CHAR GASIFICATION IN STEAM AT 1123 K CATALYZED BY K, Na, Ca AND Fe—EFFECT OF H₂, H₂S AND COS

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Abstract—Gasification of unloaded and loaded Saran char was followed at 1123 K and 0.1 MPa total pressure in a N₂ or H₂ atmosphere to which ~ 3 kPa H₂O and, in some cases, ~ 500 ppm H₂S or COS were added. Potassium, Na and Ca are excellent catalysts for the gasification of Saran char by steam. Hydrogen inhibits catalysis by K, Na and Ca and reduces the catalytic activity by Fe. The extent of the effect of H₂S or COS on inhibiting char gasification by steam depends upon whether it is added to wet N₂ or wet H₂. The inhibitory effect is much more marked in wet H₂ in all cases. Likewise, the time required to recover catalyst activity, following exposure to H₂S or COS, is much greater in the presence of wet H₂ than in the presence of wet N₂.

Key Words—Saran char, catalysts, steam, gasification.

1. INTRODUCTION

It is known that H₂ inhibits the uncatalyzed C-H₂O reaction by dissociative chemisorption onto carbon active sites[1]. The effect of H₂ on the catalyzed C-H₂O reaction is more complex. For example, H₂ acts as a promoter for the Fe-catalyzed reaction[2] and an inhibitor for the Ca-catalyzed reaction[3]. Frequently, chars, which are being gasified, contain organic and/or inorganic forms of sulfur. In the presence of steam gasification, H₂S and COS are produced. It is thus of interest to study the effect of these sulfur compounds on the rate of the uncatalyzed and catalyzed C-H₂O reaction.

2. EXPERIMENTAL

The char used in this study was a 40 x 70 U.S. sieve series particle size cut of Saran char, which was derived from Saran copolymer by heating it at 1173 K for 1 h in 0.1 MPa N₂. The char had an ash content of <50 ppm and a surface area of 1050 m²/g, as determined from CO₂ adsorption at 298 K. Catalyst loading on the char was effected by impregnation using either nitrate or acetate solutions[3]. The char was soaked for 48 h at room temperature with stirring, then filtered and dried overnight at 378 K in a vacuum oven. Loadings in wt% were: K, 1.93%; Na, 1.18%; Ca, 1.93%; and Fe, 2.58%. Loadings in mmole/g char were: K, 0.493; Na, 0.314; Ca, 0.481; and Fe, 0.462.

Reactivities were measured in a vertical TGA system (Fisher thermogravimetric analyzer model 422) at 0.1 MPa total pressure and 1123 K. The 50 mg sample (held in a quartz bucket) was heated to gasification temperature at a rate of 20 K/min and bathed at this temperature for 30 min in dry N₂ before introducing the reactant gas. The reactant gas was water saturated N₂ or H₂ at 298 K (H₂O: 3.1 kPa). In this case, the gas stream consisted of 3.1% H₂O and 96.9% N₂ or H₂. The flow rate of the dry gas was kept at 100 ml (STP)/min. Sometimes H₂S or COS was added to the reactant gas by mixing 10 ml/min of 0.5% H₂S or 0.5% COS in H₂ or N₂ with 90 ml/min of water saturated H₂ or N₂. In this case, the mixed gas stream contained ~500 ppm (0.05%) of H₂S or COS and 2.7% H₂O.

3. RESULTS

3.1 Reactivities in wet N₂ and wet H₂

Figures 1–5 present reactivity plots for the Saran char and samples loaded with catalysts in wet N₂ and wet H₂. As previously noted by us[3] and others, K and Na are particularly good catalysts for the C-H₂O reaction. Hydrogen is seen to inhibit catalysis of the C-H₂O reaction by K, Na and Ca. When the reaction gas is changed from wet N₂ to wet H₂ or vice versa, there is an abrupt change in rate, the rate decreasing in the former case and increasing in the latter case. For the char loaded with Fe, results are different. As seen in Fig. 5, the first replacement of wet N₂ by wet H₂ initially leads to a decrease in rate for about 40 min. This is followed by an abrupt increase in gasification rate—markedly above that found previously in wet N₂. Subsequent replacement of the wet H₂ by wet N₂ results in an abrupt and large decrease in gasification rate. Subsequent replacement of wet N₂ by wet H₂ results again in a large increase in gasification rate, following an induction period of ~10 min.

The effect of H₂ on the gasification of the unloaded Saran char by steam is less marked than for the samples with a catalyst present. Substitution of wet H₂ for wet N₂ initially produces a decrease in gasification rate; however, the rate increases with burn-off and after about 5% burn-off (3.5 h) the rate in wet H₂ is comparable to the previous rate in wet N₂. Subsequent substitution of wet N₂ results in little change in rate. Reactivity of char in 0.1 MPa dry H₂ is low—about 0.25% burn-off/h. Thus,
most of the gasification in wet \( \text{H}_2 \) can be attributed to the C-H\(_2\)O reaction.

3.2 Effect of \( \text{H}_2\text{S} \) and \( \text{COS} \) on reactivities in wet \( \text{H}_2 \) and wet \( \text{N}_2 \)

Figures 6 and 7 present results for the introduction of 500 ppm \( \text{H}_2\text{S} \) into wet \( \text{N}_2 \) and wet \( \text{H}_2 \) over Saran char. In both cases, \( \text{H}_2\text{S} \) significantly reduces the gasification rate, but the inhibitory effect is more marked in wet \( \text{H}_2 \). There are other more subtle differences. Inhibition is essentially immediate when \( \text{H}_2\text{S} \) is introduced into wet \( \text{H}_2 \); whereas, in wet \( \text{N}_2 \) there is a finite induction period before the gasification rate is reduced. Further, upon removal of \( \text{H}_2\text{S} \), inhibition continues for a longer period in wet \( \text{H}_2 \) than it does in wet \( \text{N}_2 \). In the absence of \( \text{H}_2\text{S} \), the gasification rate in wet \( \text{N}_2 \) is again essentially independent of extent of burn-off. In wet \( \text{H}_2 \), the gasification rate again changes with burn-off. Before the introduction of \( \text{H}_2\text{S} \), the rate increases with increasing burn-off; but following the introduction and then removal of \( \text{H}_2\text{S} \), the rate continuously decreases with increasing burn-off once the induction period is over.

Figures 8 and 9 present results for the introduction of 500 ppm \( \text{H}_2\text{S} \) into wet \( \text{N}_2 \) and wet \( \text{H}_2 \) over the K-loaded char. Introduction of \( \text{H}_2\text{S} \) into wet \( \text{N}_2 \) has no detectable effect on gasification rate. In contrast, introduction of \( \text{H}_2\text{S} \) into wet \( \text{H}_2 \) has an immediate and large inhibitory effect on char reactivity. Further, upon removal of \( \text{H}_2\text{S} \) from wet \( \text{H}_2 \), an extended period exists (60 min) before the more rapid gasification rate is again attained. As with the unloaded char, the gasification rate in wet \( \text{H}_2 \) increases with burn-off prior to the introduction of \( \text{H}_2\text{S} \) and decreases with burn-off following the removal of \( \text{H}_2\text{S} \) and completion of the induction period. Introduction of 500 ppm \( \text{COS} \), in place of \( \text{H}_2\text{S} \), shows very similar results in wet \( \text{N}_2 \) and wet \( \text{H}_2 \) to those found with \( \text{H}_2\text{S} \).

Figures 10 and 11 present results for the introduction of 500 ppm \( \text{COS} \) into wet \( \text{N}_2 \) and wet \( \text{H}_2 \) over the Na-loaded char. Introduction of \( \text{COS} \) into wet \( \text{N}_2 \) has minor effects on gasification rate. In contrast, introduction of \( \text{COS} \) into wet \( \text{H}_2 \) has an immediate and large inhibitory effect on char reactivity. Following removal of \( \text{COS} \) from wet \( \text{H}_2 \), the low reactivity continues for another 90 min.
Fig. 5. Reactivity of Fe-loaded char in wet N\textsubscript{2} and wet H\textsubscript{2}.

Similar results were found for H\textsubscript{2}S—little effect on reactivity in wet N\textsubscript{2}, a large inhibitory effect in wet H\textsubscript{2}.

Figures 12 and 13 present results for the introduction of 500 ppm H\textsubscript{2}S or COS into wet N\textsubscript{2} over the Ca-loaded char. Unlike results over the K or Na loaded char, some reduction in gasification rate is obvious. The effects of H\textsubscript{2}S and COS are very similar. Introduction of H\textsubscript{2}S to wet H\textsubscript{2} also lowers the gasification rate of the Ca-loaded char, but H\textsubscript{2} alone is such a marked inhibitor of the C-H\textsubscript{2}O reaction catalyzed by Ca that the effect is not as dramatic as that found over the K and Na-loaded chars.

Figures 14 and 15 present results for the introduction of 500 ppm H\textsubscript{2}S into wet N\textsubscript{2} and wet H\textsubscript{2} over the Fe-loaded char. Introduction of H\textsubscript{2}S into wet N\textsubscript{2} reduces the gasification rate significantly, but the inhibitory effect is not as marked as when H\textsubscript{2}S is introduced into wet H\textsubscript{2}. In wet H\textsubscript{2}, the presence of H\textsubscript{2}S almost stops gasification; and inhibition continues for at least 30 min following removal of H\textsubscript{2}S from the gas stream. Figure 16 presents results where gasification in wet H\textsubscript{2} is followed by gasification in wet N\textsubscript{2} to which H\textsubscript{2}S has been added. Inhibition of char gasification in the latter gas mixture is strong but not as strong as that found in wet H\textsubscript{2} to which H\textsubscript{2}S is added (Fig. 15). Even though H\textsubscript{2} is an accelerator for the Fe-catalyzed char-H\textsubscript{2}O reaction, the introduction of 500 ppm H\textsubscript{2}S converts the H\textsubscript{2}-H\textsubscript{2}S mixture to a very strong inhibitor, exceeding that of H\textsubscript{2}S itself as an inhibitor for the C-H\textsubscript{2}O reaction. It is noted in Fig. 16 that a very rapid loss in weight of about 2% occurs upon reintroduction of wet H\textsubscript{2} in place of the wet N\textsubscript{2} containing H\textsubscript{2}S.

4. DISCUSSION

4.1 Reactivities in wet N\textsubscript{2} and wet H\textsubscript{2}

Regardless of the precise mechanism for each step in the uncatalyzed gasification of carbon by steam, it is well accepted today that hydrogen inhibition of the reaction is through dissociative chemisorption of H\textsubscript{2} onto carbon active sites. The question, when one is working with a "pure" carbon, is whether one is able to say categorically that the overwhelming contribution to the measured gasification rate is derived from the uncatalyzed reaction. This is so because carbons of "higher purity" always contain some inorganic impurities; and since some impurities are excellent catalysts for carbon gasification[41], they may indeed result in the catalyzed gasification contributing significantly to the measured overall gasification rate. In the present study it cannot be said categorically that gasification rates measured on the unloaded Saran char represent rates of the uncatalyzed reaction. The char, for example, contains ~20 ppm Fe; and if this Fe is well dispersed and in the metallic state, it will be an excellent catalyst for the C-H\textsubscript{2}O reaction. Let us review results for the gasification of unloaded char in this light.

It is difficult to quantitatively discuss the effect of H\textsubscript{2} on the rate of char gasification by steam since the rate of gasification in wet N\textsubscript{2} is essentially independent of burn-off whereas the rate of gasification in wet H\textsubscript{2}
creases with increasing char burn-off. The latter is true whether reaction in wet $\text{H}_2$ follows some extent of gasification in wet $\text{N}_2$ (Fig. 1) or is the first reaction which the char has undergone (Fig. 7). The finding that the gasification rate is independent of burn-off in wet $\text{N}_2$ is consistent with the finding that the gasification rate of this Saran char was also independent of burn-offs up to 50% in 0.1 MPa of dry air[5]. Gasification for both the $\text{C-}H_2O$ and $\text{C-air (O)}_2$ reaction is via the oxygen complex

$$\text{C(O)} \rightarrow \text{CO(g)}.$$  \hspace{1cm} (1)

A possible explanation for the increasing gasification rate in wet $\text{H}_2$ as burn-off proceeds involves the possibility that Fe catalysis is important. When gasification first commences, $\text{H}_2$ relatively rapidly dissociates and chemisorbs on carbon active sites, thus keeping the rate of uncatalyzed carbon gasification low. In the beginning of gasification, Fe, at least on its surface, can be in an oxidized state and is not a catalyst for the $\text{C-}H_2O$ reaction[2]. As gasification proceeds, more particles of Fe can be exposed to the reacting gas; and the $\text{H}_2O/\text{H}_2$ ratio is sufficiently low that Fe will be reduced to the metallic (active catalytic) state. Thus the gasification rate shows a monotonic increase with burn-off. The problem with this explanation is that if the measured reaction rate is contributed to primarily by the Fe-catalyzed reaction, the gasification rate should decrease when the reactive gas mixture is switched from wet $\text{H}_2$ to wet $\text{N}_2$ (as is seen for the Fe-loaded char in Fig. 5). But, as seen in Fig. 1, this is not the case. Therefore, at the moment, results for the unloaded char can be simply taken as representing the “base” case prior to the deliberate loading of the char with large amounts of inorganic impurities.

As shown previously for coal chars[3,6], K, Na, and Ca are found in this study to be excellent catalysts for steam gasification of Saran char. Further, as shown previously, $\text{H}_2$ reduces the catalytic activity of the above metals for the $\text{C-}H_2O$ reaction. Mims and Pabst[6] show a linear decrease in rate of carbon gasification, as catalyzed by K, as the $\text{H}_2/\text{H}_2O$ reacting gas ratio is increased. This inhibition is attributed to the reduction in the steady-state concentration of metal–oxygen intermediate formed in the presence of $\text{H}_2O$, as a result of $\text{H}_2$ addition. This intermediate breaks down to CO, resulting in carbon gasification. This metal-oxygen intermediate has been suggested to have a phenolate and/or formate-like structure[6–10].

In contrast to the inhibiting effect of $\text{H}_2$ on the rate of carbon gasification by steam, when catalyzed by alkali and alkaline earth metals, $\text{H}_2$ acts as an accelerator when the gasification rate is catalyzed by Fe[2], as previously discussed and found in this study.
4.2 Effect of $H_2S$ and COS on reactivities in wet $H_2$ and wet $N_2$

As expected, the introduction of $H_2S$ or COS into the reactive steam environment results in a decrease in unloaded Saran char gasification rate (Figs. 6 and 7). These sulfur compounds readily dissociate over carbon active sites forming carbon–sulfur surface complexes[11,12]. Formation of these complexes would result in a decrease in the steady-state concentration of C(O) and thus a reduction in the rates of CO production and carbon gasification. Of particular interest is the finding that 500 ppm of $H_2S$ or COS are much stronger inhibitors in the presence of $H_2$ than in the presence of $N_2$. As seen in Figs. 6 and 7, immediately prior to $H_2S$ introduction, gasification rates in wet $N_2$ and wet $H_2$ are similar. After $H_2S$ introduction, the gasification rate in wet $N_2$ is reduced by about 50%; in contrast, the gasification rate in wet $H_2$ is reduced over 95% to a very low value.

As discussed previously, it is uncertain whether the predominant contribution to the measured gasification rate for the unloaded Saran char is due to the uncatalyzed or catalyzed reaction(s). Let us consider the uncatalyzed reaction first. It is known that $H_2S$ is an effective hydrogen transfer agent[13,14]. For example, it catalyzes the transfer of hydrogen between hydrocarbon reactants and free radicals. Consider the following reaction sequence, started by the interaction of $H_2S$ with a free radical carbon surface active site

\[ C \cdot + H_2S \rightarrow C(H) + HS \cdot \]  
\[ HS \cdot + H_2 \rightarrow H_2S + H \cdot \]  
\[ C \cdot + H \cdot \rightarrow C(H) \cdot \]  

In this series of reactions, $H_2S$ would not be depleted through the char bed and could lead to a greater coverage of carbon active sites by hydrogen than in the absence of $H_2S$. The problem with this scheme is that reaction (3) is estimated to have an unfavorable equilibrium constant at 1123 K, that is about $1.5 \times 10^{-3}$.

The fact that COS is also a strong inhibitor of the unloaded char–$H_2O$ reaction in the presence of $H_2$ could be attributed to a favorable equilibrium constant for the forward reaction

\[ H_2 + COS = H_2S + CO \]  

at 1123 K (31.2) and the presence of a high $H_2/C_O$ ratio when wet $H_2$ is the reacting medium. If the rate of the reaction is rapid over carbon active sites at 1123 K, COS would be converted in significant amounts to $H_2S$.

In the presence of the alkali metals, $K$ and Na, differences in the effect of $H_2S$ and COS addition to wet
N₂ compared to wet H₂ is particularly marked. Little or no effect of sulfur compound addition to wet N₂ is noted (Figs. 8 and 10). Immediate and almost complete inhibition of gasification in wet H₂ is seen (Figs. 9 and 11). In the presence of wet N₂, the stable K or Na phase will be predominantly the carbonate or hydroxide depending upon the gasification rate and thus the amount of CO produced by gasification[2]. In the presence of wet H₂, the H₂O/H₂ ratio and CO pressure are sufficiently low that K and Na will be primarily in the metallic state[2].

As discussed previously, it is thought that inhibition of the alkali metal loaded-char gasification with steam by H₂ is due to a reduction in the steady-state concentration of metal-oxide intermediate formed. If this interpretation is extended to the effect of H₂S, it appears that the addition of 500 ppm H₂S to wet N₂ has little effect on the steady-state concentration of metal-oxide intermediate formed. Conversely in wet H₂, there is a synergism between H₂S and H₂ leading to enhanced reduction of the concentration of metal-oxide intermediate formed. Such enhanced reduction may be due to an increased production of hydrogen radicals in the presence of H₂S, as discussed previously.

An alternative explanation of the effect of H₂S on the activity of alkali catalysts could be that: (i) in wet N₂, the stable catalyst phase is, as stated, the hydroxide which does not readily react with H₂S in the gas; (ii) in wet H₂, alkali metals are present which react with H₂S to form inactive sulfides. An examination of free energy values will show, for example, that the reaction

$$2 \text{NaOH} + \text{H}_2\text{S} \rightarrow \text{Na}_2\text{S} + 2\text{H}_2\text{O}$$

is not as favorable as

$$2 \text{Na} + \text{H}_2\text{S} \rightarrow \text{Na}_2\text{S} + \text{H}_2$$

Results for the Fe-loaded char gasification are particularly interesting. Again the introduction of H₂S to wet H₂ (Fig. 15) has a greater inhibitory effect than introduction of H₂S to wet N₂ (Fig. 14). In wet N₂, the initial rate was 3.3% burn-off/h; it was reduced to 1.0%h following addition of H₂S—a reduction in rate of ~69%. In wet H₂, the rate increased to 18.2%h; it was reduced to 0.15%h following addition of H₂S—a reduction in rate of >99%. Even though H₂ is a promoter of the C-H₂O reaction as catalyzed by Fe, the addition of H₂S converts the H₂S/H₂ mixture to a very strong inhibitor.

Catalysis of char gasification in steam by Fe is thought to occur by the dissociative chemisorption of H₂O at the Fe surface, followed by spillover of the oxygen atom to active carbon sites, and then carbon gasification. Iron is known to very tightly bond sulfur to its surface. We estimate from the studies of Grabke et al.[15] that at 1123 K and a H₂S/H₂ ratio of ~5 × 10⁻¹ (conditions in wet H₂ in this study), the fraction of surface Fe sites covered by sulfur is very close to 1.0. Such coverage would be expected to sharply reduce the catalytic activity...
Fig. 13. Effect of COS on reactivity of Ca-loaded char in wet N₂.

Fig. 14. Effect of H₂S on reactivity of Fe-loaded char in wet N₂.

Fig. 15. Effect of H₂S on reactivity of Fe-loaded char in wet H₂.
of Fe. At least on the basis of the H$_2$S/H$_2$ ratio, coverage of Fe sites by sulfur would be expected to approach 1.0 even more closely in wet N$_2$ to which H$_2$S is added. However, inhibition of char gasification by steam is not as marked in wet N$_2$ as in wet H$_2$. The situation is obviously complicated as H$_2$S, H$_2$, CO and H$_2$O compete for interaction with Fe surface sites. At least for Ni, steam is found to have no influence on the chemisorption of H$_2$S at 1123 K[16].

The presence of H$_2$ along with H$_2$S (or COS) not only results in strong inhibition of char gasification by steam as catalyzed by K, Na, and Fe but regeneration of the catalyst is much slower in wet H$_2$ than wet N$_2$ once the H$_2$S (or COS) is removed from the gas stream. Results on the regeneration of sulfided Ni catalysts in H$_2$O/H$_2$ atmospheres at 973 K by sulfur removal[16] may be instructive in understanding our results for Fe. The author finds that sulfur removal is enhanced when the H$_2$O/H$_2$ ratio is greater than the equilibrium constant for the oxidation of Ni. When the gas leaving the catalyst was analyzed, SO$_2$ and H$_2$S were detected. Thus the following reaction pattern was suggested:

\begin{align}
\text{Ni-S} + \text{H}_2\text{O} & = \text{NiO} + \text{H}_2\text{S} \\
\text{H}_2\text{S} + 2\text{H}_2\text{O} & = \text{SO}_2 + 3\text{H}_2.
\end{align}

Since the equilibrium constant of reaction (9) at 973 K is small (and decreases further with increasing temperature), it means that a small amount of H$_2$ will inhibit the conversion of H$_2$S. It is concluded that sulfur removal following this reaction pattern requires a total oxidation of the catalyst[16]. If some part of the Ni surface is still exposed to the gas, H$_2$ will cause H$_2$S to be retained at the surface.

At 1123 K, the equilibrium H$_2$O/H$_2$ ratio for the reaction

\[\text{Fe} + \text{H}_2\text{O} = \text{FeO} + \text{H}_2\]

is 0.56[17]. In wet H$_2$, the H$_2$O/H$_2$ ratio is considerably less than the equilibrium value, and thus removal of sulfur from the Fe could be slow.

Curiously, regeneration of the Fe activity in wet H$_2$ is much slower following exposure of the Fe-loaded char to wet N$_2$ containing H$_2$S (Fig. 16) than it is following exposure to wet H$_2$ containing H$_2$S (Fig. 15). This is despite the fact that in the former case there is an almost instantaneous weight loss of $-2\%$ when wet H$_2$ is brought into the reactor. This result points out the complexity of this reaction system.

Another complexity is how the gasification rate in wet H$_2$ changes with char burn-off. Prior to the introduction of H$_2$S or COS into wet H$_2$, the gasification rate increases with burn-off both for the unloaded and loaded char samples. Following a reaction period in wet H$_2$, with H$_2$S or COS present, reactivity, after initially increasing sharply, shows a long period of decreasing rate for the unloaded char (Fig. 7) and samples loaded with K and Na (Figs. 9 and 11). However, for the Fe-loaded char, reactivity in wet H$_2$ increases with burn-off both before and after the introduction of H$_2$S (Figs. 15 and 16). These results are not understood at this time.

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