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High temperature COS hydrolysis catalysed by γ-Al_2O_3

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The COS hydrolysis reaction (COS + H_2O = CO_2 + H_2S) using γ-Al_2O_3at 220 °C is described and discussed. The stoichiometric reaction of COS in the absence of water proceeds and the extent of reaction is comparable to the moisture content of the alumina that can be removed during TGA. The reaction of COS and H_2O is long lived at this temperature but the sulphur balance based on H_2S is ca. 80%. It is found that elemental sulphur is deposited in the reactor and on the catalyst during this reaction. Reaction in the presence of H_2 increases the sulphur balance to 100% and no sulphur is deposited on the catalyst. The beneficial effect of hydrogen is demonstrated by mixing sulphur with γ-Al_2O_3 which on reaction with H_2 leads to the formation of COS and H_2S. The addition of formic acid to the reactants leads to a reversible loss of activity, but detailed long term studies show that formic acid is not formed during the operation of the catalyst over a wide range of conditions.

KEY WORDS: COS hydrolysis; γ-alumina; formic acid.

1. Introduction

The removal of sulphur from petrochemical feedstocks is a matter of immense current concern. Sulphur is a potent catalyst poison and so must be removed effectively. However, sulphur emissions cannot be vented to the atmosphere since they represent a potent source of acid rain. Hence the chemical industry has for many years operated sulphur removal technologies that are finely tuned, and are increasingly being made more effective. Most sulphur present in hydrocarbon feedstocks is removed by hydrodesulphurisation to form H_2S that is subsequently absorbed onto ZnO. This process does not affect COS which is a potent catalyst poison, and consequently a different strategy is used to form H_2S and this is COS hydrolysis (COS + H_2O = CO_2 + H_2S). This process has been well studied and to date alumina and titania have been found to be promising catalysts [1–5].

There has been interest in improving the activity of catalysts by the addition of promoters or by variation in the operating conditions. In commercial processes γ-Al_2O_3 is a favoured catalyst and this is operated at high temperatures, typically 220 °C. It is known that the rate of COS hydrolysis can be increased by the presence of a base [6, 7] and that basic sites were essential for the reaction. To date, a wide range of alkali metals (Li, Na, K, and Cs), alkaline earth metals (Mg, Ca, Sr, and Ba), first row transition metals (Fe, Co, Ni, Cu and Zn) and Sn have been considered as catalyst promoters [4, 8–11]. In our previous studies we have investigated the COS hydrolysis reaction at low temperature, since there has been a quest to identify catalysts capable of operation at lower temperatures [12, 13]. We have shown that modification of alumina with Zn^{2+} is effective at temperatures as low as 30 °C but we did not study the effects of temperatures above 100 °C, where inhibition by water is not so pronounced. In this paper we extend our studies to the evaluation of non promoted γ-Al_2O_3 at 220 °C and in particular to determine if formic acid is a possible trace by-product at this higher temperature.

2. Experimental

γ-Al_2O_3 (Johnson Matthey, No. 55-1, BET surface area 300 $m^2\ g^{-1}$) was ground to 150–250 μm particles and used as a catalyst in all the experiments. Thermogravimetric analysis was obtained using a Perkin–Elmer TGA 7 Thermogravimetric Analyzer. COS hydrolysis was carried out using a standard laboratory microreactor with on-line analysis of the products using gas chromatography fitted with a flame photometric detector, as described previously [10–13]. Blank experiments using an empty reactor or a reactor containing glass wool showed that in both cases, within experimental error, there was no COS hydrolysis reaction occurred at 220 °C in the absence of catalyst.

^{1}H NMR (400 MHz) was used for formic acid analysis in COS hydrolysis. Formic acid was absorbed in ethanolamine solution and D_2O was used as a solvent. The characteristic formic acid peak appears around 8.2–8.3 ppm in the ^{1}H NMR spectra. Detailed

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experiments showed that levels as low as 10 ppm formic acid can be determined using this technique.

3. Results and discussion

Initial experiments were performed without the introduction of water to the feedstock. In these experiments N_2 was used as a diluent for COS and before introduction to the reactor it was dried using a zeolite bed to remove traces of H_2O. γ-Al_2O_3 was reacted at 220 °C at atmospheric pressure without pretreatment, hence there was some adsorbed water or hydroxyl groups on the surface of γ-Al_2O_3. The results are shown in figure 1, and in the initial stage of the reaction (0–2 h), COS conversion was 100%. After ca. 2 h, COS conversion declines gradually with increasing time on-line and reached ca. 40% after 7 h. H_2S selectivity increased initially and reached a maximum of ca. 60% after 1 h on-line. H_2S selectivity then decreased with increasing time on-line and a steady level of ca. 40% was reached after ca. 2 h. COS conversion declined to ca. 4% and H_2S selectivity was zero after 40 h on-line (data not shown in figure 1 for clarity). TGA analysis gave a total weight loss of 15.8% of H_2O for the untreated γ-Al_2O_3 of which the majority was associated with loss of physisorbed water at ca. 100 °C, but 7.2% occurred at >220 °C, i.e. above the reaction temperature used in this study, and it is associated with loss of surface hydroxyls. In the experiment described above the COS feedrate was 7.2×10^{-5} mol h^{-1} and the amount of water present in the γ-Al_2O_3 is estimated from the TGA data as 8×10^{-5} mol, and this is comparable to the COS converted in the absence of co-fed water. This result shows that COS hydrolysis precedes *via* reaction of COS with surface hydroxyl groups.

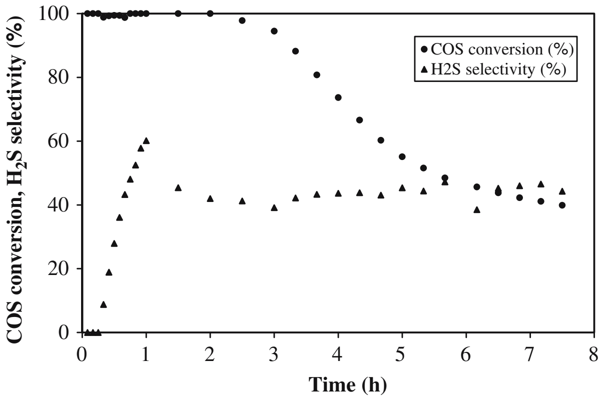

Figure 1. COS hydrolysis over γ-Al_2O_3 in the absence of H_2O. Reaction conditions: γ-Al_2O_3: 0.2 g (0.27 mL); 0.5% COS/N_2: 5.8 mL min^{-1}; N_2: 18 mL min^{-1}; 220 °C.

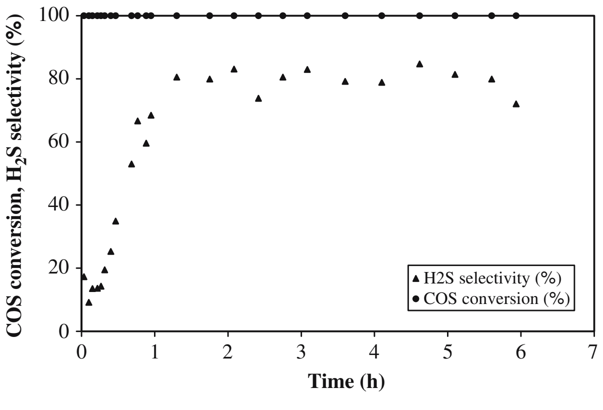

Figure 2. COS hydrolysis over γ-Al_2O_3 catalyst. Reaction conditions: γ-Al_2O_3: 0.5 g (0.68 mL); 0.5% COS/N_2: 5.8 mL min^{-1}; N_2: 18 mL min^{-1}; H_2O: 0.11 mL min^{-1}; 220 °C.

COS hydrolysis over γ-Al_2O_3 was carried out at 220 °C in the presence of water and the results are shown in figure 2. 100% COS conversion was observed during this initial test period of 6 h. H_2S selectivity increased reaching a steady level of ca. 80% after ca. 1 h. This reaction was continued for ca. 262 h and 100% conversion was maintained. When the catalyst was discharged from the reactor, a mixture of yellow solid and liquid was observed and this was confirmed by XRD and Raman spectroscopy to be sulphur. In total 0.108 g of sulphur was collected which over the 262 h timescale of the experiment represents a selectivity to elemental sulphur of ca. 18%. When this figure is combined with the selectivity to H_2S of ca. 80% (figure 2) an excellent sulphur mass balance was demonstrated in this prolonged timescale experiment.

Experiments of COS hydrolysis using COS/H_2O mixtures therefore lead to the formation of elemental sulphur, which would be detrimental to the operation of these catalysts in commercial reactors. In the industrial reactor the reaction mixture comprises $CO/CO_2/N_2/H_2$ in addition to COS/H_2O. To mimic the conditions used in industrial reactors, $CO/CO_2/N_2/H_2$ was added to the feedstock and the effect on COS hydrolysis at 220 °C was investigated. The results are shown in figure 3 and

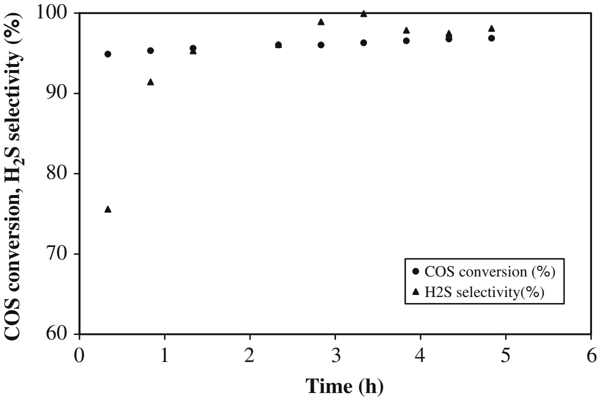

Figure 3. COS hydrolysis using γ-Al_2O_3 in the presence of $CO/CO_2/N_2/H_2$. Reaction conditions: γ-Al_2O_3: 0.5 g (0.68 mL); 0.5% COS/N_2: 5.8 mL min^{-1}; N_2: 18 mL min^{-1}; H_2O: 0.11 mL min^{-1}; 13% CO/13% CO_2/24% N_2/50% H_2: 1.0 mL min^{-1}; 220 °C.

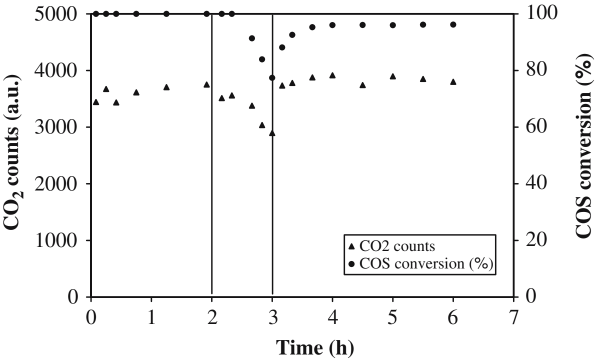

Figure 4. COS hydrolysis at 220 °C over alumina with a short period of HCOOH introduction to the feedstock. Conditions: γ-Al_2O_3 (0.2 g); 0.5% COS/N_2: 5.8 mL min^{-1}; N_2: 18 mL min^{-1}; H_2O: 0.11 mL min^{-1}; Reaction time 2–3 h: N_2 (10.4 mL min^{-1}) passed through a formic acid saturator at 0 °C.

compared with the results of COS hydrolysis in the absence of $CO/CO_2/N_2/H_2$ in the feedstock (figure 2), a slightly lower COS conversion (ca. 96%) was observed. H_2S selectivity initially increased and almost 100% H_2S selectivity was observed after ca. 1 h. No elemental sulphur was observed after 20 h reaction, which is consistent with the 100% H_2S selectivity measured.

Since no elemental sulphur was observed an experiment was carried out in which γ-Al_2O_3 (0.2 g) was mixed by grinding with elemental sulphur (0.02 g) and reacted with $CO/CO_2/N_2/H_2$ at 220 °C. COS and H_2S were detected as products indicating that a reaction between elemental sulphur and $CO/CO_2/H_2$ occurs under industrial conditions.

It is feasible that during the COS hydrolysis reactions that traces of formic acid could be formed and consequently we investigated the effect of formic acid on the COS hydrolysis reaction. Experiments showed that formic acid decomposed readily at 220 °C when fed independently as a dilute reactant; however, it is still possible that trace amounts can persist and these can affect the overall reactivity of the alumina catalyst. An experiment was carried out at 220 °C in which the steady state activity for COS hydrolysis over alumina was first established and then the reactants were doped with formic acid. The results, shown in figure 4, indicate that when formic acid is introduced the COS conversion decreases, but when formic acid is removed from the reactor feed the COS conversion recovers, indicating that formic acid acts as a temporary poison for this reaction. However, if it is formed at trace levels then it could lead to the long-term deactivation of the alumina catalyst. Hence we set out to carry out a detailed set of experiments to determine if formic acid could be formed during COS hydrolysis. After investigation of methods to determine formic acid at very low concentrations we found that ^1H NMR spectroscopy provided the most accurate and reliable method. A series of experiments were conducted using γ-Al_2O_3 as catalyst (Table 1) in which the reactor effluent was fed to an ethanolamine trap, which was subsequently analysed by ^1H NMR spectroscopy. However after these extensive studies, no formic acid was found from the COS hydrolysis reaction. It should be noted that experiments were carried out at low temperatures at which formic acid is stable over γ-Al_2O_3. Furthermore, the detection limit of the analysis technique is 10 ppm, and considering the time scale of the experiment the results are highly significant. In addition experiments were also carried out with a zinc-modified catalyst (1.4% ZnO/Al_2O_3), as in our previous studies we have shown zinc promotion can be effective at low reaction temperatures [10]. Again no formic acid was observed.

Table 1
Summary of the experiments for the investigation of formic acid formation during COS hydrolysis[a]

Feedstock	Catalyst	Temp (°C)	Running time (h)
COS + H_2O	γ-Al_2O_3	30–60	7
		220	7, 20, 119, 263, 408
	1.4% ZnO/Al_2O_3	220	591
COS + H_2O + $CO/CO_2/N_2/H_2$	γ-Al_2O_3	220	20, 162
$CO/CO_2/N_2/H_2$ + H_2O		50 220	23, 162

[a] No formic acid was detected during these experiments

4. Conclusions

Experiments show that γ-Al_2O_3 is an effective catalyst at 220 °C and that in the absence of $CO/CO_2/H_2$ elemental sulphur is formed in substantial quantities. This indicates that experiments studying this reaction are best conducted over relatively long timescales and reaction mixtures that emulate industrial feedstocks are preferred. Additionally, we have shown that formic acid acts as a reversible poison, but that it is not formed during this reaction.

Acknowledgments

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