO:H_2 = 1:1) in the absence of H_2S using α-Al_2O_3 under comparable conditions gives a lower CO conversion (*ca.* 1.3%) with significant selectivities to methane (20%), methanol (28.5%) and ethanol (21.1%). When H_2S is added to the synthesis gas feedstock, the product selectivity switches to sulfur-containing products, almost exclusively methanethiol, but some by-product thiophene is also observed. A range of other catalysts were also investigated (*e.g.*, γ-Al_2O_3, Cr_2O_3, Cr_2O_3/Al_2O_3, Cu/Cr_2O_3) but all give inferior catalytic performance when compared with α-Al_2O_3. The mechanism of the synthesis of methanethiol is discussed, based on a modification of chain propagation in the Fischer–Tropsch synthesis reaction.

Introduction

Synthesis gas (CO + H_2) reactions are used to prepare an extensive range of commodity chemicals,[1] for example, methanol, ammonia, as well as fuels using the Fischer–Tropsch synthesis reaction.[2] These reactions have been extensively studied and optimised. In contrast, there has been very limited investigation of the reactions of synthesis gas in the presence of other reactants, in particular sulfur-containing molecules such as H_2S. This is surprising since the reaction of CO:H_2:H_2S mixtures could be expected to lead to the formation of methanethiol and thiophene, both of which are useful intermediates in the synthesis of pharmaceuticals, agrochemicals and polymers.[3–5] In the reactions of CO/H_2 mixtures in the Fischer–Tropsch synthesis it should be noted that aromatic compounds are not favoured.[2] However, thiophene readily forms from the reactions of alcohols and aldehydes with sulfided surfaces[6–10] and as alcohols/aldehydes can be formed during the Fischer–Tropsch synthesis,[2] it is anticipated that thiophene could be a viable synthesis target. At present, methanethiol is produced by the reaction of methanol with H_2S[11] and thiophenes by the reaction of a sulfur source (COS, CS_2 or H_2S) with either C_{4+} alcohols[7] or α,β-unsaturated aldehydes[8] using chromia alumina or alkali/alkaline earth promoted γ-Al_2O_3 catalysts.[6–10] At first sight, the co-reaction of synthesis gas with sulfur-containing molecules would not appear to be a viable reaction pathway, since sulfur-containing molecules are known to be potent catalyst poisons for synthesis gas reactions.[1] In the Fischer–Tropsch synthesis, there have been a number of studies concerning the effects of feedstock sulfur[12–15] and some studies suggest that sulfur can act as a promoter.[14,15] To date, there have been a few studies concerning the reaction of CO + H_2 with H_2S,[16–19] using NiS,[16] MnS/Al_2O_3,[17] WO_3/Al_2O_3[18] and K_2MoO_4/SiO_2[19] as catalysts. Methanethiol is observed as the major product although, in these earlier studies, no thiophene is reported as a product. Very recently, Mul *et al.*[20] have reported the synthesis of methanethiol from the reaction of CO + H_2S in the absence of H_2 using vanadium oxide catalysts. The studies of Mul *et al.*[20] were based on previous patent disclosures[21,22] and detailed fundamental studies of the interaction of H_2O, H_2S, CO and methanethiol with TiO_2.[23–25]

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In this paper, we present our results for the reaction of a CO/H_2/H_2S mixture over alumina catalysts, demonstrating, for the first time, very high methanethiol selectivity, together with by-product thiophene formation.

Experimental

Catalyst preparation

α-Al_2O_3 (Aldrich, 1 m^2 g^{-1}), γ-Al_2O_3 (Synetix, 300 m^2 g^{-1}), Cr_2O_3 (Aldrich, 3 m^2 g^{-1}), WO_3 (Aldrich), MoO_3 (Aldrich), SiO_2 (BDH, 200 m^2 g^{-1}), $Na_2WO_4 \cdot 2H_2O$ (BDH) and H-ZSM-5 (Zeolyst, Si/Al = 80) were calcined (550 °C, 6 h) prior to use as catalysts. 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 $Cu(NO)_3 \cdot 2.5H_2O$ (Aldrich) using the incipient wetness method. In addition, composites of Cr_2O_3 or MoO_3 with α- or γ-Al_2O_3 were prepared by grinding the oxides together (1:1 by weight), followed by calcination (600 °C, 6 h). K/α-Al_2O_3 (5.0% K_2O) was prepared by impregnating α-Al_2O_3 with an aqueous solution of K_2CO_3 (Fischer) 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.*[19]

Catalyst characterisation

Powder X-ray diffraction was carried out using an Enraf Nonius FR590 powder diffractometer. Infrared spectroscopy was carried out using a Perkin–Elmer System 2000 FTIR spectrometer. Surface areas were determined using N_2 adsorption according to the BET method using a Micromeritics Gemini 2360 surface area analyser. Carbon deposition was determined using thermal gravimetric analysis using a Perkin–Elmer TGA-7 analyser.

Catalyst testing

The reaction of carbon monoxide and hydrogen ($CO:H_2 = 1:1$ by volume) and the reaction of carbon monoxide, hydrogen and hydrogen sulfide ($CO:H_2:H_2S = 4:5:1$ by volume) were carried out using a stainless steel tubular fixed bed microreactor as previously described.[26] Products were analysed using an on-line GC fitted with both flame ionisation and thermal conductivity detectors. Off-line analysis of sulfur-containing compounds was carried out using a pulsed flame photometric detector.[27]

Results

The reaction of a CO/H_2 mixture (1:1 mol ratio) was investigated using non-modified α-Al_2O_3 as catalyst at 340 °C and 20 bar total pressure (Table 1). In the absence of added H_2S, the CO conversion was very low (1.3%) but sustained over the test period of 72 h without perceptible deactivation. The products comprised mainly methane (20%), methanol (28.5%) and ethanal (21.1%). The presence of a significant selectivity to ethanal is indicative of a deactivated Fischer–Tropsch catalyst. When H_2S is added to the reactant gases ($CO:H_2:H_2S = 4:5:1$ mol ratio), the CO conversion increases markedly to 6% and the products switch almost exclusively to methanethiol (98%) with a small amount of by-product thiophene (0.6%). This catalytic performance was sustained throughout the test period of 72 h at these reaction conditions. To ensure that the reaction of the $CO/H_2/H_2S$ mixture was due to a catalytic reaction with α-Al_2O_3, three additional blank experiments were conducted using either an empty reactor containing a small amount of silica wool packing, SiC or BN. SiC and BN were selected as examples of chemically inert surfaces and with similar particle sizes to that for the α-Al_2O_3 used and, hence, this is an evaluation of wall effects. The results, shown in Fig. 1, clearly indicate that α-Al_2O_3 gives a sustained CO conversion of *ca.* 6.0%, but a very slight deactivation is observed over the time scale of the experiment. In contrast, in the empty reactor, BN and SiC all give much lower CO conversion. Hence, we conclude that the higher conversion and enhanced methanethiol selectivity are due to a catalytic reaction occurring on the surface of α-Al_2O_3. In the empty reactor, the only product observed was methane whereas, with BN and SiC, methanethiol was observed with selectivities of 84.5% and 88.0% respectively. In the presence of α-Al_2O_3, the selectivity to methanethiol was maintained at more than 98% throughout the 72 h experiment and, additionally, thiophene synthesis was also maintained at a low, but significant, level (mean selectivity 0.6%). Thiophene was not observed with SiC and BN.

Table 1 Effect of addition of H_2S to $CO + H_2$ using α-Al_2O_3 as catalyst[a]

	CO/H_2	$CO/H_2/H_2S$
% CO conversion	1.3	6.0
% Product selectivity		
CH_4	20.0	0.6
C_2H_4	3.7	–
C_2H_6	5.6	–
C_3H_8	1.5	–
C_3H_6	1.6	–
C_4H_{10}	6.1	0.1
C_4H_8	0.6	–
C_{5+}	0.2	0.2
CH_3OH	28.5	0
CH_3CHO	21.1	0
C_2H_5CHO	6.6	0.3
CH_3COOH	2.6	0
C_3H_7CHO	1.9	0.2
CH_3SH	–	98.0
C_4H_4S	–	0.6

[a] Reaction conditions: 340 °C, total pressure = 20 bar, GHSV = 200 h^{-1}, α-Al_2O_3 (2 ml), $CO:H_2 = 1:1$, $CO:H_2:H_2S = 4:5:1$, time on-line 72 h.

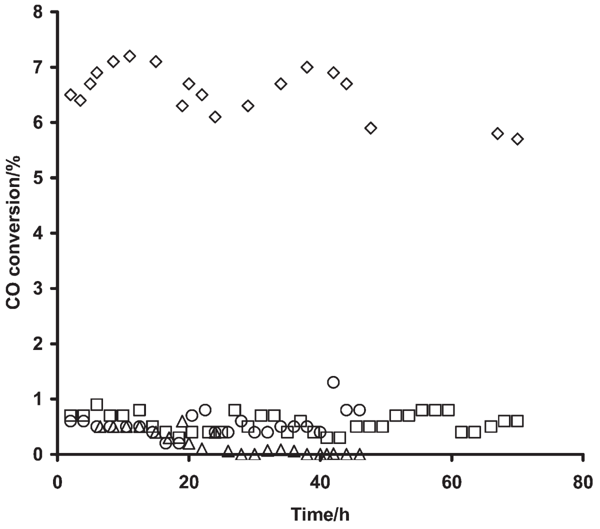


Fig. 1 CO conversion as a function of time on-line for the reaction of a $CO/H_2/H_2S$ mixture at 340 °C and total pressure 20 bar ($CO:H_2:H_2S = 4:5:1$, 200 h^{-1}): (◇) α-Al_2O_3, (□) SiC, (○) BN, (△) empty reactor

Detailed analysis of the products confirmed that the major by-product formed along with the carbon-containing products (CH_3SH and C_4H_4S) was water. Only slight trace amounts of CO_2 were observed at higher reaction temperatures. Further analysis of the sulfur-containing products was carried out using a GC equipped with a flame photometric detector and no COS was detected as a co-product. Based on thermodynamics COS can be expected to be formed at these reaction temperatures. However, we have previously shown that alumina is a highly effective catalyst for COS hydrolysis ($COS + H_2O \rightleftharpoons CO_2 + H_2S$) at temperatures below 100 °C. Since significant amounts of water are formed as a by-product, the non-detection of COS in this study is not unexpected.

Experiments were carried out using a range of temperatures (Table 2) and pressures (Table 3). As expected, the CO conversion increased with increasing temperature and pressure. As the temperature increased from 200 to 440 °C, the selectivity to methane increased markedly and the optimal temperature for methanethiol and thiophene selectivity is *ca.* 300–340 °C, although much higher yields of methanethiol can be observed at higher temperature. This effect is probably caused by the

Table 2 Effect of temperature on the synthesis of methanethiol and thiophene using α-Al_2O_3 as catalyst[a]

	Temperature/°C				
	200	250	300	340	440
% CO conversion	0.6	1.8	3.3	6.1	15.4
% Product selectivity					
CH_4	Trace	Trace	0.1	0.3	3.6
CH_3SH	97.5	97.9	98.4	98.2	94.3
C_4H_4S[b]	0	0	Trace	0.6	0.2

[a] Reaction conditions: $CO:H_2:H_2S = 4:5:1$, total pressure 20 bar, GHSV = 200 h^{-1}, α-Al_2O_3 (2 ml), time on-line 72 h. [b] C_4H_4S analysis ±0.05%.

Table 3 Effect of pressure on the synthesis of methanethiol and thiophene using α-Al_2O_3 as catalyst[a]

	Pressure/bar				
	1	5	10	15	20
% CO conversion	2.1	3.5	3.3	4.5	6.0
% Product selectivity					
CH_4	1.5	1.7	1.1	0.7	0.5
CH_3SH	94.0	95.7	97.4	98.1	98.0
C_4H_4S[b]	0.5	0.4	0.3	0.4	0.6

[a] Reaction conditions: CO:H_2:H_2S = 4:5:1, 340 °C, GHSV = 200 h^{-1}, α-Al_2O_3 (2 ml), time on-line 72 h. [b] C_4H_4S analysis ±0.05%.

higher rate of hydrogenation at the elevated temperatures. Interestingly, the by-product thiophene selectivity decreases when the temperature is increased from 340 to 440 °C, although thiophene is a very stable molecule and its formation could be expected to be enhanced at the higher temperatures. The selectivity to methane decreases with increasing reaction pressure, which is a standard feature of synthesis gas reactions.[2] The reactions were carried out using a standard flow rate of reactant gases and experiments using higher flow rates resulted in almost negligible conversion being observed. It should be noted that the flow rates utilised in this study are much lower than those usually used in synthesis gas reactions,[2] consequently further effort is required to improve the activity of the catalysts described in the present work.

Cr_2O_3, a material with the corundum structure of α-Al_2O_3, was also investigated as a catalyst for this reaction (Fig. 2). At a similar level of CO conversion, Cr_2O_3 gave enhanced methane selectivity and no by-product thiophene was observed. The addition of K^+ as an alkali additive was also investigated (Fig. 2) and this led to a decrease in CO conversion but had no effect on the product selectivity and thiophene was still observed as a by-product. The addition of Cu to the catalysts (Fig. 2) did not lead to an enhancement in catalytic performance. It was hoped that the addition of Cu could aid the formation of alcohols,[2] although under these reaction conditions methanol would not be expected to be formed in significant amounts.

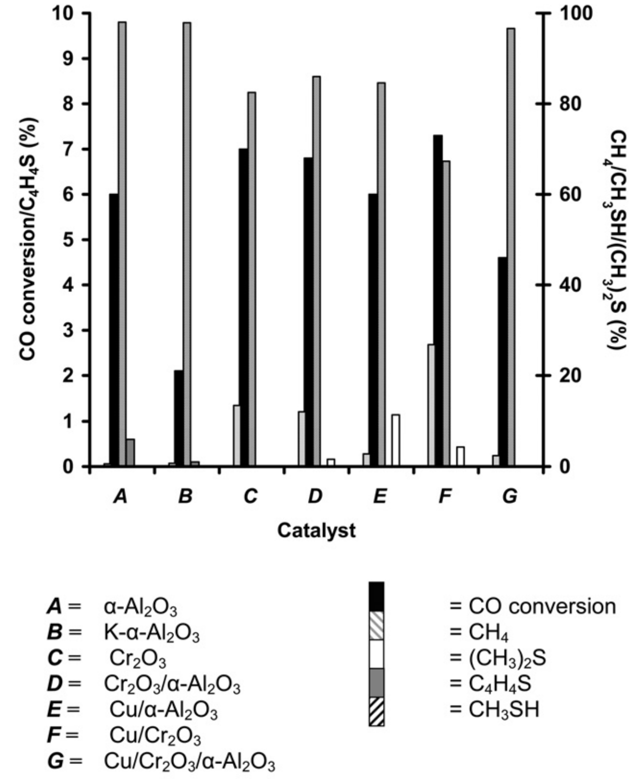


Fig. 2 Catalytic performance of catalysts for the conversion of a CO/H_2/H_2S mixture to methanethiol, thiophene and methane. Reaction conditions: 340 °C, 20 bar total pressure, CO:H_2:H_2S = 4:5:1, 200 h^{-1}, catalyst (2 ml), time on-stream 72 h.

Unmodified α-Al_2O_3 gave the best observed catalytic results for the synthesis of methanethiol. Following reaction, the used α-Al_2O_3 was characterised using powder X-ray diffraction and FTIR spectroscopy. No changes in the bulk corundum structure of the α-Al_2O_3 was discernible and analysis confirmed that there was no significant deposition of carbonaceous material on the α-Al_2O_3 as a result of the catalytic reaction.

To examine the effect of the alumina structure further, γ-Al_2O_3 was investigated as a catalyst for the reaction of $CO + H_2 + H_2S$ and the results are shown in Table 4. γ-Al_2O_3 gives very similar results to α-Al_2O_3, although the conversion is slightly lower. In addition, $(CH_3)_2S$ is observed as a product, presumably formed *via* a subsequent acid-catalysed reaction of CH_3SH. In contrast to α-Al_2O_3, the addition of Cu induces high selectivity to methane (Table 4). Also, in contrast to α-Al_2O_3, only traces of thiophene (<0.1%) are observed with γ-Al_2O_3.

Previous studies[18,19] have shown that more acidic catalysts based on W and Mo compounds are effective for the reaction of $CO + H_2 + H_2S$ to form methanethiol. In view of this, a series of catalysts were evaluated and the results are shown in Table 5. All W- and Mo-based catalysts tested give higher selectivities to methane than observed with α-Al_2O_3 and only K_2MoO_4/SiO_2 and MoO_3/α-Al_2O_3 give a higher CO conversion under these reaction conditions. Hence, on the basis of selectivity, α-Al_2O_3 appears to be the preferred catalytic material. γ-Al_2O, is much less active and consequently it is apparent that surface area is not an important parameter in this reaction. H-ZSM-5 gives significant selectivities to C_2–C_{5+} hydrocarbons as well as benzene and toluene.

Discussion

There are two significant results that require comment with α-Al_2O_3 as catalyst: the high sustained selectivity to methanethiol ($\geq$98%) and the synthesis of by-product thiophene. This is the first study to report the formation of thiophene from the reaction of CO/H_2/H_2S mixtures and the molar ratio

Table 4 Reaction of a CO/H_2/H_2S mixture over γ-Al_2O_3 and Cr_2O_3 catalysts[a]

	Catalyst			
	γ-Al_2O_3	Cr_2O_3	Cr_2/γ-Al_2O_3	Cu-γ-Al_2O_3
% CO conversion	4.5	7.0	4.5	5.1
% Product selectivity				
CH_4	0.4	13.5	3.4	60.4
C_2H_4	Trace	0.1	0.1	0.9
C_2H_4	0.1	Trace	Trace	Trace
C_3H_8	Trace	Trace	Trace	Trace
C_3H_6	0.5	Trace	Trace	Trace
C_4H_{10}	Trace	Trace	Trace	Trace
C_4H_8	0.3	Trace	Trace	Trace
C_{5+}	Trace	Trace	Trace	Trace
CH_3SH	92.1	82.5	95.7	12.5
$(CH_3)_2S$	6.0	3.9	0.5	25.9
C_3H_7SH	0.3	Trace	0.3	0.2
C_4H_4S	Trace	Trace	–	–

[a] Reaction conditions: 340 °C, CO:H_2:H_2S = 4:5:1, 200 h^{-1}, 20 bar total pressure, catalyst (2 ml), time on-line 72 h.

Table 5 Reaction of a $CO/H_2/H_2S$ mixture over H-ZSM-5, Mo- and W-based catalysts[a]

	Catalyst						
	H-ZSM-5	SiO_2	K_2MoO_4/SiO_2	WO_3	Na_2WO_4	MoO_3	$MoO_3/\alpha\text{-}Al_2O_3$
% CO conversion	6.0	0.8	20.8	0.8	3.0	2.2	10.2
% Product selectivity							
CH_4	4.0	4.6	5.0	68.0	21.8	91.2	11.1
C_2H_6	1.7	–	Trace	8.4	Trace	13.9	0.1
C_2H_4	3.8	–	Trace	Trace	–	Trace	Trace
C_3H_8	1.3	–	Trace	0.6	–	0.2	Trace
C_3H_6	0.5	–	Trace	–	–	–	–
C_{4+}	3.4	–	–	–	–	–	–
CH_3SH	79.8	95.4	93.9	22.9	75.0	4.7	84.9
$(CH_3)_2S$	4.7	–	0.8	–	3.2	–	3.7
C_4H_4S	Trace	–	–	–		–	–

[a] Reaction conditions: 340 °C, $CO:H_2:H_2S = 4:5:1$, 200 h^{-1}, total pressure 20 bar, time on-line 4 h. [b] C_5+ non-aromatic hydrocarbons.

of the reactants was selected in an attempt to maximise thiophene formation, that is in a $CO:H_2:H_2S = 4:5:1$ molar ratio.

Thiophene is a very stable molecule and, hence, its formation under the reaction conditions employed should not be unexpected. Thiophene is currently synthesised from the reaction of C_{4+} alcohols[6] or α,β-unsaturated aldehydes[7] using chromia–alumina or alkali/alkaline earth promoted γ-Al_2O_3 catalysts.[6–10] The formation of thiophene in our reaction probably results from the reaction of a higher hydrocarbon or oxygenated species with surface –SH groups. This is consistent with both the loss of these products from the reaction of $CO + H_2$ on the introduction of H_2S and, also, the previous literature concerning the mechanism of thiophene formation over oxide catalysts.[9] The mechanism of thiophene formation on oxide catalysts from alcohols with H_2S or CS_2 is known to be very complex, involving a range of interconnecting pathways of dehydrogenation and O/S exchange/insertion.[28] However, it was somewhat unexpected that conventional catalyst for thiophene synthesis, that is $Cr_2O_3/\gamma\text{-}Al_2O_3$, 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. Furthermore, the inclusion of Cu into the catalyst formulation would be expected to enhance the formation of alcohols,[2] which are precursors for the synthesis of thiophenes,[6–10] but no thiophene was formed with the Cu-containing catalysts. This may indicate that a different pathway for thiophene synthesis may be operating when the $CO/H_2/H_2S$ mixture is reacted over α-Al_2O_3. Furthermore, even with α-Al_2O_3 as catalyst, only very low levels of thiophene are observed. To examine the mechanism further, the reactivity of a range of C_4 alcohols and hydrocarbons were evaluated by reacting them with a sulfided γ-Al_2O_3 catalyst at 300–450 °C, the temperature range in which the low levels of thiophene are observed. The order of reactivity of thiophene formation decreased in the following order:

$$\text{butenol} > \text{butanal} > \text{butanol} \gg \text{butanethiol} > \text{2-methylbutene}$$

It is clear that the highest yields of thiophene are obtained from unsaturated oxygenates and yields were very low with non-oxygenated substrates or saturated sulfur-containing molecules. The reaction of CO and H_2 over α-Al_2O_3 at 340 °C (Table 1) produces very low concentrations of C_4 hydrocarbons and oxygenates. In particular, the oxygenates, for example C_3H_7CHO, are formed in much lower concentrations than the hydrocarbons. Hence, circumstances are not favourable for thiophene formation with the α-Al_2O_3 catalyst and, in the presence of H_2S, the reaction produces almost exclusively methanethiol. Another reason for the low concentration of thiophene observed is probably due to hydrosulfurisation reactions occurring, since the low partial pressure of thiophene is present with a very high partial pressure of H_2.[29] Hence, by the principle of microscopic reversibility, the decomposition of thiophene is still more favoured under the optimal reaction conditions for its formation. These two factors, low rates of formation of C_4 oxygenates with the α-Al_2O_3 catalysts and the favoured decomposition of the thiophene, contribute to the low levels of thiophene observed and will, in effect, limit the amount of thiophene that can be expected, even for catalysts with improved design.

Only a limited amount of characterisation has been conducted in this initial study. Using powder X-ray diffraction and FTIR spectroscopy, no changes were observed in the well crystalline α-Al_2O_3 sample used in these studies. This suggests that H_2S interacts solely with the surface and no structural changes to the bulk of the material occurs, such as the formation of a sulfide. Materials with the corundum structure are also used in the formation of fluorinated molecules[30] and, in this case, a similar surface modification is observed. It is envisaged that sulfur from H_2S partially exchanges with $O^{2-}_{(s)}$ on the surface of α-Al_2O_3 and thus forms the active sites for CH_3SH and C_4H_4S formation.

It is apparent that the acidity of the oxides used for the reaction of $CO + H_2 + H_2S$ needs to be minimised if the maximum selectivity to methanethiol is to be observed. For example, γ-Al_2O_3, which has surface Brønsted acid –OH groups in comparison with α-Al_2O_3, gives enhanced selectivity to $(CH_3)_2S$ formed from the acid-catalysed reaction of CH_3SH, in an analogous reaction to that observed for dimethyl ether formation from methanol over γ-Al_2O_3. However, the surface acidity of γ-Al_2O_3 is insufficient to lead to further reaction of CH_3SH and $(CH_3)_2S$ to form hydrocarbon products. Previously, we have shown that CH_3SH can be reacted over H-ZSM-5 and WO_3 catalysts and that methane is a major product;[31] these experiments were carried out to gain a fuller understanding of the mechanism for carbon-carbon bond formation from methanol with these catalysts. In general, sulfur-containing molecules were much less reactive than their oxygen-containing counterparts. Hence, in the present study, the introduction of acidity using H-ZSM-5, W- or Mo-based catalysts (Table 5) typically leads to a significant loss of CH_3SH selectivity as it is converted, *via* an acid-catalysed pathway, to hydrocarbons. Therefore, for these catalysts, the hydrocarbons observed are considered to result from the secondary reaction of CH_3SH and not from the Fischer–Tropsch synthesis reaction occurring in parallel with methanethiol formation. Further evidence for this hypothesis is supplied by the results observed when H-ZSM-5 is used as a catalyst (Table 5). Both benzene and toluene are observed together with other hydrocarbons. It is unlikely that these aromatic compounds would be formed in a Fischer–Tropsch reaction under these reaction conditions and, in general, H-ZSM-5 is inactive for $CO + H_2$ reactions in the absence of H_2S.

Therefore, for the maximum selectivity to methanethiol, a relatively non-functionalised surface is required, which has minimal acidity. Clearly, α-Al_2O_3 provides such a surface, but it is interesting to note that high methanethiol selectivities were also observed with SiO_2, BN and SiC. At the present time, the reactivity of α-Al_2O_3 is perhaps too low and it will be necessary to produce a higher area formulation; this may be achieved through comminution, which has proved successful in other catalysed systems.[32]

It is interesting to consider the possible mechanisms by which methanethiol is formed on the surface of α-Al_2O_3 from the reaction of $CO + H_2 + H_2S$. In a number of previous studies[18,20,25] COS has been proposed as an intermediate in the conversion of CO and H_2S mixtures. Although no H_2 was introduced with the reactants, H_2 could be formed *via* the formation of COS or *via* water gas shift reactions under the experimental conditions:

$$CO + H_2S \rightleftharpoons COS + H_2 \qquad (1)$$

$$COS + 3H_2 \rightleftharpoons CH_3SH + H_2O \qquad (2)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (3)$$

$$COS + H_2O \rightleftharpoons CO_2 + H_2S \qquad (4)$$

$$2COS \rightleftharpoons CO_2 + CS_2 \qquad (5)$$

The synthesis of CH_3SH *via* hydrogenation of COS is considered to involve a surface methylthiolate intermediate CH_3S_{ads}.[25] Further hydrogenation of this intermediate leads to the formation of by-product methane. In our studies, we have purposely introduced additional H_2 and, hence, this pathway could be possible. However, with the higher concentrations of H_2 present, the formation of COS *via* reaction (1) would be suppressed and the CH_3S_{ads} intermediate would be expected to be hydrogenated more readily, leading to higher selectivities of CH_4. In this way, it is not considered feasible that this mechanism would lead to the, almost, exclusive formation of CH_3SH, which is observed in our studies.

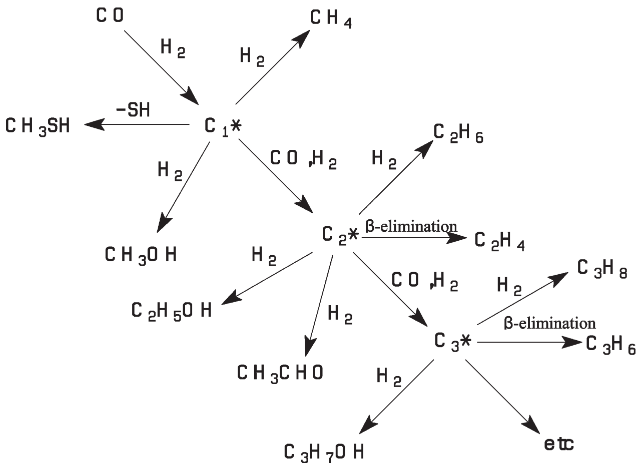
It is, of course, possible that methanethiol is formed by the reaction of H_2S with methanol:

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad (6)$$

$$CH_3OH + H_2S \rightleftharpoons CH_3SH + H_2O \qquad (7)$$

The precedence for such a proposal comes from the present industrial route for the synthesis of methanethiol *via* reaction (7)[11] and the observation that furan can exchange sulfur with sulfided alumina catalysts as part of the mechanism by which thiophene is formed.[9] However, in our studies with γ-Al_2O_3 in the absence of H_2S, the rate of methanol formation is low and the CO conversion is considerably enhanced when H_2S is introduced. Also, at low temperatures and low CO conversion (Table 2) no methanol is observed, but if this was the primary product from the reaction of CO with H_2 then some residual methanol could have been expected to be observed at 200 °C. Both of these observations suggest that, for α-Al_2O_3, reaction (7) is not the main pathway by which methanethiol is formed.

An alternative possibility is that a modification of the process occurring during the Fischer–Tropsch reaction takes place. The Fischer–Tropsch process is considered to follow a surface polymerisation mechanism in which a surface C_1 intermediate reacts to form a surface C_2 intermediate as outlined in Scheme 1.[2] When H_2S is introduced into the reactant mixture the surface of the α-Al_2O_3 catalyst can be expected to comprise –SH. These would be much more nucleophilic with respect to carbon compared with the surface –OH groups present in the absence of H_2S. It is possible that the –SH groups could intercept a C_1 surface intermediate formed in the hydrogenation of CO to form either an adsorbed $CH_3S^-_{ads}$ intermediate or adsorbed CH_3SH. The high nucleophility of the sulfur in the surface –SH groups would disrupt the chain propagation step and lead exclusively to the formation of a C_1 product, namely CH_3SH, which is wholly consistent with Schulz–Flory polymerisation kinetics.[2] This mechanism would also readily explain the observation that when H_2S is present the products are almost exclusively thiols or sulfur-containing molecules.



Scheme 1 Modified mechanism of the Fischer–Tropsch process incorporating a reaction of a C_1 intermediate with a surface ^-SH group (* denotes surface intermediates).

In conclusion, in this study of methanethiol formation from the reaction of a $CO/H_2/H_2S$ mixture, we have found that very high selectivities can be observed ($\geq$98%) when using the relatively simple α-Al_2O_3 as catalyst. It is essential that surface acidity is minimised, since when acid sites are present hydrocarbon formation *via* the consecutive reaction of CH_3SH is observed. A small amount of by-product thiophene is formed along with the methanethiol, and if the activity of the α-Al_2O_3 catalyst can be significantly improved, then this reaction may be of interest for the syntheses of these valuable chemical intermediates.

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