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COS hydrolysis using zinc-promoted alumina catalysts

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The effect of doping alumina catalysts with zinc oxide is investigated for the COS hydrolysis reaction ($COS + H_2O = CO_2 + H_2S$) at 150 °C. The effect of the catalyst preparation method is described and discussed, and two methods are compared, namely: impregnation by incipient wetness of zinc nitrate followed by calcination to form the oxide and coprecipitation to form a hydroxide followed by calcination. The most effective zinc-promoted catalysts are prepared using the incipient wetness impregnation method. The promotional effect of zinc oxide on alumina is only observed on the basis of intrinsic activity and is not particularly significant at the initial time on stream, but becomes more marked with increased reaction time. The addition of the zinc oxide therefore decreases the deactivation and experiments using catalysts pretreated with H_2S and H_2O show that the alumina is deactivated by adsorption of these reactants. However, the effect is related to ZnO acting as a sulfur scavenger at 150 °C and we conclude that any promotional effect is likely to be relatively short lived.

KEY WORDS: COS hydrolysis; γ-alumina; catalyst promotion.

1. Introduction

There is presently significant interest in environmental issues and in particular there is general concern about emissions of pollutants to the atmosphere. While much of the focus of this interest concerns carbon dioxide and global warming, there have been sustained efforts concerning the reduction of sulfur containing emissions for many years. The reason for this is sulfur emissions from the combustion of hydrocarbon fuels leads to the formation of sulfur dioxide which is a potent precursor of acid rain. Consequently there has been continued interest in removing sulfur from process streams in chemicals production. Most sulfur present in hydrocarbon feedstocks is removed by hydrodesulfurisation 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 [1–6].

There has been interest in improving the activity of catalysts by the addition of promoters and to date most of these studies have concerned the modification of alumina to affect its acid/base properties. George [7] and Fiedorow *et al.* [8] demonstrated that the rate of COS hydrolysis could be increased by the presence of a base and that basic sites were essential for the reaction. To date, a wide range of alkali metals (Li, Na, K, Cs), alkaline earth metals (Mg, Ca, Sr, Ba), first row transition metals (Fe, Co, Ni, Cu, Zn) and Sn have been considered as catalyst promoters [9–13]. In our previous studies 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 earlier studies concerning the promotional effect of zinc and present our results for the use of zinc-promoted catalysts for the hydrolysis of COS at 150 °C.

2. Experimental

2.1. *Catalyst preparation*

Catalysts were prepared using impregnation with incipient wetness and coprecipitation as follows.

2.1.1. *Incipient wetness impregnation*

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 support. The appropriate amount of metal nitrate was dissolved in distilled water (0.9 mL) to form an aqueous solution. The solution was added dropwise to γ-Al_2O_3 particles (1 g) and the solid was shaken for 10 min to ensure uniform distribution of the solution. The wet solid was dried in air (90 °C, 16 h). TGA results showed that metal nitrate on alumina decomposed at 450 °C, the catalyst precursors were calcined at 500 °C for 3 h in static air, at the temperature ramp rate of 10 °C min^{-1}, to obtain the final catalysts.

About 1.3%ZnS/Al_2O_3 was prepared using a two-step incipient wetness method as follows: $Zn(NO_3)_2.6H_2$

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O (0.0480 g) was dissolved in distilled water (0.9 mL) to form an aqueous solution. The solution was added dropwise to γ-Al_2O_3 particles (1 g), which was shaken manually to ensure uniform distribution of the solution. The wet solid was dried at 90 °C overnight. $(NH_4)_2S$ (1 mL, 0.159 mol L^{-1}) solution was added dropwise to the dried precursor and the mixture was shaken. The wet solid was dried at 90 °C overnight and then calcined in air (500 °C, 3 h) to obtain the final catalyst.

2.1.2. Coprecipitation

The preparation procedure, using 1.3%ZnO/Al_2O_3 as an example, is as follows: $Zn(NO_3)_2.6H_2O$ (0.2350 g) and $Al(NO_3)_3.9H_2O$ (20.9 g) were dissolved in distilled water (30 mL) at room temperature and the solution was stirred continuously. Aqueous ammonia (17.5%) was added dropwise to the solution until a pH of 7.0–8.0 was attained. The suspension solution was kept stirring at room temperature for 2 h. The precipitate was recovered by filtration and dried in air (90 °C, 16 h). Calcination at 500 °C for 3 h in static air was used to obtain the final catalyst. The catalyst was crushed and sieved to particle size 150–250 μm and used for catalytic test.

2.2. Catalyst characterisation and COS hydrolysis

The catalysts were characterised using a number of techniques. The specific surface area was measured according to the BET method with the N_2 isotherm adsorption at 77 K using a Gemini 2360 Surface Analyser (Micromeritics). Before measurement, the samples were treated in N_2 (150 °C, 2 h). XRD patterns were obtained using an Enraf Nonius FR590 X-ray generator employing a CuK_α source ($\lambda = 1.5418$ Å), fitted with an Inel CPS 120° position sensitive detector. The tube voltage was set to 40 kV and the current was set to 30 mA. Each sample was scanned for 30 min. Thermogravimetric analysis was obtained using a Perkin Elmer TGA 7 Thermogravimetric Analyzer. Elemental analysis was carried out using atomic absorption spectroscopy (Varian 55B Atomic Absorption Spectrometer).

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 [12,13].

3. Results and discussion

A series of catalysts were prepared using the incipient wetness and coprecipitation methods. TGA of the uncalcined 0.4, 1.3, 2.6 and 4.1%ZnO/Al_2O_3 nitrate-doped catalyst precursors show very similar weight loss profiles with maxima at ca. 100, 300 and 500 °C respectively with the total mass loss being consistent with the loading of $Zn(NO_3)_2.6H_2O$ and its decomposition to the oxide. $Zn(NO_3)_2.6H_2O$ in the absence of alumina showed three weight losses at ca. 150, 260 and 420 °C, indicating that the nitrate is stabilised by being supported on alumina. Consequently catalysts were calcined at 500 °C to ensure the nitrate was decomposed to the oxide. Elemental analysis of the catalysts after calcination at 500 °C showed that the loading of ZnO was as expected.

The 1.3%ZnO/Al_2O_3 catalyst precursor prepared by coprecipitation was similarly investigated and three weight loss maxima are observed at ca. 100, 340 and 500 °C. A reference sample of $Zn(OH)_2$ also prepared by coprecipitation showed weight losses at ca. 80, 220 and 330 °C. Consequently, the ZnO/Al_2O_3 catalyst precursor was calcined at 500 °C and elemental analysis confirmed the loading of ZnO was as expected.

The XRD patterns of γ-Al_2O_3 and Zn modified alumina catalysts are shown in figure 1. Similar XRD patterns have been observed for all the ZnO/Al_2O_3 catalysts, and all the broad reflections can be referenced

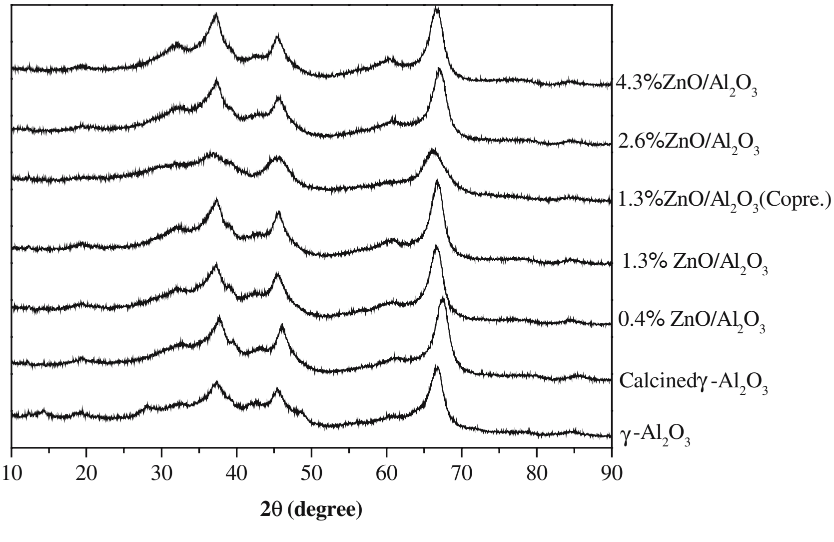

Figure 1. XRD patterns for γ-Al_2O_3 and zinc modified alumina catalysts.

to γ-Al_2O_3. Compared with the ZnO/Al_2O_3 catalysts prepared using the impregnation method, the 1.3%ZnO/Al_2O_3 catalyst prepared by a coprecipitation method shows slightly broader reflections, indicating smaller crystallites in this sample.

Based on the TGA data it is clear that the calcination temperature will have a significant effect on the nature of the material prepared and hence our initial catalyst testing was carried out to examine this parameter. We have previously shown [13] that the calcination temperature of alumina is important with respect to activity in COS hydrolysis activity at low temperatures (30–60 °C). In particular two maxima in activity are observed for alumina calcined at ca. 150 and 500 °C. At the lower temperature this is assigned to loss of physisorbed water and at the higher temperature it is due to surface dehydroxylation. Hence we examined the effect of calcination on the reactivity of the alumina for the COS hydrolysis reaction at 150°C. Figure 2 shows the conversion data for reaction at 1 h time on stream. It is clear that the same effects are observed but the effects at the higher temperature are not so marked. Alumina is significantly more active at this reaction temperature when heat treated at or below this reaction temperature, and this has consequences for catalyst preparation strategies. Similar experiments were carried out for the 1.3%ZnO/Al_2O_3 sample prepared by the impregnation method in the temperature range of 150–600 °C and these data are also shown in figure 2. The COS conversion for this material is clearly lower at all temperatures, but shows a maxima at ca. 500 °C. Hence on a catalyst mass basis the addition of this level of zinc is not beneficial during the initial time on stream.

To investigate the promotion effect of ZnO on alumina, a series of ZnO/Al_2O_3 with different ZnO loadings (0.4, 1.3 and 4.1%), were prepared using an impregnation method, calcined at 500°C and tested at 150 °C for COS hydrolysis. Results presented as intrinsic activities are compared with γ-Al_2O_3 in table 1. At initial time on stream modification with zinc oxide does not significantly enhance activity. After 400 min on line, the activities of all catalysts decline, but marked differences are observed. γ-Al_2O_3 and 0.4%ZnO/Al_2O_3 catalysts show very similar activity while 1.3%ZnO/Al_2O_3 and 4.1%ZnO/Al_2O_3 are more active than the unmodified alumina, and this is in agreement with our previous findings at lower reaction temperatures [6,12].

Comparison of the intrinsic activities for COS hydrolysis at 150 °C of 1.3%ZnO/Al_2O_3 catalysts prepared by impregnation and the coprecipitation methods with calcination at 500 °C has also been carried out and the results are given in table 1. The 1.3%ZnO/Al_2O_3 catalyst prepared by the impregnation method has better activities for COS hydrolysis at 150 °C than that prepared by coprecipitation. A sample of undoped

Table 1
Rates of COS hydrolysis for the range of catalysts studied

Catalyst[a]	Intrinsic activity[b]/10^{-8} mol COS conv m^{-2} s^{-1}	
	5 min	400 min
γ-Al_2O_3(i)	4.6	1.8
0.4%ZnO/Al_2O_3(i)	4.2	1.8
1.3%ZnO/Al_2O_3(i)	5.1	3.2
4.1%ZnO/Al_2O_3(i)	4.3	3.1
1.3%ZnO/Al_2O_3(p)	4.0	2.4
Al_2O_3(p)	2.5	1.0

[a] (i) catalysts prepared using impregnation, (p) catalysts prepared using precipitation.
[b] activity per m^2 at the times stated.

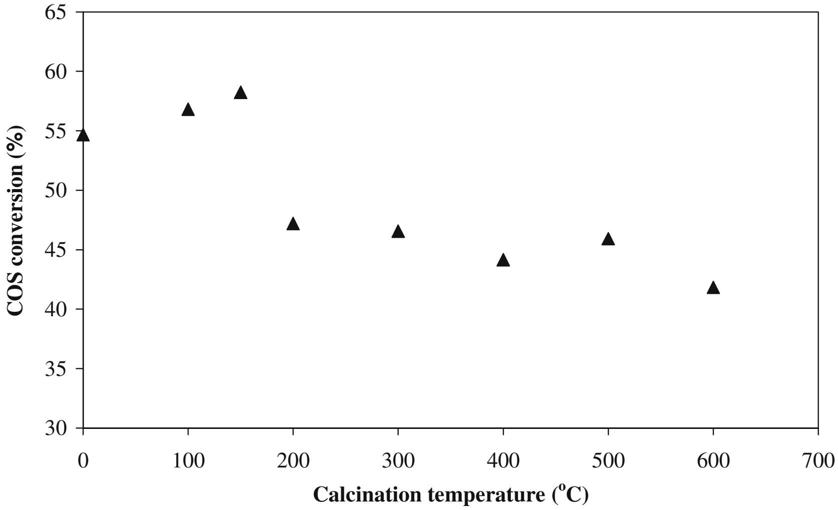

Figure 2. Effect of γ-Al_2O_3 thermal treatment on the activity for COS hydrolysis. Calcination temperature "0" denotes untreated alumina. Conditions: γ-Al_2O_3: 10 mg diluted by 500 mg silicon carbide; 0.5%COS/N_2: 58 mL min^{-1}; N_2: 180 mL min^{-1}; H_2O: 4559 ppm; reaction temperature: 150 °C.

alumina was prepared by precipitation and this was found to have the lowest activity. The key finding is that the addition of zinc decreases the rate of deactivation that is very pronounced with the undoped alumina catalysts (Table 1).

We investigated the effect of zinc addition on deactivation during COS hydrolysis using pre-treatment with H_2S and H_2S/H_2O (150 °C, 1 h, 0.28%H_2S/N_2 41 mL min^{-1}, 0.28%H_2S/0.26%H_2O/N_2 41 mL min^{-1}). The results for γ-Al_2O_3 and 1.3%ZnO/Al_2O_3 are shown in figures 3 and 4 respectively. The untreated alumina catalyst rapidly deactivates in the initial stages of the reaction (0–2 h) and the activity in terms of COS conversion decreases rapidly from ca. 68% to ca. 40% under the conditions investigated. Subsequently after 2 h on line, the activity only decreases slightly with increasing time. For the catalysts pre-treated using H_2S and H_2S/H_2O, different activity profiles are observed and a steady activity corresponding to that observed with alumina after ca. 2 h on line is observed with both treatments from the start. This shows that the initial deactivation is caused by sulfiding the alumina surface.

The same pre-treatment procedure was performed with 1.3%ZnO/Al_2O_3 and the catalysts were tested using the same conditions. The results are presented in figure 4. The two catalysts pre-treated using H_2S and H_2S/H_2O respectively demonstrate almost the same activity for COS hydrolysis, and, in contrast to the pre-treated alumina catalysts, both show deactivation throughout the timescale of the experiment. For

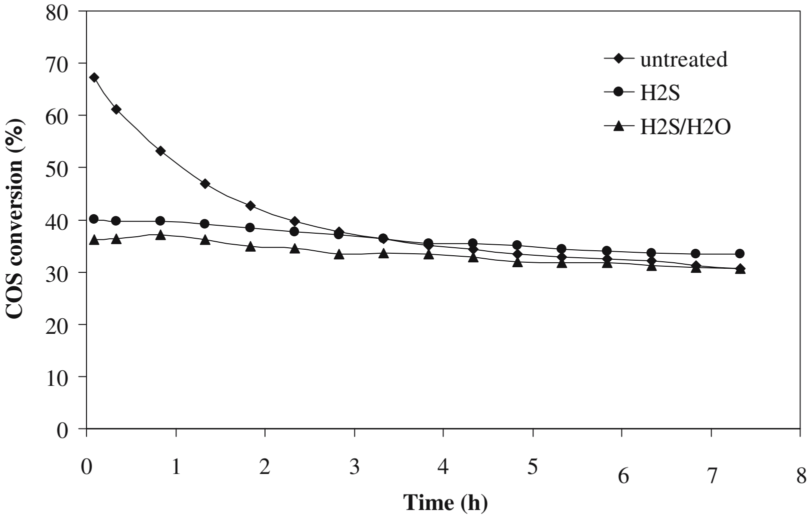

Figure 3. Effect of pre-treatment with H_2S/N_2 and $H_2S/H_2O/N_2$ on the activity of alumina for COS hydrolysis. Conditions: catalyst: 10 mg diluted by 500 mg silicon carbide; 0.5%COS/N_2: 58 mL min^{-1}; N_2: 180 mL min^{-1}; H_2O: 4559 ppm; reaction temperature: 150 °C.

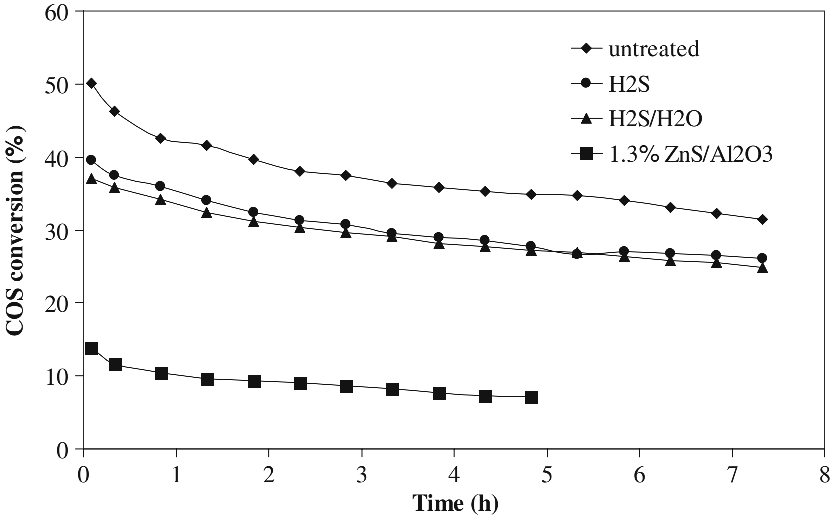

Figure 4. Effect of pre-treatment with H_2S/N_2 and $H_2S/H_2O/N_2$ on the activity of 1.3%ZnO/Al_2O_3 for COS hydrolysis at 150 °C. Conditions: catalyst: 10 mg diluted by 500 mg silicon carbide; 0.5%COS/N_2: 58 mL min^{-1}; N_2: 180 mL min^{-1}; H_2O: 4559 ppm; reaction temperature: 150 °C.

comparison, the results for 1.3%ZnS/Al_2O_3 prepared using a two stage preparation procedure is also shown in figure 4. This is much less active than 1.3%ZnO/Al_2O_3, although the surface area is comparable. We have found that non-supported ZnS, prepared by precipitation and sulfiding, is totally inactive for this reaction, whereas non-supported ZnO is active with an intrinsic activity comparable to the supported ZnO/Al_2O_3 catalysts. These data confirm that a fully sulfided zinc-modified alumina catalyst is likely to show limited activity. However, these results do help to explain the manner in which zinc modification decreases the rate of deactivation during the COS hydrolysis reaction. We consider that the role of zinc is to act as a sink for sulfur species that would decrease the activity of the alumina. The sulfur balance during use with an alumina catalyst is almost 100% and so very little sulfur is retained on the catalyst on the timescale of these experiments, but this is very effectively scavenged by stoichiometric reaction with ZnO.

Consequently, we conclude that the promotional effect on the intrinsic activity observed on addition of ZnO to alumina is likely to be short lived. Hence, we are reconsidering our strategy with respect to the identification of promoters for alumina for the COS hydrolysis reaction since we need to identify additives that act as long term promoters.

Acknowledgments

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