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 N_2 or H_2 atmosphere to which ~ 3 kPa H_2O and, in some cases, ~ 500 ppm H_2S 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 but promotes catalysis by Fe. The extent of the effect of H_2S (or COS) on inhibiting char gasification by steam depends upon whether it is added to wet N_2 or wet H_2. The inhibitory effect is much more marked in wet H_2 in all cases. Likewise, the time required to recover catalyst activity, following exposure to H_2S or COS, is much greater in the presence of wet H_2 than in the presence of wet N_2.

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

1. INTRODUCTION

It is known that H_2 inhibits the uncatalyzed C–H_2O reaction by dissociative chemisorption onto carbon active sites[1]. The effect of H_2 on the catalyzed C–H_2O reaction is more complex. For example, H_2 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, H_2S 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–H_2O reaction.

2. EXPERIMENTAL

The char used in this study was a 40 × 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 N_2. The char had an ash content of <50 ppm and a surface area of 1050 m²/g, as determined from CO_2 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, 0.514; 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 N_2 before introducing the reactant gas. The reactant gas was water saturated N_2 or H_2 at 298 K (H_2O:3.1 kPa). In this case, the gas stream consisted of 3.1% H_2O

and 96.9% H_2 or N_2. The flow rate of the dry gas was kept at 100 ml (STP)/min. Sometimes H_2S or COS was added to the reactant gas by mixing 10 ml/min of 0.5% H_2S or 0.5% COS in H_2 or N_2 with 90 ml/min of water saturated H_2 or N_2. In this case, the mixed gas stream contained ~500 ppm (0.05%) of H_2S or COS and 2.7% H_2O.

3. RESULTS

3.1 *Reactivities in wet N_2 and wet H_2*

Figures 1–5 present reactivity plots for the Saran char and samples loaded with catalysts in wet N_2 and wet H_2. As previously noted by us[3] and others, K and Na are particularly good catalysts for the C–H_2O reaction. Hydrogen is seen to inhibit catalysis of the C–H_2O reaction by K, Na and Ca. When the reaction gas is changed from wet N_2 to wet H_2 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 N_2 by wet H_2 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 N_2. Subsequent replacement of the wet H_2 by wet N_2 results in an abrupt and large decrease in gasification rate. Subsequent replacement of wet N_2 by wet H_2 results again in a large increase in gasification rate, following an induction period of ~10 min.

The effect of H_2 on the gasification of the unloaded Saran char by steam is less marked than for the samples with a catalyst present. Substitution of wet H_2 for wet N_2 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 H_2 is comparable to the previous rate in wet N_2. Subsequent substitution of wet N_2 results in little change in rate. Reactivity of char in 0.1 MPa dry H_2 is low—about 0.25% burn-off/h. Thus,

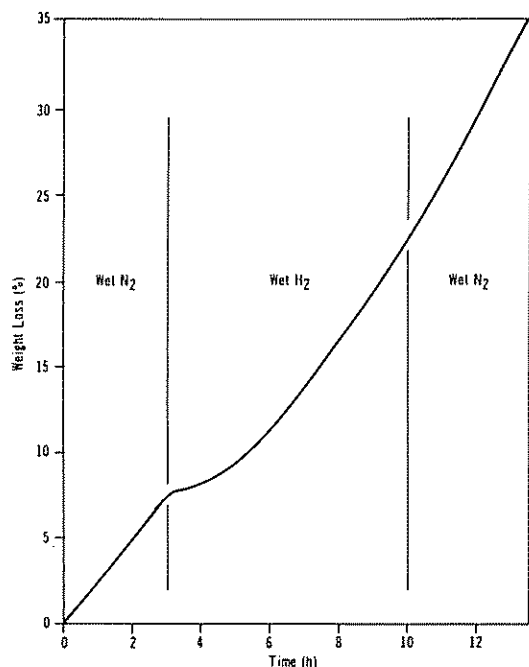*Present Address: Government Industrial Research Institute, Kyushu, Tosu, Saga, 841 Japan.

Fig. 1. Reactivity of unloaded Saran char in wet N_2 and wet H_2.

most of the gasification in wet H_2 can be attributed to the C–H_2O reaction.

3.2 Effect of H_2S and COS on reactivities in wet H_2 and wet N_2

Figures 6 and 7 present results for the introduction of 500 ppm H_2S into wet N_2 and wet H_2 over Saran char. In both cases, H_2S significantly reduces the gasification rate, but the inhibitory effect is more marked in wet H_2. There are other more subtle differences. Inhibition is essentially immediate when H_2S is introduced into wet H_2; whereas, in wet N_2 there is a finite induction period before the gasification rate is reduced. Further, upon removal of H_2S, inhibition continues for a longer period in wet H_2 than it does in wet N_2. In the absence of H_2S,
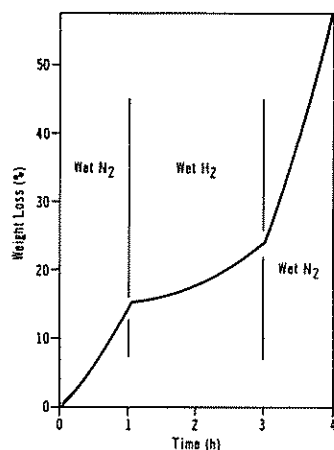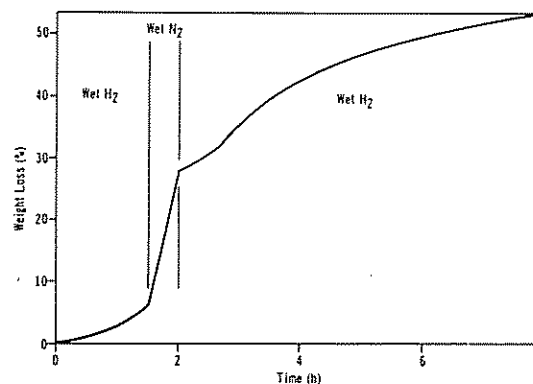

Fig. 3. Reactivity of Na-loaded char in wet N_2 and wet H_2.

the gasification rate in wet N_2 is again essentially independent of extent of burn-off. In wet H_2, the gasification rate again changes with burn-off. Before the introduction of H_2S, the rate increases with increasing burn-off; but following the introduction and then removal of H_2S, 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 H_2S into wet N_2 and wet H_2 over the K-loaded char. Introduction of H_2S into wet N_2 has no detectable effect on gasification rate. In contrast, introduction of H_2S into wet H_2 has an immediate and large inhibitory effect on char reactivity. Further, upon removal of H_2S from wet 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 H_2 increases with burn-off prior to the introduction of H_2S and decreases with burn-off following the removal of H_2S and completion of the induction period. Introduction of 500 ppm COS, in place of H_2S, shows very similar results in wet N_2 and wet H_2 to those found with H_2S.

Figures 10 and 11 present results for the introduction of 500 ppm COS into wet N_2 and wet H_2 over the Na-loaded char. Introduction of COS into wet N_2 has minor effects on gasification rate. In contrast, introduction of COS into wet H_2 has an immediate and large inhibitory effect on char reactivity. Following removal of COS from wet H_2, the low reactivity continues for another 90 min.

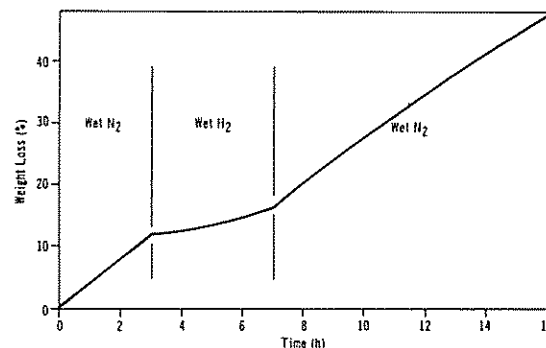Fig. 2. Reactivity of K-loaded char in wet N_2 and wet H_2.

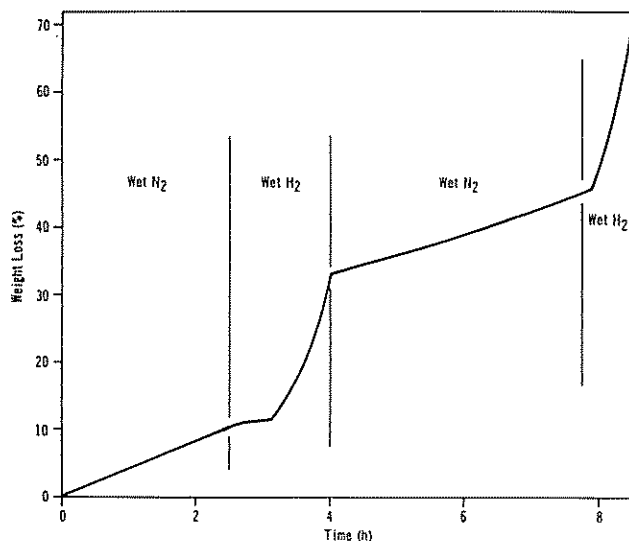Fig. 4. Reactivity of Ca-loaded char in wet N_2 and wet H_2.

Fig. 5. Reactivity of Fe-loaded char in wet N_2 and wet H_2.

Similar results were found for H_2S—little effect on reactivity in wet N_2, a large inhibitory effect in wet H_2.

Figures 12 and 13 present results for the introduction of 500 ppm H_2S or COS into wet N_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_2S and COS are very similar. Introduction of H_2S to wet H_2 also lowers the gasification rate of the Ca-loaded char, but H_2 alone is such a marked inhibitor of the C–H_2O 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_2S into wet N_2 and wet H_2 over the Fe-loaded char. Introduction of H_2S into wet N_2 reduces the gasification rate significantly, but the inhibitory effect is not as marked as when H_2S is introduced into wet H_2. In wet H_2, the presence of H_2S almost stops gasification; and inhibition continues for at least 30 min following removal of H_2S from the gas stream. Figure 16 presents results where gasification in wet H_2 is followed by gasification in wet N_2 to which H_2S has been added. Inhi-

Fig. 6. Effect of H_2S on reactivity of unloaded Saran char in wet N_2.

bition of char gasification in the latter gas mixture is strong but not as strong as that found in wet H_2 to which H_2S is added (Fig. 15). Even though H_2 is an accelerator for the Fe-catalyzed char–H_2O reaction, the introduction of 500 ppm H_2S converts the H_2–H_2S mixture to a very strong inhibitor, exceeding that of H_2S itself as an inhibitor for the C–H_2O reaction. It is noted in Fig. 16 that a very rapid loss in weight of about 2% occurs upon reintroduction of wet H_2 in place of the wet N_2 containing H_2S.

4. DISCUSSION

4.1 Reactivities in wet N_2 and wet H_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_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[4], 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_2O reaction. Let us review results for the gasification of unloaded char in this light.

It is difficult to quantitatively discuss the effect of H_2 on the rate of char gasification by steam since the rate of gasification in wet N_2 is essentially independent of burn-off whereas the rate of gasification in wet H_2 in-
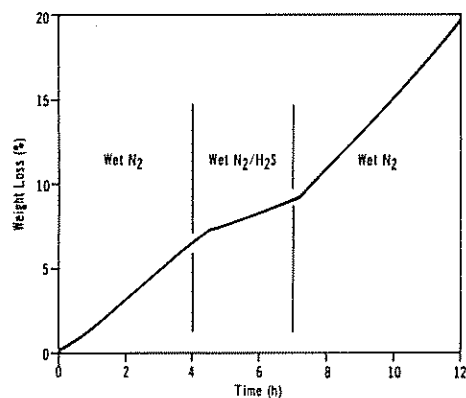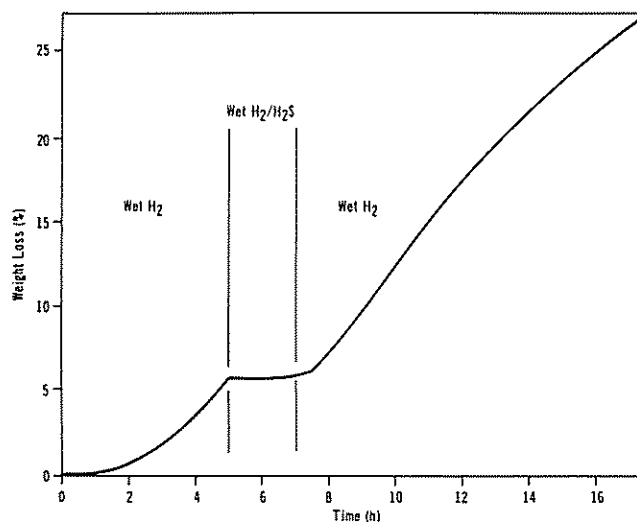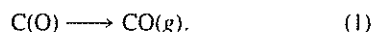
Fig. 7. Effect of H₂S on reactivity of unloaded Saran char in wet H₂.

creases with increasing char burn-off. The latter is true whether reaction in wet H_2 follows some extent of gasification in wet 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 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 C–H_2O and C–air (O_2) reaction is via the oxygen complex

$$C(O) \longrightarrow CO(g). \qquad (1)$$

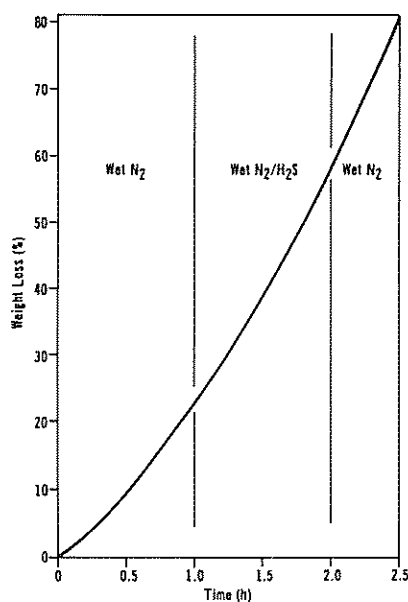A possible explanation for the increasing gasification rate in wet H_2 as burn-off proceeds involves the possibility

Fig. 8. Effect of H₂S on reactivity of K-loaded char in wet N₂.

that Fe catalysis is important. When gasification first commences, 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 C–H_2O reaction[2]. As gasification proceeds, more particles of Fe can be exposed to the reacting gas; and the H_2O/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 H_2 to wet 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, H_2 reduces the catalytic activity of the above metals for the C–H_2O reaction. Mims and Pabst[6] show a linear decrease in rate of carbon gasification, as catalyzed by K, as the H_2/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 H_2O, as a result of 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 H_2 on the rate of carbon gasification by steam, when catalyzed by alkali and alkaline earth metals, H_2 acts as an accelerator when the gasification rate is catalyzed by Fe[2], as previously discussed and found in this study.
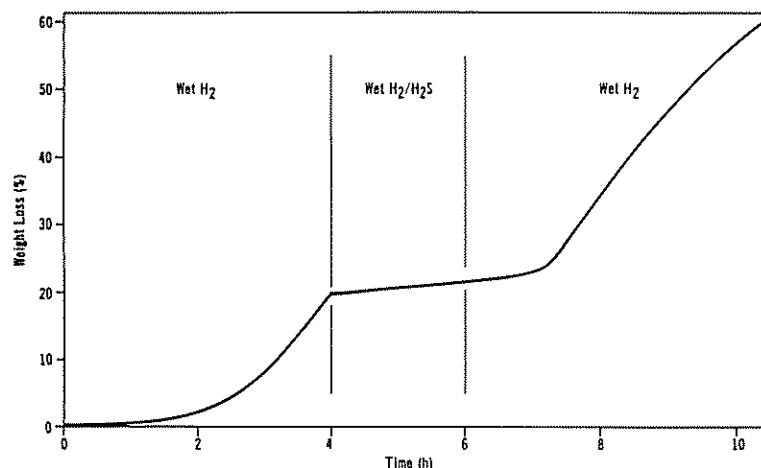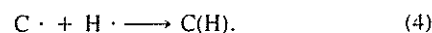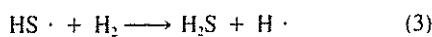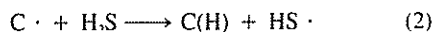
Fig. 9. Effect of H₂S on reactivity of K-loaded char in wet H₂.

4.2 Effect of H₂S and COS on reactivities in wet H₂ and wet N₂

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.


Fig. 10. Effect of COS on reactivity of Na-loaded char in wet N₂.

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

$$C \cdot + H_2S \longrightarrow C(H) + HS \cdot \qquad (2)$$

$$HS \cdot + H_2 \longrightarrow H_2S + H \cdot \qquad (3)$$

$$C \cdot + H \cdot \longrightarrow C(H). \qquad (4)$$

In this series of reactions, H_2S would not be depleted down 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 1.5×10^{-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

$$H_2 + COS = H_2S + CO \qquad (5)$$
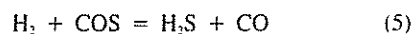
at 1123 K (31.2) and the presence of a high H_2/CO ratio when wet H_2 is the reacting medium. If the rate of the reaction is rapid over carbon active sites at 1123 K, COS would be converted in significant amounts to H_2S.

In the presence of the alkali metals, K and Na, differences in the effect of H_2S and COS addition to wet
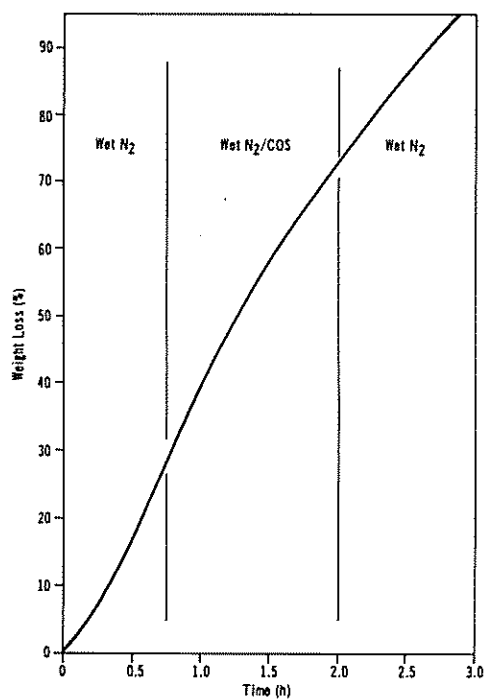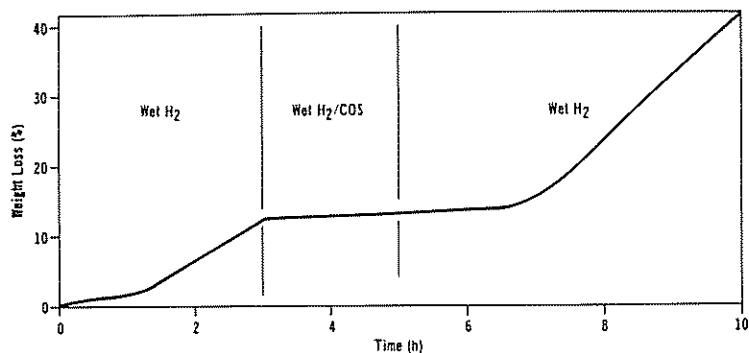
Fig. 11. Effect of COS on reactivity of Na-loaded char in wet H_2.

N_2 compared to wet H_2 is particularly marked. Little or no effect of sulfur compound addition to wet N_2 is noted (Figs. 8 and 10). Immediate and almost complete inhibition of gasification in wet H_2 is seen (Figs. 9 and 11). In the presence of wet N_2, 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 H_2, the H_2O/H_2 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 H_2 is due to a reduction in the steady-state concentration of metal-oxide intermediate formed. If this interpretation is extended to the effect of H_2S, it appears that the addition of 500 ppm H_2S to wet N_2 has little effect on the steady-state concentration of metal-oxide intermediate formed. Conversely in wet H_2, there is a synergism between H_2S and H_2 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 H_2S, as discussed previously.

An alternative explanation of the effect of H_2S on the activity of alkali catalysts could be that: (i) in wet N_2 the stable catalyst phase is, as stated, the hydroxide which does not readily react with H_2S in the gas; (ii) in wet H_2 alkali metals are present which react with H_2S to form inactive sulfides. An examination of free energy values

will show, for example, that the reaction

$$2 NaOH + H_2S \longrightarrow Na_2S + 2H_2O \qquad (6)$$
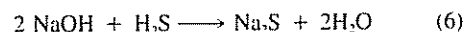
is not as favorable as

$$2 Na + H_2S \longrightarrow Na_2S + H_2. \qquad (7)$$

Results for the Fe-loaded char gasification are particularly interesting. Again the introduction of H_2S to wet H_2 (Fig. 15) has a greater inhibitory effect than introduction of H_2S to wet N_2 (Fig. 14). In wet N_2, the initial rate was 3.3% burn-off/h; it was reduced to 1.0%/h following addition of H_2S—a reduction in rate of ~69%. In wet H_2, the rate increased to 18.2%/h; it was reduced to 0.15%/h following addition of H_2S—a reduction in rate of >99%. Even though H_2 is a promoter of the C–H_2O reaction as catalyzed by Fe, the addition of H_2S converts the H_2S/H_2 mixture to a very strong inhibitor.

Catalysis of char gasification in steam by Fe is thought to occur by the dissociative chemisorption of H_2O 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 H_2S/H_2 ratio of ~5 × 10^{-4} (conditions in wet H_2 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
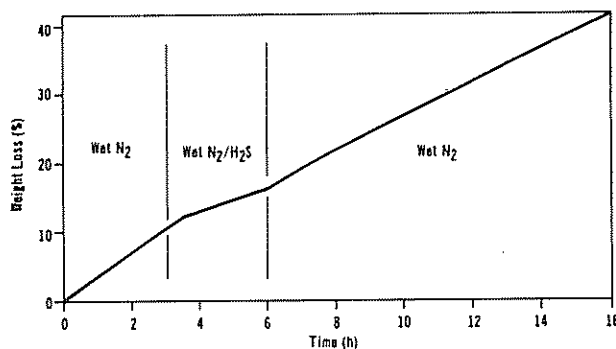

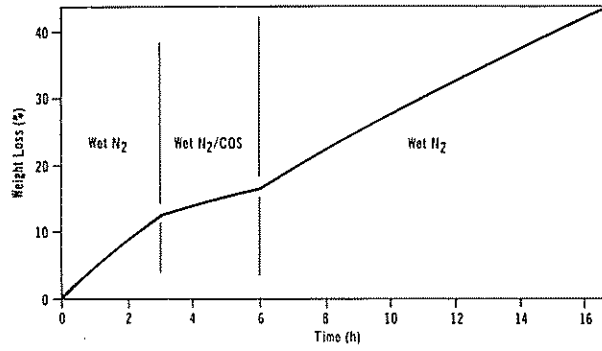Fig. 12. Effect of H_2S on reactivity of Ca-loaded char in wet N_2.

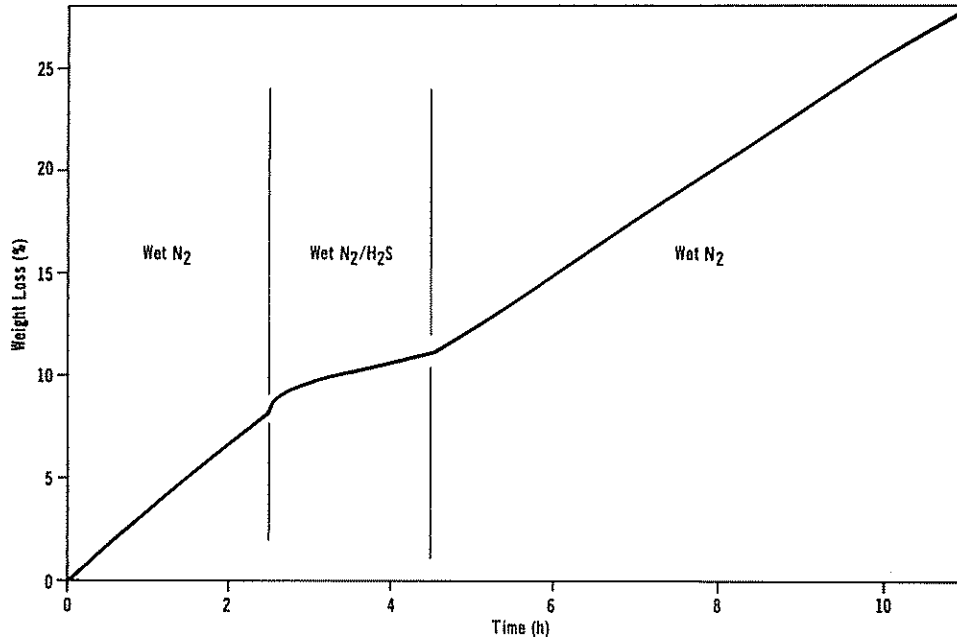Fig. 13. Effect of COS on reactivity of Ca-loaded char in wet N_2.

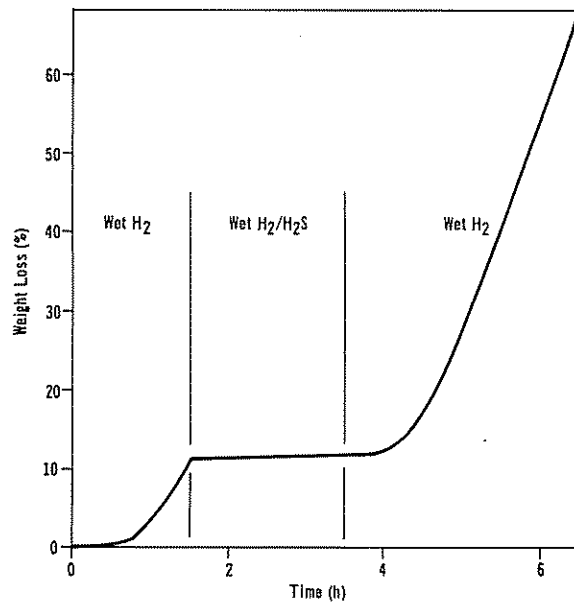Fig. 14. Effect of H_2S on reactivity of Fe-loaded char in wet N_2.

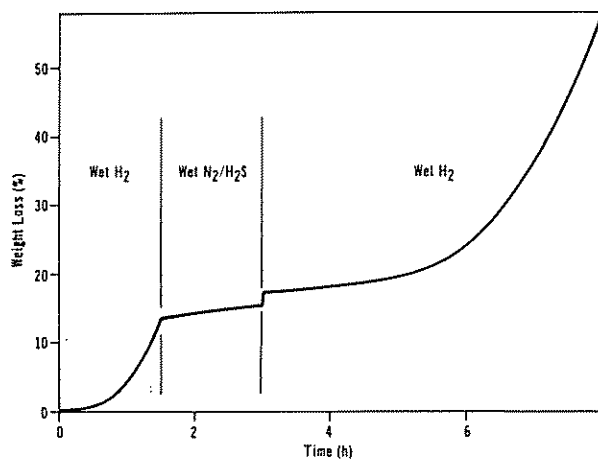Fig. 15. Effect of H_2S on reactivity of Fe-loaded char in wet H_2.

Fig. 16. Effect of H_2S on reactivity of Fe-loaded char in wet N_2 following and preceding reactivity in wet H_2.

of Fe. At least on the basis of the H_2S/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_2S 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_2S, H_2, CO and H_2O compete for interaction with Fe surface sites. At least for Ni, steam is found to have no influence on the chemisorption of H_2S at 1123 K[16].

The presence of H_2 along with H_2S (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_2S (or COS) is removed from the gas stream. Results on the regeneration of sulfided Ni catalysts in H_2O/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_2O/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_2S were detected. Thus the following reaction pattern was suggested:

$$Ni\text{–}S + H_2O = NiO + H_2S \qquad (8)$$

$$H_2S + 2H_2O = SO_2 + 3H_2. \qquad (9)$$
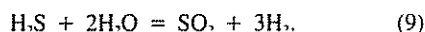
Since the equilibrium constant of reaction (9) at 973 K is small (and decreases further with increasing temperature), it means that a small amount of H_2 will inhibit the conversion of H_2S. It is concluded that sulfur removal following this reaction pattern requires a total oxidation of the catalyst[16]. If some part of the Ni surface is still exposed to the gas, H_2 will cause H_2S to be retained at the surface.

At 1123 K, the equilibrium H_2O/H_2 ratio for the reaction

$$Fe + H_2O = FeO + H_2 \qquad (10)$$
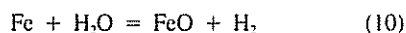
is 0.56[17]. In wet H_2, the H_2O/H_2 ratio is considerably

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_2S (Fig. 16) than it is following exposure to wet H_2 containing H_2S (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_2S 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_2S 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_2S (Figs. 15 and 16). These results are not understood at this time.

REFERENCES

1. P. L. Walker, Jr., F. Rusinko, Jr. and L. G. Austin, Advances in Catalysis (Edited by D. D. Eley, P. W. Selwood, and P. B. Weisz), Vol. 11, pp. 133–221, Academic Press, New York (1959).
2. D. W. McKee, Chemistry and Physics of Carbon (Edited by P. L. Walker, Jr. and P. A. Thrower), Vol. 16, pp. 1–118, Marcel Dekker, New York (1981).
3. P. L. Walker, Jr., S. Matsumoto, T. Hanzawa, T. Miura and I. M. K. Ismail, Fuel 62, 140 (1983).
4. P. L. Walker, Jr., M. Shelef and R. A. Anderson, Chemistry and Physics of Carbon (Edited by P. L. Walker, Jr.), Vol. 4, pp. 287–383, Marcel Dekker, New York (1968).
5. R. L. Taylor, Ph.D. thesis, The Pennsylvania State University, 1982.
6. C. A. Mims and J. K. Pabst, Fuel 62, 176 (1983).
7. C. Ishizaki and I. Marti, Carbon 19, 409 (1981).
8. T. Wigmans, J. van Doorn and J. A. Moulijn, Fuel 62, 190 (1983).

9. B. J. Wood, R. H. Fleming and H. Wise, *Fuel* **63**, 1600 (1984).

10. S. J. Yuh and E. E. Wolf, *Fuel* **63**, 1604 (1984).

11. O. C. Cariaso and P. L. Walker, Jr., *Carbon* **13**, 233 (1975).

12. B. R. Puri, *Chemistry and Physics of Carbon* (Edited by P. L. Walker, Jr.), Vol. 6, pp. 191–282, Marcel Dekker, New York (1970).

13. C. Rebick, *Frontiers of Free Radical Chemistry* (Edited by W. A. Pryor), pp. 117–137, Academic Press, New York (1980).

14. M. B. Abdel-Baset and C. T. Ratcliffe, *Preprints Am. Chem. Soc. Div. Fuel Chem.* **25**(1), 1 (1980).

15. H. J. Grabke, E. M. Petersen and S. R. Srinivasan, *Surface Sci.* **67**, 501 (1977).

16. J. R. Rostrup-Nielsen, *J. Catalysis* **21**, 171 (1971).

17. H. J. Grabke, *Ann. N.Y. Acad. Sci.* **213**, 110 (1973).