CATALYSIS OF THE CONCURRENT C-H₂O-H₂ AND METHANATION REACTIONS—INHIBITION BY SULFUR

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Abstract—In an attempt to maximize CH_4 production from the C-H_2O reaction, two catalysts were used. Iron or K was added to a high surface area char, which in turn was mixed with a methanation catalyst, either Ni or Co-Mo supported on γ-Al_2O_3. If the γ-Al_2O_3 contained negligible sulfur, as was the case with a commercial Ni/Al_2O_3 catalyst, mixing this catalyst with the Fe-loaded char was seen to yield synergism in the rate of char gasification in a H_2O/H_2 gas mixture of molar ratio 0.032. Further, significant production of CH_4 is realized via the reaction of CO, produced by the C-H_2O reaction, with H_2. However, if the γ-Al_2O_3 contained traces of sulfur, Fe- or K-loaded char gasification by steam exhibited a long induction period of low reactivity and concurrent low rates of CH_4 production. Only when the sulfur content in the mixture was apparently reduced to a very low level did char reactivity attain a higher level, with the catalyst mixture again exhibiting synergism.
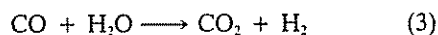
KEY WORDS—Catalysis, sulfur, methanation, carbon-steam reaction.

1. INTRODUCTION

There is continuing interest in the production of methane via the gasification of carbon by steam. That is,

$$2C + 2H_2O \longrightarrow CH_4 + CO_2 \qquad (1)$$

This overall reaction is the combination of the following reactions:

$$2C + 2H_2O \longrightarrow 2CO + 2H_2 \qquad (2)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (3)$$

$$CO + 3H_2 \longrightarrow CH_4 + H_2O \qquad (4)$$

Reaction (1) is of interest since it is essentially thermoneutral. The endothermicity of reaction (2) is closely balanced by the exothermicity of reactions (3) and (4); therefore, there is great advantage in carrying out these reactions within the same reactor. Methane can also be produced via the reaction,

$$C + 2H_2 \longrightarrow CH_4 \qquad (5)$$

but this reaction is about three orders of magnitude slower than the C-H_2O reaction[1].

Since conversion in reaction (2), at equilibrium, is favored by increasing temperature (Fig. 1) and the rate increases sharply with increasing temperature (an activation energy of about 334 kJ/mole[1]), it is

advantageous to conduct this reaction at elevated temperatures. However, as seen in Fig. 1, equilibrium conversion via eqns (3) and (4) decreases sharply with increasing temperature. Thus, there is interest in catalyzing these reactions so that reaction temperature can be lowered. It is also desirable, in practice, to operate at elevated pressures to accelerate the rate and increase maximum equilibrium conversion of eqn (4), as shown in Fig. 1.

Iron is a good catalyst for the C–H_2O reaction when sufficient H_2 is present to keep the iron in a reduced state[2]. Nickel is an excellent catalyst for both the water-gas shift reaction[3] and the methanation reaction[4]. It is also a reasonable catalyst for the C–H_2O reaction, again as long as Ni remains in the reduced state. Unfortunately, sulfur strongly poisons the catalytic activity of both Fe and Ni for the preceding reactions[3,4]. There is some indication, however, that the hydrogenation activity of Co/Mo on alumina is not impaired by the presence of sulfur[5].

In this study, the effect of sulfur on catalytic activities of Fe, Ni, Co/Mo, and K have been examined.

2. EXPERIMENTAL

The char used in this study was a 40 × 70 mesh U.S. standard sieve 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 with nitrate solutions[6]. The char was soaked for

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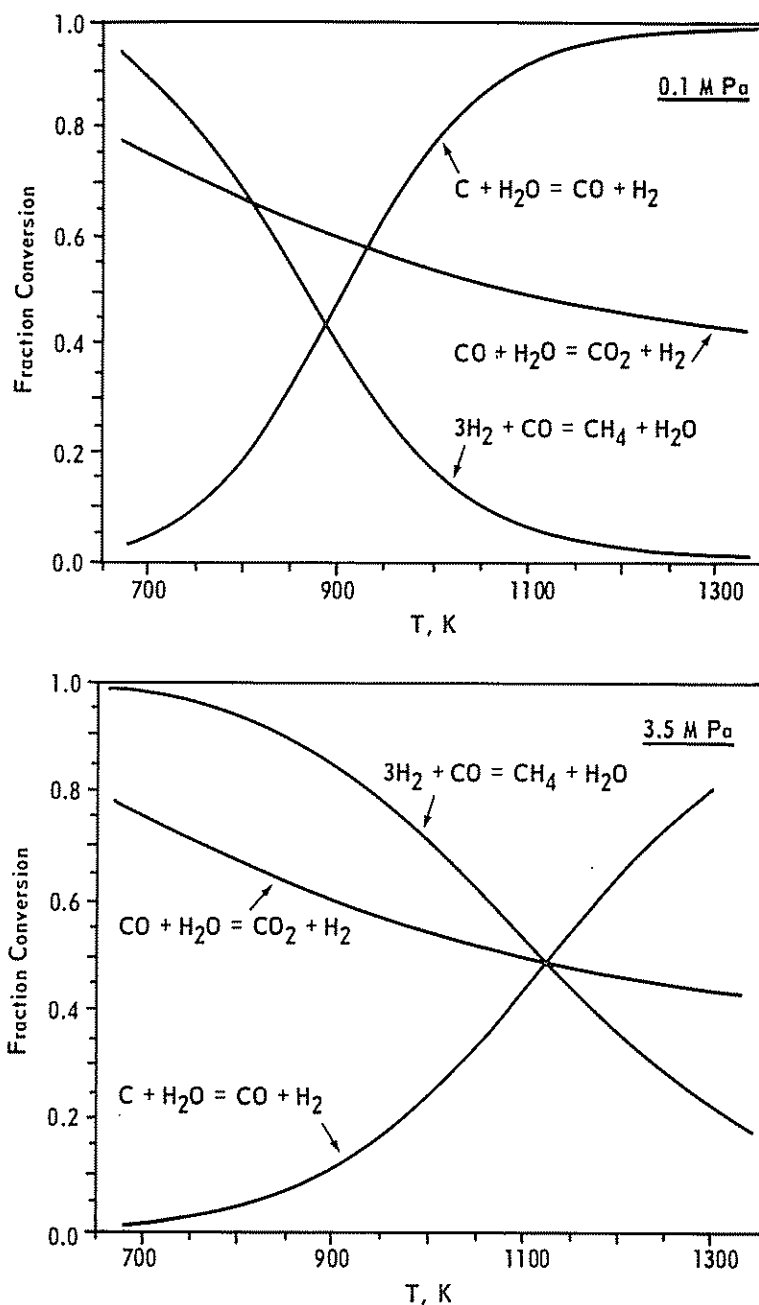†Present address: Government Industrial Research Institute, Kyushu, Tosu, Saga, 841 Japan.

Fig. 1. Equilibrium conversions for reactions of importance in the production of CH₄ via the carbon-steam reaction.

48 h at room temperature with stirring, then filtered and dried overnight at 378 K in a vacuum oven. Loadings in percent weight (wt %) were: Fe, 2.58%, and K, 11.0%. Loadings in mmole/g char were: Fe, 0.462, and K, 2.80.

The following water-gas shift and methanation catalysts were used: Ni/γAl₂O₃ (designated catalyst A) and Co-Mo/γ-Al₂O₃ (catalyst B). Nickel (67 wt %) was supported on Al₂O₃ having a BET surface area of 117 m²/g. This catalyst had a negligible sulfur content. This commercial catalyst was characterized previously in this laboratory by magnetic measurements and methanation activity[7]. The as-received

catalyst had a degree of metal dispersion (percent of total Ni atoms on the surface) of 10%. Following heating to 1173 K in N₂, it is estimated that dispersion decreased to ~6%. The Co-Mo commercial catalyst, 3 wt% Co as CoO and 10 wt% Mo as MoO₃, was supported on a standard hydrodesulfurization (HDS) γ-Al₂O₃ catalyst support having a surface area of 140 m²/g. The HDS Al₂O₃ support was also available for our studies. This support contained 0.23 wt% sulfur. Most of its surface area was in pores 14 nm in diameter[8]. This support was impregnated in this laboratory with Ni, using the nitrate solution, to a loading of 30 wt% Ni (catalyst C). Catalysts A,
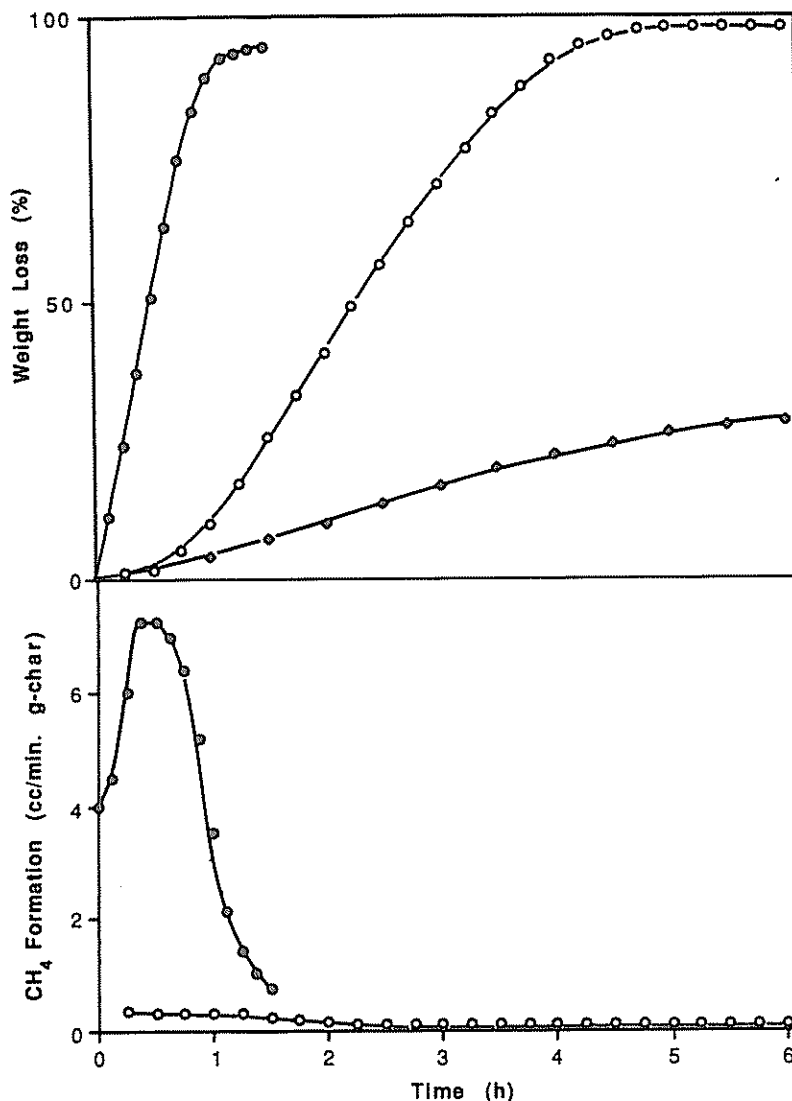
Fig. 2. Char reactivity and CH_4 production in the systems Fe-loaded char/catalyst A (◉), Fe-loaded char (○), and char/catalyst A (♦) at 1123 K.

B, and C were used in a particle size of 40 × 70 mesh U.S. standard sieve, that is the same particle size as the char.

Char reactivities were measured in a vertical TGA (Fisher thermogravimetric analyzer model 422) at 0.1 MPa total pressure and at temperatures ranging from 973 K to 1123 K. Char weight was 50 mg; it was ordinarily mixed with the same bulk volume of catalyst supported on Al_2O_3 (catalyst A, B, or C). The sample, held in a quartz bucket, was heated to reaction temperature at a rate of 20 K/min in dry N_2 and held at this temperature for 30 min. before commencing reaction. The reactant gas was H_2 (flow rate 100 ml (STP)/min) saturated with water vapor at 298 K (H_2O: 3.1 kPa), yielding a H_2O/H_2 molar ratio of 0.032. The effluent gas stream was analyzed for CH_4 concentration using an IR detector, with a sensitivity as low as 2 ppm.

Introduction of wet H_2 led to a rapid weight decrease of catalysts A, B, or C, which was completed in several minutes at 1123 K. This was attributed primarily to weight loss due to catalyst reduction. Weight loss, attributed to char gasification, was measured starting at this point.

3. RESULTS AND DISCUSSION

With the large excess of H_2 to water in the incoming gas stream used in this study, essentially all the carbon gasified through eqn (2) can be converted to CH_4 through eqn (4) at equilibrium. Also because of the large excess of H_2 used, eqn (3) will occur to a negligible extent.

3.1 Reaction in the Fe-char/Ni-Al₂O₃ system

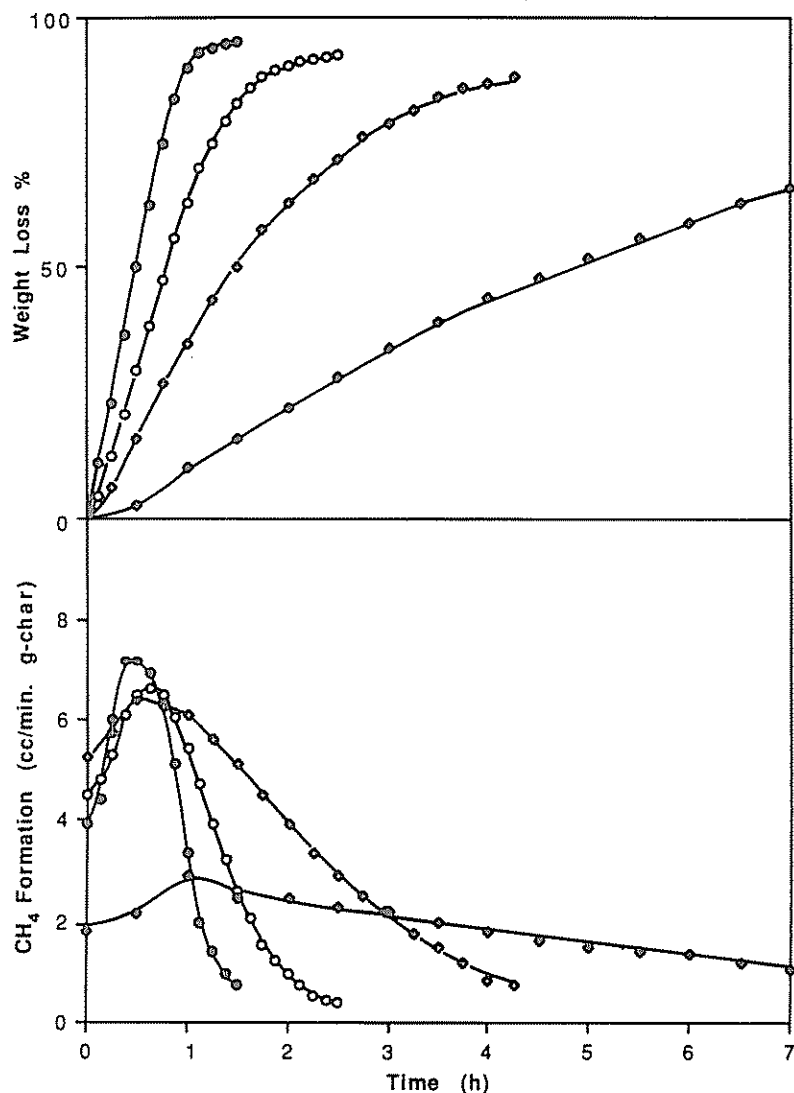Figure 2 presents results for the reactivity of Fe-loaded char in the absence and presence of catalyst

Fig. 3. Char reactivity and CH_4 production in the system Fe-loaded char/catalyst A at various temperatures: 1123 K (◉), 1073 K (○), 1023 K (◊), 973 K (♦).

A at 1123 K. In the absence of catalyst A, maximum reactivity is 31.4%/h. If it was assumed that gasification was due entirely to the reaction of H_2 with char to produce methane, 9.6 ml CH_4/min g-char would be produced. As seen from Fig. 2, little CH_4 is produced from this reaction; therefore, most of the gasification can be attributed to the $C–H_2O$ reaction. However, in the absence of a good methanation catalyst, little of the CO produced via the $C–H_2O$ reaction is converted to CH_4. Again, ~9.6 ml CH_4/min g-char could be produced if all the CO resulting from char gasification at its maximum rate were methanated via eqn (4).

When catalyst A was added to the Fe-loaded char, char reactivity increased sharply to ~100%/h and significant CH_4 was produced. Synergism resulting from mixing catalyst A with the Fe-loaded char is seen since maximum char reactivity for the char/Ni-Al_2O_3 system is only 6.6%/h. Nickel is known to be

an active catalyst for dissociation of H_2[9]. Following dissociation to H atoms, it has been shown that these atoms diffuse rapidly on Al_2O_3 surfaces and can spill over to adjoining surfaces[9]. It is suggested that spillover of H atoms to the Fe supported on the char is effective at maintaining a higher fraction of this surface in a reduced state and, hence, more catalytically active for the $C–H_2O$ reaction.

Figure 3 presents results for the reactivity of Fe-loaded char in the presence of catalyst A at temperatures ranging from 973 to 1123 K. As expected, char gasification rates increased sharply with increasing temperature, the maximum reactivity showing an eightfold increase over the temperature range. However, increasing temperature has much less of an effect on the maximum rate of CH_4 production, increasing it only 2.5-fold. As stated earlier, with the large excess of H_2 used, CH_4 production via the methanation reaction is restricted little by equilib-
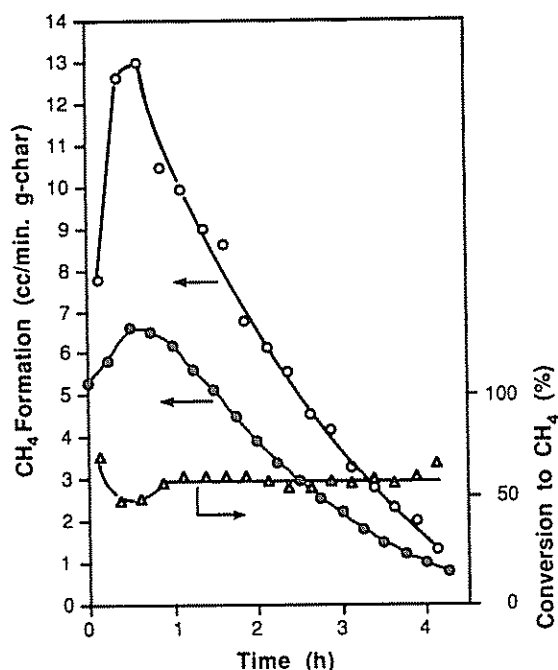
Fig. 4. Comparison of amount of CH_4 formed in the system Fe-loaded char/catalyst A (●) with amount that could have formed at equilibrium as a result of char gasification (O) at 1023 K.

rium. Rather, with increasing temperature above 773 K, we have shown in this laboratory that increased sintering of Ni supported on Al_2O_3 occurs[7]. This leads to decreasing specific reactivity of Ni for the methanation reaction[7]. Under the experimental conditions used here, if maximizing CH_4 production rate is the ultimate aim, it is not necessary to exceed a temperature of ~1023 K.

Figure 4 presents results for measured and equi-librium CH_4 production at 1023 K as a function of reaction time (or gasification rate). Over the 4-h reaction time ~60% of the CH_4, which could have been produced at equilibrium as a result of char gasification, is, in fact, produced. At 1123 K the amount of CH_4 produced decreased to only ~24% of that possible at equilibrium.

As discussed earlier, the HDS Al_2O_3 support was also impregnated with Ni to a loading of 30 wt% Ni (catalyst C). Figure 5 presents the reactivity of the Fe-loaded char in the presence of catalyst C at 1123 K. The shape of the reactivity plot is sharply different from that found for the Fe-loaded char in the pres-ence of catalyst A. Whereas char reactivity in the presence of catalyst A immediately assumed its max-imum value (Fig. 2), in the presence of catalyst C a long induction period lasting for ~2 h occurred. Such an induction period is reminiscent of the effect of H_2S on the reactivity of Fe-loaded char in steam at 1123 K[10]. Hydrogen sulfide is extremely effective at sulfiding the surface of Fe and consequently re-ducing its catalytic activity. For example, at 1123 K only 1 ppm H_2S in H_2 is needed to sulfide 60% of surface Fe sites[11]. The HDS Al_2O_3 support con-tained measurable amounts of sulfur. This is con-sistent with our finding when we studied the coking of high purity anthracene over the HDS Al_2O_3 sup-port in an autoclave in this laboratory[12]. The odor of H_2S was detected when the autoclave was opened following the completion of a run. This result again emphasizes the deleterious effect of sulfur on the activity of Fe as a catalyst for the $C–H_2O$ reaction.

To further emphasize the inhibiting effect of sulfur on char gasification in steam, the HDS-alumina sup-port was added to the Fe-loaded char and to the Fe-loaded/char catalyst A system. As is seen in Fig. 6, char gasification and CH_4 production rates at 1073 K are sharply reduced over that with no HDS catalyst
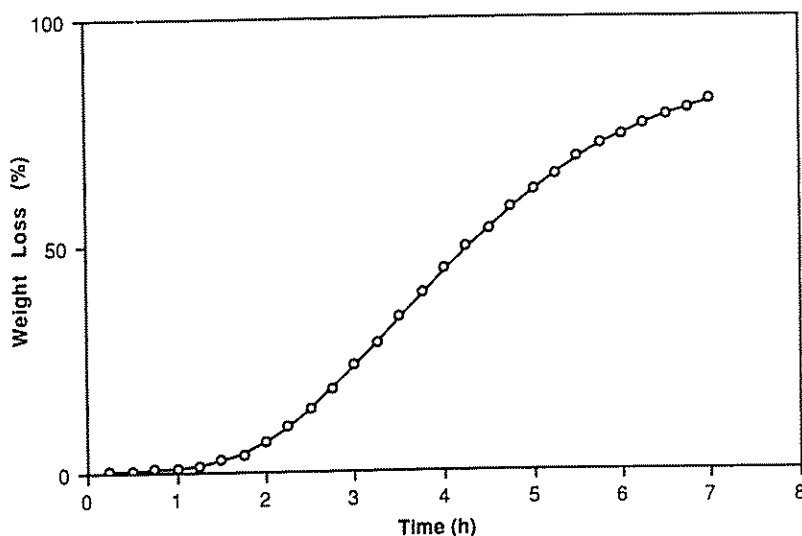

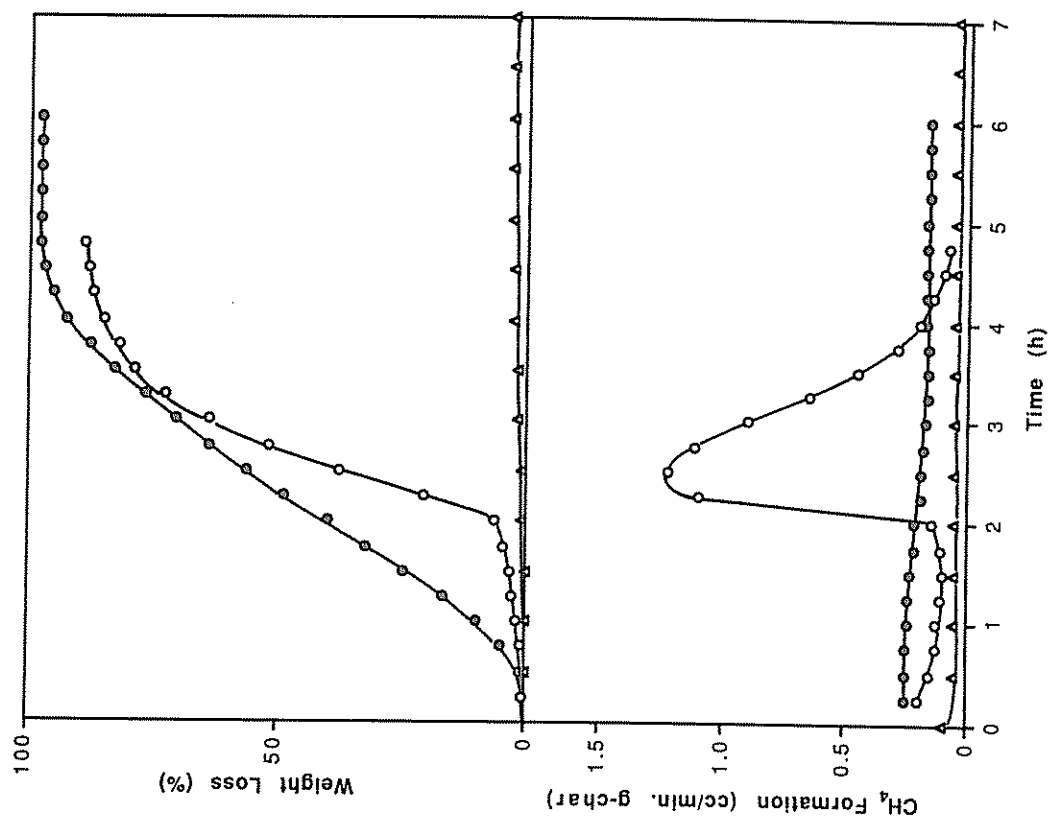Fig. 5. Char reactivity in the system Fe-loaded char/catalyst C at 1123 K.

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Fig. 7. Char reactivity and CH₄ production in the systems Fe-loaded char/catalyst B at 1123 K. Fe-loaded char (○), Fe-loaded char (⊘), and char/catalyst B (△) at 1123 K.

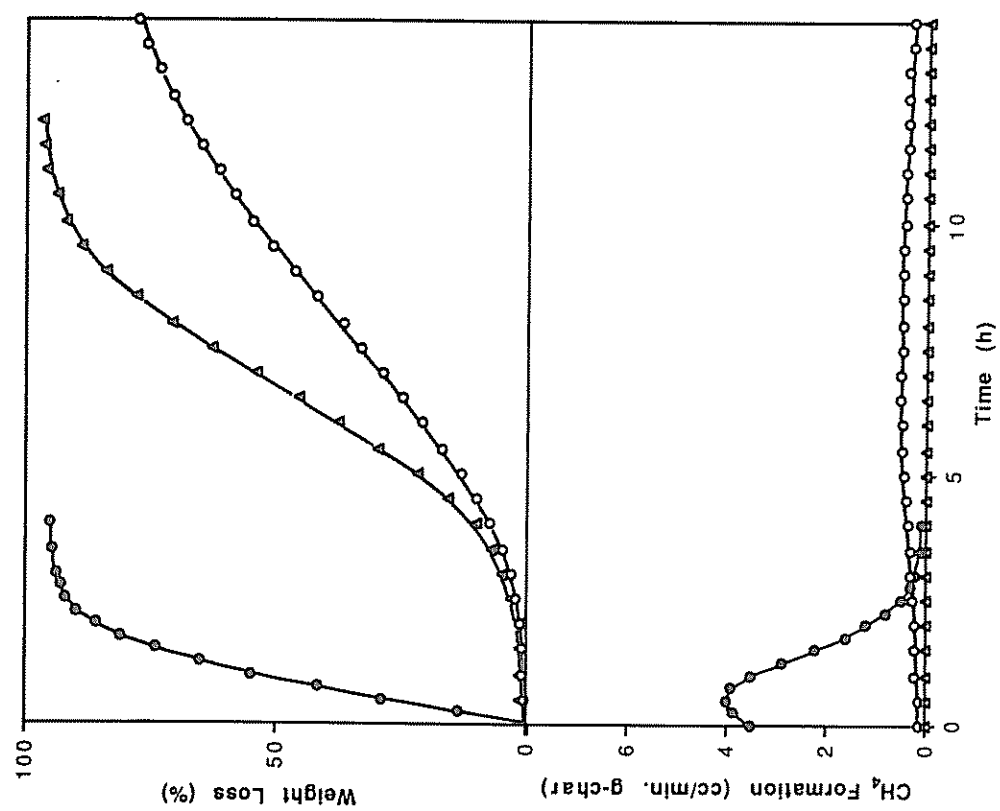

Fig. 6. Effect of HDS alumina support on char reactivity and CH₄ production at 1073 K. Fe-loaded char/catalyst A (⊘), Fe-loaded char/HDS-Al₂O₃ (△), Fe-loaded char/catalyst A/HDS-Al₂O₃ (○). Bulk volume: 1.0/0.5/0.5.

present. Again a long induction period is observed before maximum gasification rates are achieved.

3.2 *Reaction in the Fe-char/Co-Mo-Al$_2$O$_3$ system*

Figure 7 presents results for the reactivity of Fe-loaded char in the absence and presence of catalyst B at 1123 K. The reactivity for the Fe-loaded char/catalyst system exhibits a long induction period of low char reactivity. This was as expected since Co-Mo is supported on HDS Al$_2$O$_3$ in this system. Following the induction period, char reactivity attains a maximum value of 77%/h. This char gasification would yield a maximum CH$_4$ production rate of 23.5 ml CH$_4$/min g-char, assuming equilibrium was attained in the methanation reaction. In fact, with an experimental maximum rate of CH$_4$ production of 1.22 ml CH$_4$ min g-char, only 5.2% of CH$_4$ production possible at equilibrium was realized. This is considerably poorer than the performance shown by the water-gas shift catalyst A.

Catalyst B alone has little catalytic activity for char gasification. However, it is interesting that maximum char reactivity (77%/h) in the Fe-loaded char/catalyst B system exceeds maximum char reactivity (31.4%/h) for the Fe-loaded char alone. This is similar to the synergism in char reactivity found when catalyst A was added to the Fe-loaded char. It again suggests that catalyst B, following sulfur elimination, is effective in dissociating molecular hydrogen, with the H atoms produced spilling over onto Fe surface

sites and maintaining them in a more active state for catalysis of the C–H$_2$O reaction.

Figure 8 shows results of an experimental run confirming the strong inhibiting effect of H$_2$S on catalytic activity for char gasification in the system Fe-loaded char/catalyst B. As was seen in Fig. 7, following an induction period of ~2 h, char reactivity at 1123 K increases sharply. However, following a char burn-off of ~31%, 480 ppm H$_2$S was introduced into the wet H$_2$ gas stream. Char reactivity is rapidly reduced to a negligible value as long as the H$_2$S is present. Following removal of H$_2$S from the gas stream, ~3 h is apparently required to rid the system of H$_2$S and to again attain a high-char reactivity in steam.

3.3 *Reaction in the K-char/Co-Mo-Al$_2$O$_3$ system*

Potassium is an excellent catalyst for the C–H$_2$O reaction[10]. However, its catalytic activity is strongly retarded by sulfur in a wet H$_2$ atmosphere[10]. Figure 9 indicates that char reactivity at 1073 K for the K-loaded char is rapid (a maximum rate of 36.4%/h) with no induction period present. Further, K shows some activity for the production of CH$_4$. However, when catalyst B is added to the K-loaded char, char reactivity is essentially killed. Significant reactivity is ultimately expected when sulfur is removed from the system, but an induction period of at least 7 h is seen. Clearly, K (like Fe) tightly bonds sulfur to its surface; and this sulfur is extremely difficult to remove.
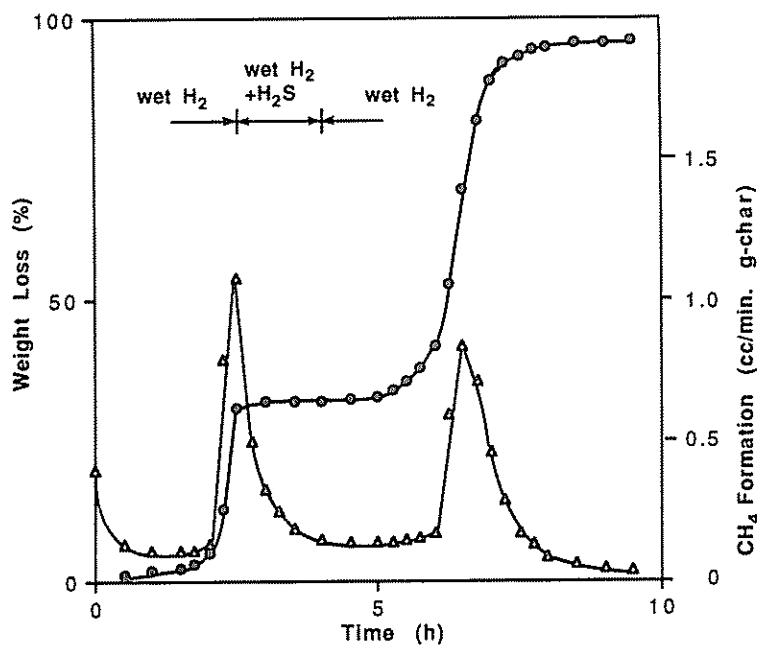

Fig. 8. Effect of H$_2$S introduction on catalytic activity in the Fe-loaded char/catalyst B system for char gasification (⬤) and methane production (△).
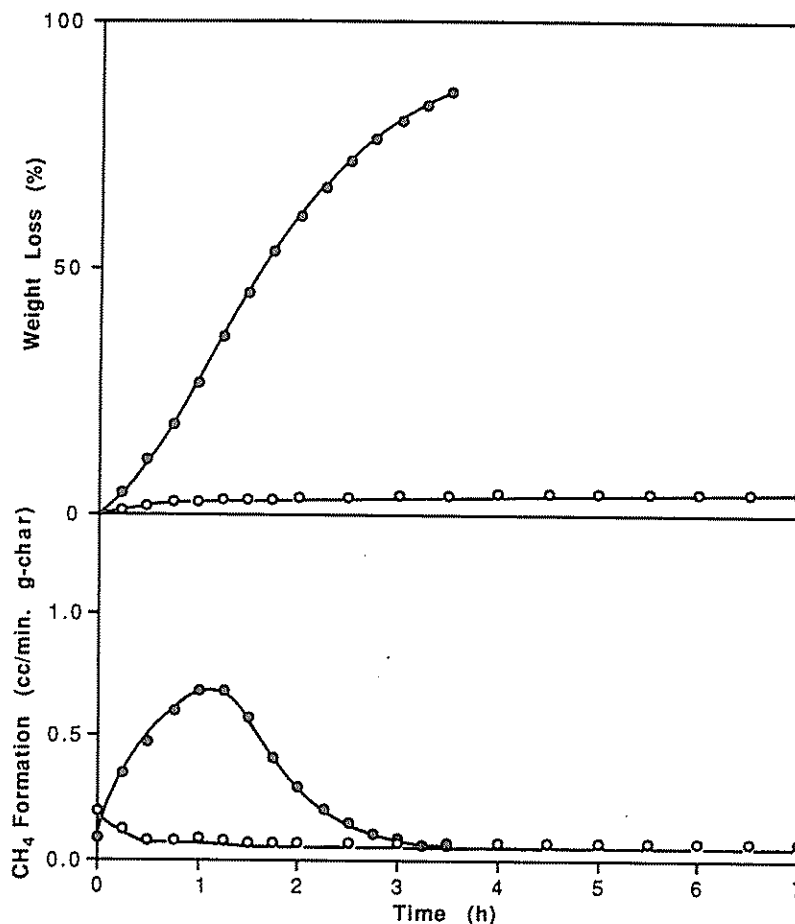
Fig. 9. Char reactivity and CH_4 production at 1073 K in the systems K-loaded char (◉) and K-loaded char/catalyst B (○).

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