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Water–gas shift conversion using a feed with a low steam to carbon monoxide ratio and containing sulphur

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Abstract

Based on thermodynamic calculations a discussion was given on the need for operation of the water–gas shift (WGS) reaction with a low H_2O/CO ratio when a H_2-separation membrane is combined with the reaction and on the degree of possible formation of C and CH_4 as the result of side reactions occurring in the mixture of CO, H_2O, CO_2 and H_2 under WGS conditions. The behaviour of a number of materials including Fe–Cr, Cu–Zn, Co–Cr and Pt/ZrO_2 were examined under the conditions where the ratio of H_2O to CO in the feed was low, with and without the presence of H_2S in the feed. The experimental results suggested that Pt/ZrO_2 has potential for use in these conditions.

Keywords: Water–gas shift conversion; Steam to carbon monoxide ratio; Sulphur

1. Introduction

The water–gas shift (WGS) reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$$\Delta H^\circ = -40.6\,\mathrm{kJ\,mol^{-1}} \qquad (1)$$

is used for the conversion of CO and H_2O to CO_2 and H_2 in ammonia synthesis and methanol synthesis [1]. As the reaction is exothermic the conversion of CO decreases with increase of temperature. A two-step CO shift is usually employed: the high temperature (ca. 350 to 420°C) CO shift using a Fe–Cr based catalyst; and the low temperature (ca. 180 to 250°C) shift using a Cu–Zn based catalyst. In order to achieve higher CO conversions, the steam to carbon monoxide ratio in the feed, R, is usually higher than that actually required by the reaction stoichiometry ($R = 1$) and the energy efficiency is therefore low.

When a H_2-separation membrane is combined with the WGS reaction through which the H_2 produced by the reaction is continuously removed from the reaction stream, this would allow the reaction to be operated at a low ratio of H_2O to CO without suffering the thermodynamic constrain [2,3]. The operation cost would be lowered. The use of a H_2-separation membrane would also make it possible for the WGS reaction to be carried out in one step, provided that a suitable catalyst is used.

However, problems may arise when using a feed with a low H_2O to CO ratio. Side reactions may become important when the H_2O/CO ratio is low, producing undesired products such as carbon and/or methane. For instance, in a gas

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system containing CO, CO_2, H_2O and H_2, the following side reactions may occur:

$$2CO \rightleftharpoons C + CO_2 \tag{2}$$

$$CO + H_2 \rightleftharpoons C + H_2O \tag{3}$$

$$CO_2 + 2H_2 \rightleftharpoons C + 2H_2O \tag{4}$$

$$2CO + 2H_2 \rightleftharpoons CO_2 + CH_4 \tag{5}$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \tag{6}$$

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \tag{7}$$

$$C + 2H_2 \rightleftharpoons CH_4 \tag{8}$$

In these reactions, carbon and methane can be formed either as final products or they can take part in further reactions. The extent to which these reactions proceed depends greatly on the catalyst system used, the reaction conditions and the kinetics of each reaction. If these reactions occur significantly during the WGS reaction, a series of problems can arise. For example, the formation of carbon would block the catalyst bed and would cause catalyst deactivation, an increase in pressure drop across the catalyst bed, plugging and fouling of equipment, and eventually lead to a run-down of the process [1]. If a H_2-separation membrane is involved, the coke formed may also block the pores of the membrane, hence lowering its permeability. The formation of methane would also consume valuable hydrogen and change the final product composition, this might cause difficulties in subsequent steps in the process involved. The selectivity of a catalyst for the WGS reaction, when operated at a low H_2O/CO ratio, is therefore very important.

In this paper we will firstly discuss the desirable features of a membrane for the reaction and the thermodynamics of the reaction, we then present data for a number of different catalysts when operated at low H_2O/CO ratios and show the behaviour of these catalysts when in the presence of H_2S. We show that a Pt/ZrO_2 catalyst has potential for use in these conditions.

2. Thermodynamic considerations

2.1. The effect of the H_2O to CO ratio on the maximum gain in CO conversion by using a H_2-separation membrane

The WGS reaction (1) is a moderately exothermic reaction. As shown in Fig. 1, the equilibrium constant of the reaction decreases as the reaction temperature increases, as does the equilibrium conversion of CO at a fixed H_2O to CO ratio, R, in the feed; at a fixed temperature, without using a H_2-separation membrane, the

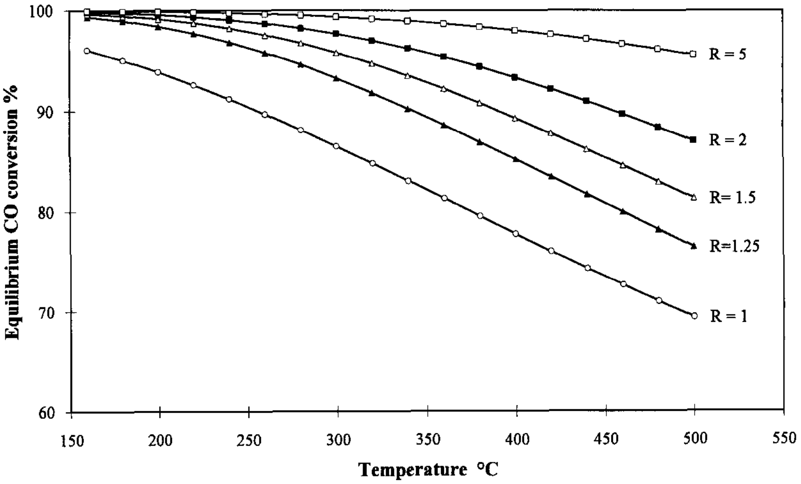

Fig. 1. Variation of the equilibrium conversion of CO as a function of the H_2O to CO ratio (R) in the feed at different temperatures.

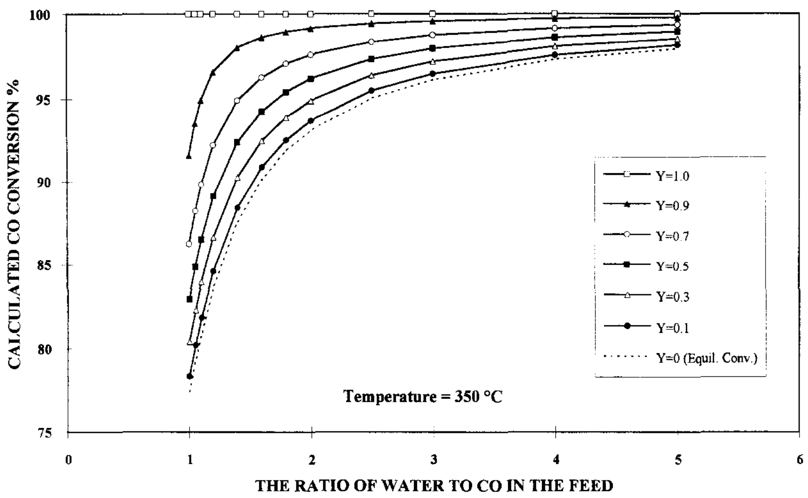

Fig. 2. The enhancement of CO conversion when a H_2-separation membrane having different H_2 separation efficiencies (Y denotes the fraction of H_2 being separated through a membrane) is incorporated with the WGS reaction as a function of the H_2O to CO ratio, R, in the feed at a constant temperature of 350°C.

equilibrium conversion of CO will increase as R increases. When a H_2-separation membrane is incorporated, the equilibrium for CO conversion will be shifted by removing H_2 selectively from the reaction mixture; the maximum benefit in the conversion of CO by using such a membrane will be obtained at the point where the equilibrium conversion (in the absence of a membrane) is the lowest, i.e. when R approaches 1. This is illustrated more clearly in Fig. 2, in which the CO conversion enhancement due to the use of a membrane having different H_2 separation efficiencies, Y, (the Y value in Fig. 2 denotes the mole fraction of total H_2 being separated through a membrane) is plotted as a function of the H_2O to CO ratio, R, at a constant temperature of 350°C. Fig. 2 shows that the lower the R value, the higher is the CO conversion enhancement obtained by using the membrane. Fig. 2 also shows that a membrane

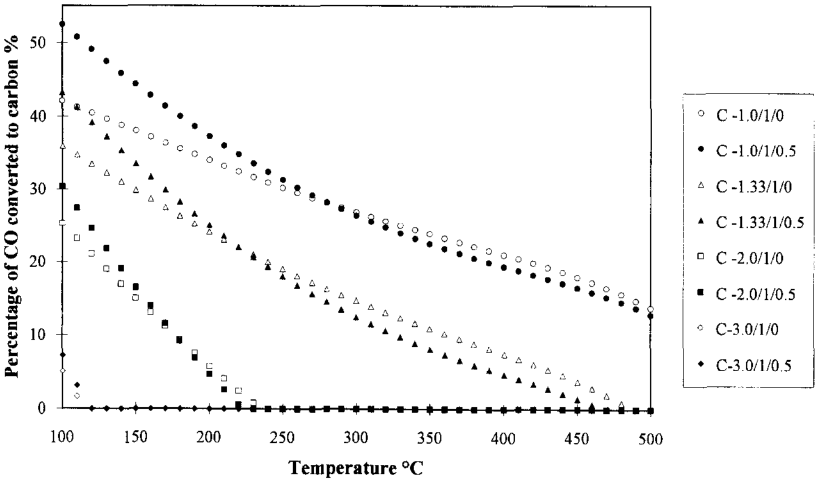

Fig. 3. Possible formation of carbon as a function of temperature with various $H_2O/CO/H_2$ ratios in the feed, calculated from the thermodynamic equilibrium composition of the reactions concerned. C-$x/y/z$ denotes the mole ratio of $H_2O/CO/H_2$ in the feed.

with a high H_2 separation efficiency (higher Y value) is preferred as the gain in CO conversion is proportional to the Y value. When only the H_2 formed during the reaction is removed by the membrane ($Y = 1$, e.g. with a Pd-based membrane), the CO conversion is increased to 100%.

A membrane with a high H_2 separation efficiency (high Y), i.e. a high permeability and permselectivity, is preferable when it is to be used with the WGS reaction; the enhancement of CO conversion due to the use of a membrane is however more pronounced when the feed H_2O/CO ratio is low. The maximum enhancement is achieved when R approaches unity.

2.2. The effect of the H_2O to CO ratio on the possible formation of C and CH_4

As discussed in Introduction, several side reactions may occur in a gas mixture containing CO, CO_2, H_2O and H_2 under WGS conditions. The equilibrium composition of such a reaction system will be altered if the ratio of H_2O to CO in the feed varies. A thermodynamic calculation of the equilibrium composition with various ratios of $H_2O/CO/H_2$ in the feed was thus performed, considering a system in which reactions (1) to (8) can occur. Figs. 3 and 4 show the calculation results on the amounts of carbon (C) and methane (CH_4) being formed at equilibrium, on the basis of the CO in the feed, at different temperatures for various feed ratios of $H_2O/CO/H_2$.

Fig. 3 shows that the formation of carbon is in general favoured at low temperature, particularly at a low H_2O to CO ratio. When the H_2O to CO ratio, R, is larger than 2, carbon will not exist in the equilibrium mixture when the reaction temperature is higher than 230°C. However, as the ratio decreases, the risk of carbon formation due to the side reactions increases. When $R = 1$, the formation of carbon becomes thermodynamically favourable over the entire temperature range examined. The presence of H_2 in the feed has less effect on the temperature range for carbon-free operation than does the R value. Results of calculation of the effect of CO_2 (not shown here) indicated that the presence of CO_2 in the feed has negligible influence on the shape and position of the curves in Fig. 3.

The effect of the feed gas composition on the formation of CH_4 (see Fig. 4) is more complicated. In general, methane can exist in the equilibrium composition over the whole temperature range examined with maximum formation

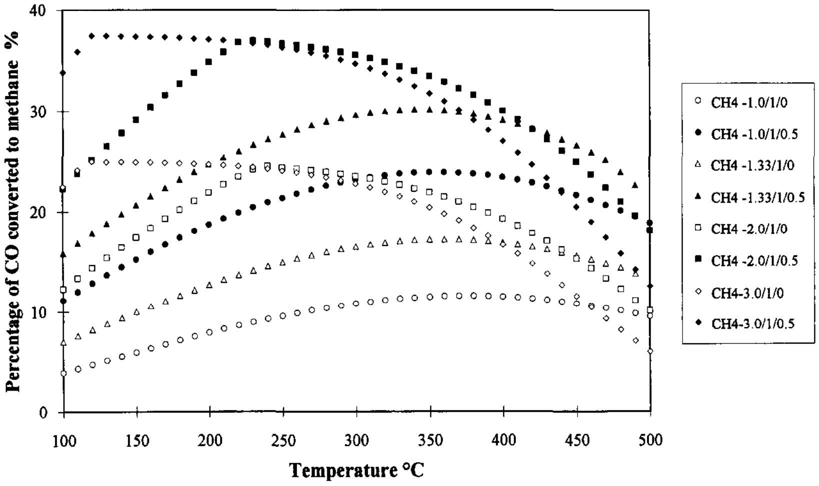

Fig. 4. Possible formation of CH_4 as a function of temperature with various $H_2O/CO/H_2$ ratios in the feed, calculated from the thermodynamic equilibrium composition of the reactions concerned. CH_4-$x/y/z$ denotes the mole ratio of $H_2O/CO/H_2$ in the feed.

(except when $R \geq 3$) occurring between 200 and 450°C, the practical temperature range in which the WGS reaction is operated. An increase in the H_2O/CO ratio, R, from 1 to 2 tends to give more CH_4 in the equilibrium gas composition; a further increase of R to 3 leads to a lower percentage of CO being converted to CH_4 at the high temperature side. The presence of H_2 in the feed appears to have a significantly positive influence of the formation of CH_4.

It should be stressed that the above examination is solely based on the thermodynamic calculation of the reaction system, and that it is therefore only an indication of the possibility of the formation of C and CH_4 in such a system if the thermodynamic equilibrium is reached. In practice, the extent to which those side reactions actually proceed will depend greatly on the kinetics of each reaction for the catalyst used. Nevertheless, these calculations point out the potential risk of C and CH_4 formation if the WGS reaction is to be operated at a low H_2O/CO ratio and emphasise the importance of the catalyst selectivity. The results also suggest that the use of a H_2-separation membrane in the WGS reaction can reduce the potential driving force for CH_4 formation by removing H_2 selectively from the reaction stream.

3. Experimental

3.1. Catalysts

The catalysts which were examined in this work are given in Table 1. All the catalyst samples were made into grains of 0.212 to 0.425 mm in size. The catalyst load for the activity experiments was 200 mg, unless otherwise specified. The catalyst was reduced before the activity measurement commenced. The reduction treatment varied from catalyst to catalyst and details will be given in the Results section.

Table 1
The catalysts examined in this work

Fe–Cr	Commercial high-temperature shift catalyst
Cu–Zn	Commercial low-temperature shift catalyst
Co–Cr	Laboratory-made sample with a Co:Cr molar ratio of 3:1
Pt/ZrO_2	Laboratory-made sample with 1 wt% of platinum

3.2. Activity measurements

The activity of each catalyst for the WGS reaction was examined in a quartz tubular reactor located in a Eurotherm-controlled furnace. The experiments were normally carried out over the temperature range 150 to 450°C and at approximately atmospheric pressure, with a total feed flow of 50 cm^3 (STP) min^{-1}. The feed mixture in most of the activity experiments had a H_2O to CO ratio of 1.33, consisting of CO (15%), H_2O (20%), CO_2 (5%), H_2 (5%) and N_2 (balance), unless otherwise specified. The H_2O was introduced by passing the dry gas mixture through a water saturator, the temperature of which was determined by the required water partial pressure and maintained with ±0.5°C. A HP 5980 II GC equipped with a Carboxen1000 column was used to determine the concentrations of CO, CO_2, H_2 and CH_4 (if formed) in the gas streams before and after the reactor.

The WGS activity of each catalyst was expressed in terms of the percentage of CO converted, calculated using the following equation:

$$X_{CO}(\%) = \frac{Y_{CO,in} - Y_{CO,out}}{Y_{CO,in}} \times 100\% \qquad (9)$$

where $Y_{CO,in}$ and $Y_{CO,out}$ are the number of moles of CO in the feed and in the reactor effluent, respectively. The data obtained from CO_2 and H_2 measurement were used to cross-check the CO conversion as calculated from those of CO. A satisfactory carbon balance was obtained as long as there was no carbon deposition on the catalyst.

4. Results and discussion

4.1. Reaction without a catalyst

It is known that the WGS reaction proceeds very slowly in gas phase at practical temperatures [1]. A blank test was performed and the results showed no detectable CO conversion at temperatures from 150 to 450°C. However, it was observed that a thin layer of carbon was formed gradually on the inner wall of the quartz reactor when the reaction mixture was heated to above 375°C, although no detectable deterioration of the carbon balance was found. The thermodynamic calculation described in the preceding section indicated that carbon could be formed below 450°C with a feed with a H_2O to CO ratio of 1.33. It is not clear whether this small amount of carbon forms by gas phase reactions or by reactions catalysed by the reactor wall. No methane was detected in the reactor effluent stream, indicating that no gas phase or reactor-wall catalysed reactions leading to the formation of CH_4 occurred in the temperature range examined.

4.2. Behaviour of commercial Fe–Cr and Cu–Zn catalysts when using a feed with low H_2O to CO ratio

The activities and selectivities of two commercial shift catalysts were examined under the standard experimental conditions and the results are presented as CO conversion vs. temperature in Fig. 5. The equilibrium conversion is also plotted in the figure as the dotted line.

The LT shift Cu–Zn catalyst appeared to be very active under the experimental conditions used, a CO conversion ca. 70% being obtained at about 200°C and equilibrium conversions were achieved at temperatures above 350°C. Neither carbon nor CH_4 was observed during the reaction, indicating that the Cu–Zn catalyst is not only very active but also very selective for the WGS reaction when operated with a low H_2O/CO ratio in the feed ($R = 1.33$).

The HT shift Fe–Cr catalyst, however, demonstrated WGS activity only at reaction temperatures above 300°C under the same conditions, the conversion of CO approaching equilibrium only at temperatures above 450°C. After an initial temperature cycle from 150 to 450°C

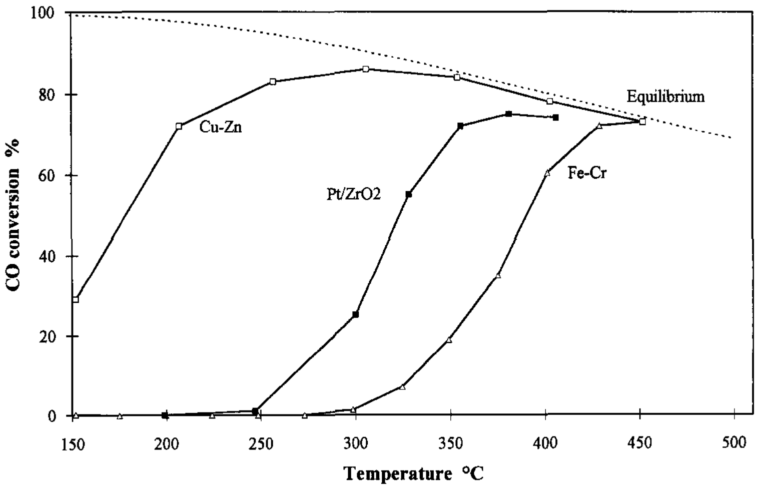

Fig. 5. The conversions of CO as a function of temperature over various catalysts.

the sample was left in the reaction stream at 350°C to test stability; a gradual decrease in the CO conversion, from 25 to 17%, was observed after 50 h. No pressure drop across the catalyst bed was recorded during the experiment nor was CH_4 formation observed in the effluent stream.

As in the blank experiments described above, a thin layer of carbon was formed on the inner wall of the reactor, but only touching the top layer of the catalyst bed from the feed side of the reactor; the rest of the reactor wall (that part in touch with and after the catalyst bed) remained carbon-free. It is likely that there was no carbon accumulation in the catalyst bed as there was neither an increase in the pressure drop across the catalyst bed nor was there any change in the carbon-balance from 100%. This was also found to be the case when a prolonged ageing test was conducted and even when the reaction was carried out using a feed with a H_2O/CO ratio as low as $R = 0.36$.

From these observations we may conclude that both LT Cu–Zn and HT Fe–Cr catalysts retain their high selectivity for the WGS reaction when operated with a feed having a low H_2O/CO ratio; there is no carbon accumulation nor detectable CH_4 formation on the catalysts during the reaction. Within the experimental range examined the selectivity of these catalysts for the WGS reaction does not change upon varying the H_2O/CO ratio in the feed.

4.3. Behaviour of the Co–Cr catalyst when using a feed with a low H_2O to CO ratio

Hutchings and co-workers [4,5] have recently reported that Co–Cr based catalysts are effective for the WGS reaction; since they become active in the temperature range 250–300°C Hutchings and his colleagues classified them as HT shift catalysts and showed that the Co–Cr materials were more active than a commercial Fe–Cr catalyst, the highest activity being obtained with the catalyst having a Co to Cr molar ratio of 3:1. They found that a small amount of CH_4 was formed and that these materials were relatively sulphur-resistant in comparison with the commercial ones.

However, most of the results reported by Hutchings and his colleagues were obtained using a feed with a H_2O/CO ratio of 4.5:1, very high in comparison with that used practically. To see how well the catalyst would work when operated at a low feed H_2O/CO ratio, a sample with a Co–Cr molar ratio of 3:1, prepared using

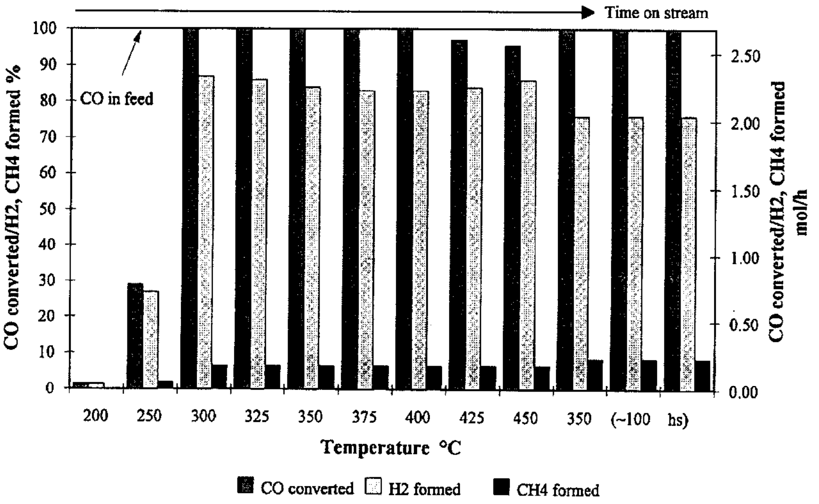

Fig. 6. CO converted and H_2 and CH_4 formed at different temperatures over the Co–Cr catalyst (the last two sets of data represent the results obtained at the beginning and the end of a period of 100 h at 350°C). Feed gas: $H_2O = 20\%$, $CO = 10\%$ and balance N_2.

a similar method to that reported in [4] and [5], was examined using a feed with H_2O:CO = 1.33:1. After a reduction treatment in H_2 at 400°C for about 12 h, the catalyst was subjected to the reaction temperature which was programmed to increase from 200 to 450°C in step of 50°C and hold for 4 h at each temperature step. The catalyst became active at a temperature of around 250°C; however, when the temperature reached 350°C, a significant amount of CH_4 was recorded in the reactor effluent stream, and the pressure drop across the reactor increased from less than 0.1 bar to larger than 0.5 bar in less than 2 h. Reactor blockage then occurred and the gas flow through the reactor decreased significantly so that the experiment was then terminated. The carbon balance calculated from the experimental data revealed that the number of carbon molecules leaving the reactor at temperatures above 250°C was considerably less than that entering the reactor, i.e. there was carbon accumulation in the reactor. A considerable amount of fine carbon powder was found within the catalyst bed after the experiment. Repeating the experiment gave exactly the same results.

The thermodynamic calculations reported above indicated that both C and CH_4 could formed when using a feed of H_2O:CO = 1.33 (Figs. 3 and 4). It appeared that the Co–Cr catalyst did catalyse side reactions producing both C and CH_4. The calculation also showed that no carbon would be present in the equilibrium composition if the ratio R is larger than 2 when the temperature is above about 230°C. A further experiment was thus carried out using a feed with H_2O:CO = 2 (H_2O 20%, CO 10% and balance N_2), the results of which are presented in Fig. 6.

At temperatures above 300°C, all the CO in the feed was converted; however, not all the CO and H_2O were converted to H_2 and CO_2 via the WGS reaction because the H_2 formed was less than 100% and there was also CH_4 formed as the reaction product. The last two series of data of Fig. 6 represent data taken at intervals at 350°C. Surprisingly, the conversion of CO was 100% (equilibrium conversion ca. 96% at 350°C if only the WGS reaction takes place) and the formation of H_2 was 76% and that of CH_4 was 8.5%, indicating the occurrence of side reactions. If all the reactions (1) to (8) reached equilibrium, the amounts of CH_4 formed would be the same as the values predicted in Fig. 4 and these would be about 24% of CO converted to CH_4 at 350°C. The much lower value observed implies that not all of reactions (1) to (8) were in equilibrium. Considering the reactions which form CH_4 form CO, CO_2 and H_2 (reactions (5), (6) and (7)), if reaction (1) occurred simultaneously with reaction (5) or reaction (6), or reaction (7) occurred sequentially after reaction (1), one would expect that the formation of each mole of CH_4 would correspond to a decrease of 4 moles of H_2 in the number that could be produced from the WGS reaction, so the amount of H_2 produced when 100% of feed CO is converted and 8.5% CH_4 is formed would be:

$$100\% - (4 \times 8.5\%) = 66\%$$

The actual value observed for H_2 formation was 76% (Fig. 6). We can therefore conclude that neither of these two reaction routes occurs and carbon formation reactions may also involved on this catalyst. The mechanism for the CH_4 formation may be very complicated and it is beyond the scope of the present study.

Carbon deposition was also observed on the Co–Cr catalyst when using the feed with H_2O:CO = 2, although the rate of carbon formation was much lower in this case than that when using a feed having H_2O:CO = 1.33. This observation is also an indication that reactions (1) to (8) were not all at equilibrium; if they had been, we should not have observed the formation of carbon at temperatures above 230°C (see Fig. 4).

These results allow us to conclude that the Co–Cr catalyst is very active but is not as selective as the Cu–Zn or Fe–Cr catalysts for the WGS reaction. It also catalyses other reactions producing both carbon and methane; the formation of C and CH_4 could be significant when the ratio of H_2O to CO in the feed is low. A further modification of the catalyst is therefore necessary to improve its selectivity if it is to be used for the WGS reaction.

4.4. *Behaviour of the Pt/ZrO_2 catalyst when using a feed with low H_2O to CO ratio*

During screening of various other catalysts [6], we found that a Pt/ZrO_2 catalyst was very active for the WGS reaction, in comparison to the commercial Fe–Cr based HT shift catalyst. Typical activity data for a Pt/ZrO_2 catalyst are shown in Fig. 5. It can be seen that the Pt/ZrO_2 catalyst gave a CO conversion of 72% at 350°C; under the same experimental conditions, the Fe–Cr catalyst gave only 19% conversion. A prolonged ageing test also showed that the Pt/ZrO_2 catalyst suffered less deactivation than did the Fe–Cr catalyst.

During the activity measurements a trace amount of CH_4 was observed in the reactor effluent stream when the temperature was increased to above 400°C in the first temperature cycle, but disappeared in a subsequent temperature cycle. The amount of CH_4 formed during the initial run, depending on the type of Pt/ZrO_2 catalysts tested, was estimated to be between 0.1 to 0.5% of the total CO in the feed. It is not clear why CH_4 was formed at the start of reaction and later disappeared; some surface sites, which can catalyse the methane formation reactions, may have been less stable under the WGS conditions and were therefore destroyed during initial stages of use of the catalyst.

As with the Fe–Cr catalyst, a small amount of carbon was found on the Pt/ZrO_2 catalyst, this being located at the very top layer of the catalyst bed in addition to that formed on the reactor wall above the catalyst bed. There seemed to no further accumulation of carbon as evidenced by the fact that there was no noticeable increase in the pressure drop across the catalyst bed even after the catalyst had been in contact with the reaction mixture for a few hundred hours. Further lowering of the water to CO ratio to $R = 0.33$ did not lead to any CH_4 formation nor to C accumulation on the catalyst.

4.5. *The behaviour of the catalysts in the presence of sulphur*

Sulphur compounds are major impurities present in the process gas derived from coal gasification and these are capable of causing deactivation of the WGS catalysts. Under WGS con-

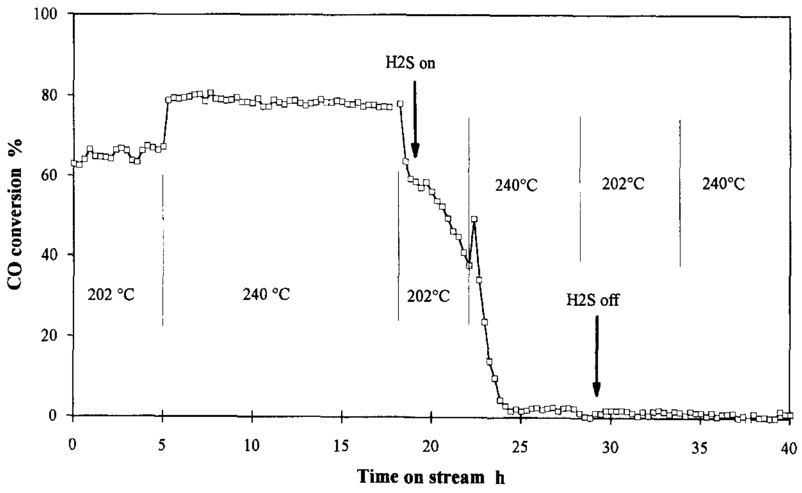

Fig. 7. The WGS activity of the Cu–Zn catalyst before and after the addition of 50 ppm of H_2S.

ditions, the sulphur is most likely to be in the form of H_2S. An investigation of the effect of sulphur on the performance of catalysts was therefore carried out by adding H_2S to the feed at different concentrations levels. Prior to H_2S addition, the catalyst was first stabilised in the sulphur-free reaction mixture. The effect of sulphur was examined in most cases at three values of temperature (300, 325 and 350°C) with H_2S levels in the feed ranging from 50 to 1000 ppm. The CO conversion levels over a catalyst were usually away from equilibrium in order to obtain a clear picture of the effect of sulphur addition on the catalyst activity.

4.5.1. Low-temperature shift copper-based catalyst

The CO conversions over the Cu–Zn catalyst with and without H_2S addition, as a function of reaction time at various temperatures are shown in Fig. 7. After the copper catalyst had been stabilised at 200 and 240°C for about 18 h, a concentration of 50 ppm H_2S was admitted to the feed. The catalyst deactivated completely and removal of H_2S from the feed later did not result in any noticeable return of the catalyst activity. This result indicates that the Cu–Zn catalyst is extremely susceptible to poisoning by sulphur, and this is consistent with results reported in the literature [7].

4.5.2. High-temperature shift iron-based catalyst

Table 2 shows the CO conversions over the HT Fe–Cr catalyst at different concentrations of H_2S. The catalyst was first stabilised by ageing in the sulphur-free reaction stream at 350°C for approximately 50 h before the H_2S was introduced; the concentrations of H_2S introduced into the feed were 50, 200 and 1000 ppm. The CO conversions over the catalyst were measured at 300, 325 and 350°C, the catalyst being kept for about 4 h at each temperature. The CO conversions after the H_2S was removed from the feed are also given in Table 2. It can be seen that the decrease in the activity on sulphur addition is proportional to the concentration of H_2S added; when 1000 ppm H_2S was present in the feed, the catalyst retained nearly a half of its activity and the initial activity was almost completely restored upon the removal of H_2S from the feed. These observations also agree well with those reported in the literature [1,8].

Table 2
The WGS activities of the Fe–Cr catalyst at various concentration levels of H_2S addition

Run conditions	X_{CO} (%)			E_a (kJ mol^{-1})
	300°C	325°C	350°C	
After 50 h at 350°C	3	7.3	17	117
50 ppm H_2S addition	2.4	6	14	105
200 ppm H_2S addition	2.4	6	11	100
1000 ppm H_2S addition	1.8	4	7.5	90
H_2S removal from the feed	1.5	7	17	

The effect of H_2S concentration in the feed on the activity of the Fe–Cr catalyst, shown in Table 2 can be correlated with the equation:

$$X_{CO} = k_1 P_{CO} \tag{11}$$

$$k_1 = a[H_2S]^b \tag{12}$$

where k_1 is the pseudo first order rate constant of the WGS reaction; a and b are constants related to the catalyst and to the experimental conditions used; and $[H_2S]$ denotes the H_2S concentration in the feed. For example, at 350°C, assuming P_{CO} remains constant, we have:

$$k_1 = 6.57 \times 10^{-5}[H_2S]^{-0.22} \tag{13}$$

when k_1 is in mol g^{-1} s^{-1} atm^{-1} and $[H_2S]$ in ppm. The apparent activation energy for the reaction of CO was found to decrease as the H_2S concentration in the feed increases and is also given in Table 2.

4.5.3. Co–Cr catalysts

The performance of a Co–Cr catalyst in the presence of sulphur was also evaluated using a feed with a H_2O to CO ratio of 2. In this experiment the catalyst load in the reactor was 100 mg and only one concentration level of H_2S of 200 ppm was used; the temperature of

Table 3
The WGS activity of the Co–Cr catalyst before and after H_2S addition

Condition	X_{CO} (%)		
	300°C	325°C	350°C
Fresh catalyst	58 → 39	72 → 78	98
200 ppm H_2S addition	18 → 12	24 → 21	45 → 29
After H_2S removal from the feed	2.5 → 3	7 → 8.5	16 → 17
After heating to 450°C and kept another 28 h at 350°C			23

the reaction was programmed to increase from 250 to 350°C in steps of 50°C. Table 3 shows the CO conversions measured under different situations. As the activity of the catalyst while staying at certain temperature levels (ca. 4 h at each temperature level) was found to decrease or increase continuously, the CO conversions at those temperatures are therefore shown as two values in the columns of Table 3, the first one being taken at the beginning of each temperature step and the second at the end. It appeared that the Co–Cr material showed very high activity in the absence of H_2S; an addition of 200 ppm of H_2S in the feed, however, caused the catalyst to deactivate severely. That the conversion was still decreasing at the end of 4 h at each value of temperature and that the conversion values measured immediately after the H_2S was removed from the feed were lower than those in the presence of H_2S indicated that the process of sulphur poisoning to the Co–Cr material was slow in comparison to Fe–Cr. After H_2S was removed from the feed, the conversion values climbed back only slightly and reached only 23% after the catalyst was heated to 450°C and then kept at 350°C for another 28 h.

These results indicate that the poisoning of the Co–Cr catalyst by sulphur is irreversible. However, the Co–Cr catalyst was more active than the HT shift Fe–Cr catalyst, either in the presence or the absence of the feed sulphur. This is consistent with the conclusions of Hutchings and co-workers [4,5]. That they did not observe deactivation of the Co–Cr (3:1) catalyst after ageing the catalyst for nearly 500 h may be due to their operation of the catalyst at high temperature (400°C) with high residence time (CO GHSV = 510 h^{-1}), so that the equilibrium conversion level was maintained during their experiments. The higher H_2O/CO ratio ($H_2O:CO = 4.5:1$) used in their experiment also certainly had a beneficial effect on the CO conversions which they measured.

4.5.4. *Pt/ZrO_2 catalyst*

The effect of adding H_2S to the feed on the WGS activity of the Pr/ZrO_2, as well as the effect of different treatments of the Pt/ZrO_2 catalysts after being poisoned by H_2S were also investigated. For example, one of the Pt/ZrO_2 catalysts tested showed a CO conversion $> 70\%$ at 300°C after ageing in the sulphur-free reaction stream for more than 100 h and still gave a conversion of 50% on addition of 50 ppm H_2S to the feed; furthermore, the activity was fully restored after H_2S was removed from the feed. Detailed results will be published in a separate paper [6].

In general, the Pt/ZrO_2 catalyst was found to deactivate when H_2S was present in the feed; however, the catalyst retained the highest WGS activity, in comparison with the Fe–Cr and Co–Cr catalysts, at all the H_2S addition levels studied. The S-deactivated catalyst was also found to be easily regenerated either by hydrogen treatment or by heating in the reaction mixture containing no H_2S.

5. Conclusions

1. Thermodynamic calculations show that in a reaction system containing a mixture of H_2O, CO, CO_2 and H_2, a considerable fraction of the feed CO can be converted to C and/or CH_4 as the result of side reactions occurring under WGS reaction conditions. The formation of CH_4 is possible over the entire temperature range regardless of the H_2O/CO ratio in the feed under

the conditions examined. However, the possibility of the formation of carbon depends greatly on the ratio of H_2O to CO in the feed. An increase of the H_2O/CO ratio lowers the risk of carbon formation by lowering the temperature range in which carbon could be formed. The calculations reveal that a shift catalyst operating with a feed with a low H_2O/CO ratio should not only be active but also selective.

2. When operated with a feed having a low H_2O to CO ratio, the commercial LT shift Cu–Zn catalyst, retained its high activity and selectivity for the WGS reaction. However, it lost its activity completely when sulphur was present in the feed. When operated at a low H_2O/CO ratio, the commercial HT shift Fe–Cr catalyst was also very selective for the WGS reaction, but it only became active at relatively high temperatures. The presence of sulphur in the feed deactivated the catalyst, but the activity could be restored fully after sulphur was removed from the feed.

3. The Co–Cr catalyst had very high WGS activity; however, its selectivity was relatively poor since it also catalysed side reactions producing undesired carbon and methane, especially when operating with a feed having a low H_2O/CO ratio. The formation of carbon appeared to occur rapidly on this catalyst under the conditions where thermodynamics predict carbon formation. The catalyst also suffered severe deactivation in the presence of sulphur, and this effect was not reversed after sulphur was removed from the feed.

4. The Pt/ZrO_2 catalyst showed higher activity than that of the Fe–Cr catalyst. The catalyst was also selective to the WGS reaction. In the presence of sulphur, the catalyst deactivated; however, the activity remaining was higher than any of the other catalysts tested under the same conditions. The sulphur-deactivated catalyst could easily be regenerated, either by hydrogen treatment or by heating in the reaction mixture containing no H_2S.

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References

[1] M.V. Twigg, Catalysts Handbook, 2nd edn., Wolfe Publishing, London, 1989, pp. 283–339.
[2] E. Kikuchi, S. Uemiya, N. Sato, H. Ando and T. Matsuda, Chem. Lett., (1989) 489–492.
[3] S. Uemiya, N. Sato, H. Ando and E. Kikuchi, Ind. Eng. Chem. Res., 30 (1991) 585–589.
[4] G.J. Hutchings, R.G. Copperthwaite, F.M. Gottschalk, R. Hunter, J. Mellor, S.W. Orchard and T. Sangiorgio, J. Catal., 137 (1992) 408–422.
[5] R.G. Copperthwaite, F.M. Gottschalk and T. Sangiorgiot and G.J. Hutchings, Appl. Catal., 63 (1990) L11–L16.
[6] E. Xue, M. O'Keefe and J.R.H. Ross, in preparation.
[7] H. Bohlbro and M.H. Jorgensen, Chem. Eng. World, 5 (1970) 46–49.
[8] D.S. Newsome, Catal. Rev. Sci. Eng., 21 (1980) 275–318.