



Study the Effect of H₂S on the Gas-shift Conversion

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The characteristics of conversion of carbon monoxide and hydrogen generation from a water gas shift reaction are investigated experimentally. The behaviour of catalyst (Fe-Cr) was examined with and without the presence of H₂S in the feed. With the effect of the high temperature catalyst, increasing reaction temperature will promote the performance of the water gas shift reaction. These behaviours reveal that the water gas shift reaction with the high temperature catalyst is governed by chemical kinetics. It is of interest that water decomposition also develops in the water gas shift reaction so that the concentration of H₂ is always higher than that of CO₂.

Key Words: Catalyst, H₂S, Poisoning, High temperature.

INTRODUCTION

Over the years hydrogen economy^{1,2} has received a great deal of attention. This arises from the fact that some kinds of fossil fuels, say, petroleum and natural gas, are likely to be exhausted in the next several decades³⁻⁵. In contrast, the utilization of hydrogen possesses the merits of sustainable fuel resource (*i.e.* biomass or water), no air pollutant and greenhouse gas emissions and reducing our dependence on fossil fuels as the source of energy^{6,7}. In addition, unlike wind or solar energy, hydrogen can be stored and transported. It is thus considered to be the most viable energy carrier in the future. In particular, recently there is a progressive development in fuel cells, which can be used for transportation, primary power generation and distributed generation^{8,9} and it is known that hydrogen is a vital fuel in the fuel cells. Consequently, an efficient and cost-saving hydrogen generation method becomes an important issue before the fuel cells can be applied extensively.

The reaction (eqn. 1) has been commercially used and developed over many decades.



This reaction is exothermic and the H₂ production is thermodynamically favoured at low temperature, *e.g.* 175-250 °C and high steam ratios^{10,11}. Two disadvantages arise: at low temperatures, the reaction kinetics slow, even using the preferred copper zinc alumina catalysts^{11,12} and excess steam needs to be recycled. Typically, industrial reactors use a two-step shift to optimize conversion. A high temperature shift, operating between 300 and 450 °C with a FeCr catalyst,

provides most of the reaction, followed by a low temperature stage to maximize the conversion. While the two-step shift method provides both high reaction rates and high conversion, it requires large catalyst volumes and high steam recycling.

As far as hydrogen generation is concerned, the methods can roughly be cataloged into: (1) thermochemical, (2) electrochemical, (3) photobiological and (4) photoelectrochemical¹³. Despite numerous methods developed, so far the thermochemical technique is still the most available method in that this technique is well-developed and a variety of fuel sources can be applied. In the thermochemical technique, autothermal reforming¹⁴, steam reforming¹⁵ and gasification^{5,16} in incorporating with natural gas, alcohol, coal or biomass can be applied to produce synthesis gas or syngas (*i.e.* H₂ + CO).

Claus process has been most commonly employed to remove H₂S from natural gas in facilities or refinery plants. Claus plants generally convert 94-98 % of sulfur compounds in the feed gas into elemental sulfur^{17,18}. As the restrictions on sulfur emissions are annually strengthening worldwide, a number of tail gas clean-up processes have been developed to reduce sulfur emission to permissible levels¹⁹. Nadegea *et al.*²⁰ studied the effect of H₂S on the hydrogenation activity of relevant transition metal sulfides.

In this article, we study the effect of H₂S on the activity of high temperature of water gas shift conversion.

EXPERIMENTAL

Reaction system: A schematic of the conducted reaction system is sketched in Fig. 1. The main components of the system include five units; they are: (1) the reactants input unit,

(2) the steam generation unit, (3) the reaction unit, (4) the product gas treatment unit and (5) the gas analysis unit.

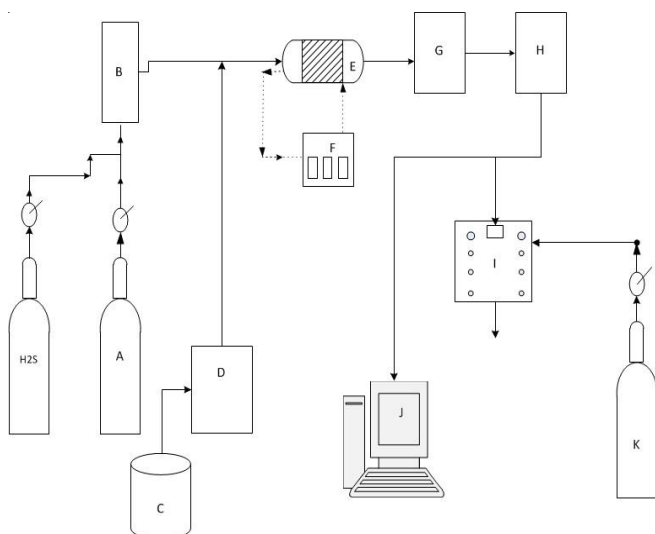


Fig. 1. A schematic of the reaction system, A=Feeding gas; B=Rotameter; C=Water; D=Rotary Pump; E=Reactor; F=Controller; G=Condenser; H=Drier; I=GC Sensor; J=Recorder; K=Carrier gas.

Experimental procedure: For running experiments, the granular catalyst with fixed bed length was first packed in the reactor. Then, the feeding gas and water with controlled volumetric flow rates were sent into the tube installed in the steam generator. It should be mentioned that CO is a toxic gas, 10 % of CO was thus mixed with 90 % of N₂ as the feeding gas to avoid the possible risk caused by CO during the experiments. The feeding gas was not only a reactant but also played a role of carrier gas to aid in transporting water into the steam generator. The temperature of the steam generator was fixed at 220 °C to vapourize water and preheat the reactants. Hence, as long as water past through the steam generator, the water would evolve into steam and mix with the feeding gas. When the mixture flew into the reactor, the water gas shift reaction was achieved. Thereafter, the product gas was washed by ice water to primarily condense the moisture, followed by flowing through the drier to completely absorb and remove the moisture. Subsequently, the treated gas was analyzed in the gas analysis unit. The electrical signals from the GA, indicating the concentrations of CO and CO₂, were sent into a computer *via* a signal receiver to monitor and record the collected data. To ensure the measurement quality, prior to performing experiments the feeding gas with fixed volumetric flow rate was blown into the reaction system. Then, the flow rate of the gas and the concentration of CO were measured at the system exit. This guaranteed that no gas leakage occurred. The calibrations of the GC and the GA were also carried out by means of standard gases to ensure that the measured quality of the product gas was reliable. Flow rates of the feeding gas (25 °C and 1 atm) were 1583 mL/min. The porosity of the two catalyst beds was 0.3; accordingly, one was able to calculate the residence time of the reactants in the catalyst beds.

Catalyst preparation: The following amounts of nitrates of the respective metals were dissolved in distilled water to make a 300 mL solution:

(i) Fe(NO₃)₃·9H₂O 30.60 g

(ii) Cr(NO₃)₃·9H₂O 3.22 g

The solution was stirred at 60 °C for 2 h and then 46.22 g of citric acid monohydrate was added to the solution; further mixing for 1 h was carried out at 60 °C and then the temperature was raised to 90 °C. The solution remained on a hot plate until complete removal of water. After dryness, the solid was heated further at 140 °C for 4 h. Finally, the solid was calcined up to 900 °C for 10 h at a heating rate of 3 °C/min. Catalyst surface areas and components are listed in Table-1.

TABLE-1
SURFACE AREAS AND MAIN COMPONENTS
OF THE ADOPTED CATALYSTS

Surface area (m ² /g)	Component (wt %)
58.3	Iron oxide: 88–94 Chromium oxide: 7–11 Chromium trioxide: 0.3–5.0

RESULTS AND DISCUSSION

Catalyst reaction was analyzed using the SEM. As can be seen from Fig. 2, light particle are Cr oxide.

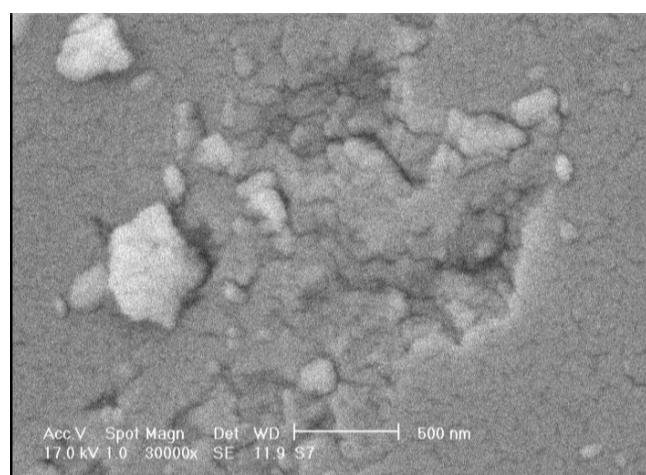


Fig. 2. SEM images of the high-temperature catalyst (Fe-Cr).

The effect of the reaction temperature on the performance of the water gas shift conversion is examined in Fig. 3. The reaction temperature in the former ranges from 200 to 450 °C and the CO/steam ratio is fixed at 1/4. Upon inspection of CO and CO₂ distributions, when the reaction temperature is 300 °C, only little amount of CO (< 5 %) is consumed so that the concentration of CO₂ is relatively low. Consequently, the CO conversion is low and its value is around 4 %, as shown in Fig. 3. with increasing reaction temperature, it is evident that the concentration of CO declines with respect to the temperature, whereas the CO₂ concentration is approximately proportional to the increase of temperature. In contrast, for the high temperature catalyst, the CO conversion is highly sensitive to the reaction temperature and an increase in temperature is conducive to the hydrogen generation (Fig. 4). It follows that the reactions with the high temperature catalyst are controlled by chemical kinetics (*i.e.* Arrhenius law). Fig. 4. shows

concentration percentage of CO, CO₂ and H₂ at different temperature, as can be seen, as temperature increase, the concentration percentage of CO₂ and H₂ increase, can also be seen that the H₂ concentration in all temperature is higher than CO₂.

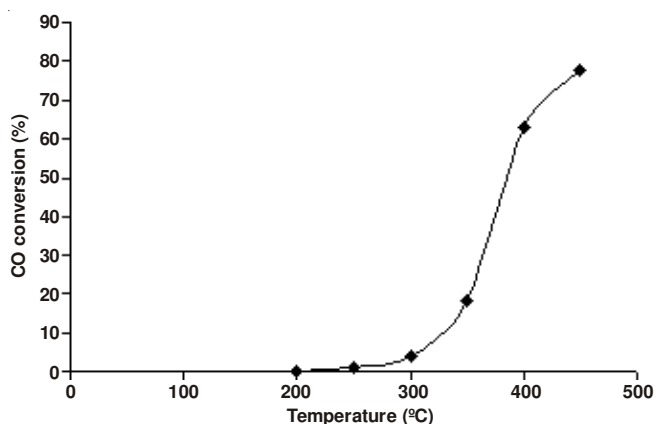


Fig. 3. The conversion of CO as a function of temperature on the Fe-Cr catalyst.

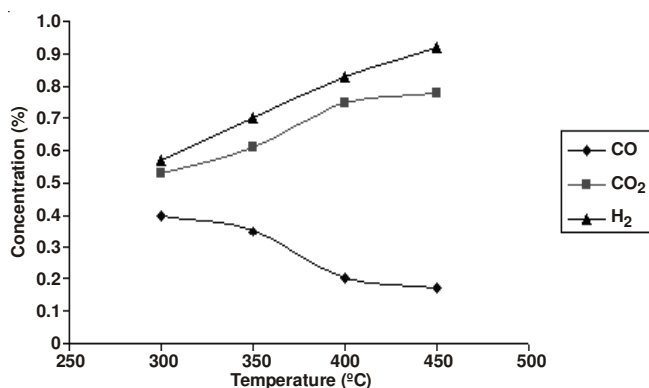


Fig. 4. The concentration of CO, CO₂ and H₂ under the effect of high temperature catalyst

Table-2 shows the CO conversions over the high temperature Fe-Cr catalyst at different concentrations of H₂S. The catalyst was first stabilized by ageing in the sulphur-free reaction stream at 350 °C for approximately 50 h before the H₂S was introduced; the concentrations of H₂S introduced into the feed were 50, 100, 200, 500 and 1000 ppm. The CO conversions over the catalyst were measured at 300, 350, 400 and 450 °C the catalyst being kept for about 4 h at each temperature. The CO conversions after the H₂S 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 H₂S added; when 1000 ppm H₂S 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 H₂S from the feed.

As can be seen in Tables 2 and 3, the concentration less than 200 ppm of H₂S, has no critical effect on activity of catalyst, but when the concentration are more than 200 ppm

of H₂S the catalyst activity decrease to half. To explain this matter, it can be said that in higher concentration of H₂S, in the reaction between H₂S and the catalyst Fe-Cr, the compound FeS is formed and this compound cause that the catalyst with this near to half conversion rate, can continue its activity.

TABLE-2
THE WGS ACTIVITIES OF THE Fe-Cr CATALYST AT VARIOUS CONCENTRATION LEVELS OF H₂S ADDITION

Run condition	X CO (%)			
	300	350	400	450
After 50 h	4.0	18.3	63.5	78.4
50 ppm H ₂ S add	4.0	17.9	61.2	76.5
100 ppm H ₂ S add	3.8	17.9	58.5	74.2
200 ppm H ₂ S add	3.8	17.3	57.0	70.0
500 ppm H ₂ S add	2.5	9.0	34.2	42.0
1000 ppm H ₂ S add	2.5	8.5	29.4	37.5

TABLE-3
THE WGS ACTIVITIES OF THE Fe-Cr CATALYST AT VARIOUS CONCENTRATION LEVELS OF H₂S ADDITION

Run condition	X CO (%)			
	300	350	400	450
After 100 h	3.9	18.3	63.2	78.1
50 ppm H ₂ S add	3.9	17.2	59.5	75.3
100 ppm H ₂ S add	3.8	16.9	58.1	73.5
200 ppm H ₂ S add	3.6	15.1	55.2	70.1
500 ppm H ₂ S add	2.3	8.5	32.1	40
1000 ppm H ₂ S add	1.9	7.5	27.4	35.2

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