SULFUR PROBLEMS IN THE DIRECT CATALYTIC PRODUCTION OF METHANE FROM COAL-STEAM REACTIONS

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The use of a multiple catalyst system consisting of potassium carbonate and a commercial nickel methanation catalyst for the direct production of methane from coal-steam reactions has been described in earlier papers (1,2). This system combines the beneficial catalytic effects of these catalysts to produce in a single-step conversion a product gas consisting primarily of methane and carbon dioxide with lesser amounts of carbon monoxide and hydrogen and has a CO_2-free heating value of about 850 Btu per SCF. Two of the apparent problems inherent with such a system are catalyst recovery and the loss of catalyst activity over prolonged periods of time at the conversion temperatures ($\geq$ 1200°F) in the presence of the various reactants produced from the coal gasification. In conjunction with the latter problem, this paper addresses the influence of sulfur compounds produced during gasification upon catalyst life and activity. This situation is compared and contrasted to the catalyst performance in the catalytic methanation of synthesis gas.

EXPERIMENTAL

Experimental Systems

The coal gasification was carried out in 1" o.d., batch-charge reactor which was constructed of 316 stainless steel. A schematic is shown in Figure 1.

The methanation studies with synthesis gas were performed in a 1/2" o.d. adiabatic flow reactor. It too was constructed of 316 stainless steel. Its schematic is shown in Figure 2.

Feed Materials

A subbituminous coal from Glenrock, Wyo., and Consol lignite from Stanton, N. Dak., both ground to 60-100 mesh were used in this investigation. Tables I and II contain the proximate and ultimate analyses of these materials. Although it was intended to use only anhydrous potassium carbonate (K_2CO_3) as the alkali catalyst x-ray studies indicated that it had taken up water to form some $K_2CO_3 .3/2\ H_2O$. The methanation catalyst, which contains approximately 35% nickel, was purchased from Harshaw Chemical Company. Additional chemicals and reagents that were used in conjunction with this investigation are commercially available or readily prepared by routine procedures.

Gas Analyses

The product gas volume was measured with a calibrated wet test meter, while the composition was periodically monitored with a gas chromatograph equipped with two thermal conductivity detectors. A Porapak Q column with helium carrier gas was used in conjunction with one detector while a molecular sieve column with argon carrier was used with the other. A total analysis required about 15 minutes. Data reduction was facilitated with an Auto Lab System IV digital integrator equipped with a calculation module.

Sulfur Analyses

The total sulfur and sulfate sulfur in the nickel methanation catalyst were determined by ASTM Method E39. The sulfide sulfur was calculated as the difference

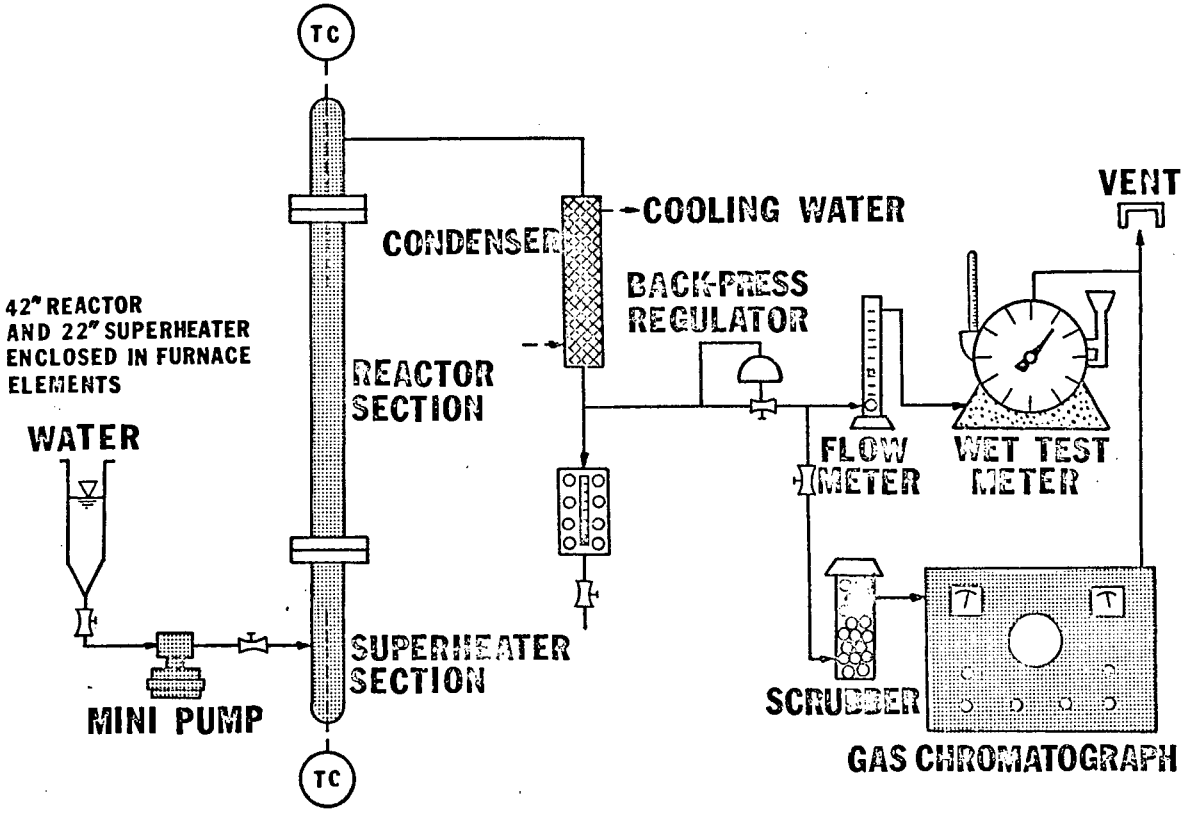

FIGURE 1. SCHEMATIC FLOW DIAGRAM ONE INCH REACTOR

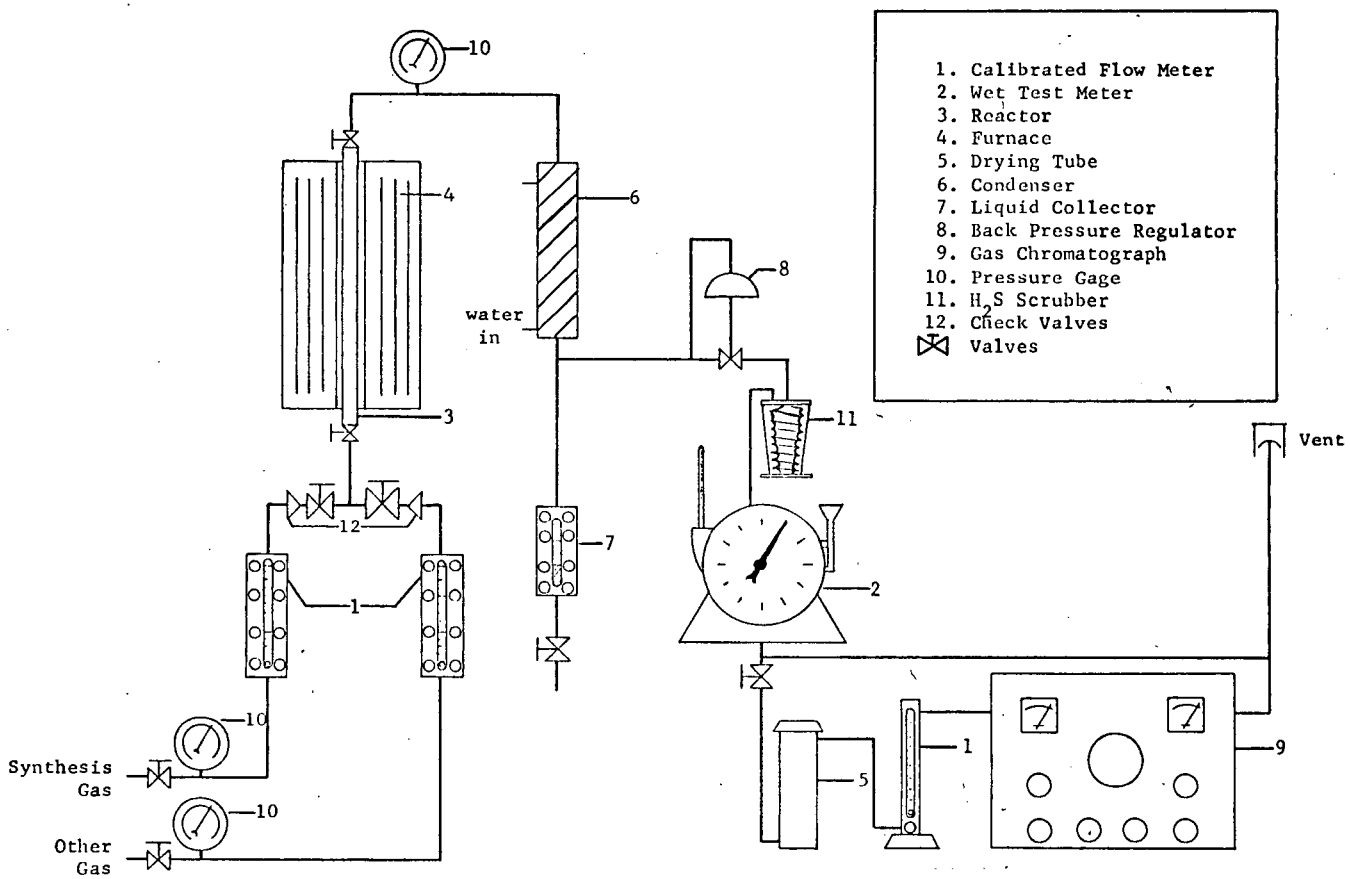

FIGURE 2 SCHEMATIC FLOW DIAGRAM 1/2" FLOW REACTOR

between the total sulfur and sulfate sulfur. A LECO sulfur analyzer was used to determine total sulfur in the coal and ash as well as in the nickel methanation catalyst. In addition some sulfur determinations employed the ASTM method D1757.

X-Ray Diffraction

Coal, ash and catalysts were examined with a General Electric XRD-5 diffractometer. Copper radiation at 35-50 kvp and 16 ma was used for the analyses. Scanning was started at an angle 2θ of 4-6° and continued through 70°. The patterns were recorded on a strip chart. Interplanar spacings were determined from CuKα (λ=1.5418 A) tables, whereas compound identifications employed the ASTM x-ray powder diffraction file.

Methodology

The coal gasification experiments were conducted by dry mixing the coal, catalysts and other additives and charging them to the reactor. Generally the runs employed 100g of coal, 20g K_2CO_3 and 100g of nickel methanation catalyst. The reactor temperature was brought to an operating value of about 650°C in less than two hours. A predetermined operating pressure was employed. These conditions were maintained throughout the remainder of the run. The total run time was about seven and half hours. During the run the gaseous product was monitored every half-hour and the results presented as time rated averages.

Methanation investigations with the half-inch adiabatic flow reactor employed rather standard operating procedures. A catalyst bed one inch in length was charged to the reactor. The temperature was monitored by a thermocouple positioned in the catalyst bed while means for varying the temperature, pressure, space velocity and gas composition were provided by external control. The product gas composition was periodically monitored with a gas chromatograph set-up similar to the one described above under Gas Analyses.

Table I. Analysis of Glenrock Coal (wt.%)

	As Received	Moisture Free
Proximate Analysis		
Moisture	12.2	--
Volatile Matter	39.6	45.1
Fixed Carbon	36.1	41.1
Ash	12.1	13.8
Heating Value (Btu/lb)	9140	10410
Ultimate Analysis		
Hydrogen	5.1	4.3
Carbon	52.7	60.0
Nitrogen	0.6	0.7
Oxygen	28.6	20.2
Sulfur	0.8	1.0
Ash	12.1	13.8

Table II. Analysis of Consolidation Lignite (wt.%)

	As Received	Moisture Free
Proximate Analysis		
Moisture	25.1	--
Volatile Matter	31.8	42.5
Fixed Carbon	38.3	51.1
Ash	4.8	6.4
Heating Value (Btu/lb)	9800	10720

	As Received	Moisture Free
Ultimate Analysis		
Hydrogen	6.4	4.8
Carbon	50.3	67.2
Nitrogen	0.6	0.8
Oxygen	37.5	20.3
Sulfur	0.4	0.5
Ash	4.8	6.4

RESULTS AND DISCUSSION

Multiple Catlayst Single Step Conversion

In the direct production of hydrocarbons from coal-steam reactions catalysts are employed to increase reaction rates and lower conversion temperatures. Lower temeratures result in a more favorable equilibrium. Consequently, more methane is realized in the product gas. By employing this method 850 Btu/SCF gas has been produced by the single step conversion (2).

In view of the complexity of the coal it is not surprising that a good mechanistic description of gasification has not been forwarded. Nevertheless, from several hundred experimental runs with this system, the following empirical description of the conversion has evolved. The overall objective is to increase the atomic H/C ratio and at the same time eliminate the oxygen from the hydrogen deficient coal. This in turn calls for a source of hydrogen which can be obtained from water as a coupled reactant. Hydrogen production may be ascribed to carbonization followed and accompanied by the water-gas, CO-shift and steam reforming reactions as illustrated by Eqs. 1, 2, 3 and 4.

Carbonization $$C_aH_bO_{b/2} = aC + b/_2H_2O \quad (1)$$

Water-gas $$aC + aH_2O = aCO + aH_2 \quad (2)$$

CO-shift $$aCO + aH_2O = aCO_2 + aH_2 \quad (3)$$

Steam reforming $$C_aH_bO_{b/2} + (2a-b/_2)H_2O = aCO_2 + 2aH_2 \quad (4)$$

The major product component of SNG can be arrived at by reacting the hydrogen produced from the preceding reactions with the initial feed material as shown in Eq. 5.

$$C_aH_bO_{b/2} + 2aH_2 = b/_2H_2O + aCH_4 \quad (5)$$

Combining Eqs. 4 and 5 give Eq. 6, which is a simplified form of the overall conversion reaction where the small amounts of nitrogen and sulfur in the feed material have not been accounted for.

$$2C_aH_bO_{b/2} + 2(a-b/_2)H_2O = aCO_2 + aCH_4 \quad (6)$$

Reactions also of importance in describing the direct conversion of coal are devolatilization and methanation. The devolatilization reactions can be viewed as Eqs. 7-10 or Eq. 11 overall, whereas the methanation reaction is demonstrated by Eq. 12.

$$C_aH_bO_c = C_{(a-c/2)}H_b + c/_2CO_2 \quad (7)$$

$$C_aH_bO_c = C_aH_{b-2c} + cH_2O \quad (8)$$

$$C_{(a-c/2)}H_b = C_d + C_{(a-c/2-d)}H_b \quad (9)$$

$$C_aH_{(b-2c)} = C_d + C_{(a-d)}H_{(b-2c)} \quad (10)$$

$$2C_aH_bO_c = 2C_d + c/2CO_2 + cH_2O + C_{(a-c/2-d)}H_b + C_{(a-d)}H_{(b-2c)} \quad (11)$$

$$3H_2 + CO = CH_4 + H_2O \quad (12)$$

Although the extent of the catalysts' role in the above reactions is not known from a mechanistic point of view, the influence of the alkali carbonate and nickel methanation catalyst has been amply demonstrated (2). The alkali catalyzes the coal-steam and devolatilization reactions for the production of intermediate reactants while the nickel catalyzes the conversion of these intermediates on to final products.

There has been some criticism of the thermodynamics concerning the feasibility of the direct production of SNG from coal-steam reactions by a single-step conversion. However, independent calculations by Edmiston (3) and Higgins (4) have shown that the overall conversion (Eq. 6) has a favorable standard free energy change in the vicinity of 900°K. Furthermore, the National Research Council (5) has taken the position that the reaction is thermodynamically feasible. These conclusions indicate that previous thermodynamic analyses have been based on β-graphite, which does not provide a good approximation of the coal's carbon for thermodynamic considerations. Consequently, erroneous conclusions are likely to arise therefrom.

The enthalpy of Eq. 6 has been calculated (4,6) from heats of combustion and amounts to about 10 kcal/mole. This value will vary somewhat with the rank of the coal. In spite of its endothermic nature, the single-step conversion is believed to be considerably more thermally efficient than the more conventional multiple-step processes for the production of SNG from coal.

Sulfur in the Multiple Catalyst Single-Step Conversion

In previous discussions of the process concept no mention of the influence of the coal's sulfur on the conversion was made. The sulfur contained in the coal is of particular concern in a multiple catalyst single-step conversion since its derived intermediates often function as catalyst poisons (7).

During the gasification of coal under reducing conditions the organic and pyritic sulfur of the coal are converted to gaseous sulfur compounds in their most reduced state. The extent of the coal's sulfur conversion is strongly dependent upon the gasification temperature (8). Although the type of reduced sulfur gases produced have not been extensively investigated and correlated with gasification conditions, H_2S, CS_2 and COS seem to be the predominate forms. These compounds are known to act as catalyst poisons in catalytic methanators even when present in small concentrations. Although the extent of sulfur poisoning of the nickel methanation catalyst used in the single-step conversion is more difficult to predict in view of the multitude of competing equilibria here too sulfur poisoning is anticipated to be a problem.

Table III contains some sulfur material balances that were undertaken to determine the extent of sulfur buildup on the nickel catalyst in the integrated system. Representative runs for both Glenrock coal and Consol lignite are included. These runs were completely integrated using the coal or lignite dry mixed with potassium carbonate and the nickel methanation catalyst. An examination of the data demonstrates that some of the sulfur is lost to the system, some remains in the ash and some is deposited upon the nickel methanation catalyst.

It is noted that there is considerable variance in the distribution of the coal's sulfur in the grouped runs. This apparently is attributed to the sensitivity toward experimental conditions and difficulty in obtaining a homogeneous reaction mixture of the 60-100 mesh coal and alkali carbonate with the 1/8" nickel catalysts.

The sulfur loss to the system is the computed difference between total sulfur in reactants charged and that found in the nickel catalyst and ash. In addition to

Table III Sulfur Material Balances

Run No.	Coal[a]	% Coal Conv.	MSCF Gas/Ton (CO_2-free)	Btu/SCF (CO_2-free)	% Original Coal Sulfur In Ni catalyst	Ash	System Loss
714[b]	L	52	10.7	860	51.1	43.0	5.9
722[b]	L	48	9.4	780	63.6	33.5	2.9
724[b]	L	51	8.6	800	40.5	53.1	6.4
651[b]	G	62	9.7	820	40.7	50.8	8.5
652[b]	G	61	10.6	840	28.7	64.8	6.5
687[b]	G	59	8.9	780	44.2	48.3	7.5
734[c]	G	59	10.8	770	88.5	9.7	1.8
737[c]	G	61	15.4	580	87.4	11.6	1.0
738[c]	G	66	10.8	780	89.8	9.5	0.7

[a] L, Consol lignite; G, Glenrock coal. [b] Runs all at 32 psia. [c] Runs all at 112 psia.

Table IV Sulfur Scavenger Runs

Run No.	% Coal Conv.	Scavenger, g/g coal	MSCF Gas/Ton (CO_2-free)	Btu/SCF (CO_2-free)	% Original Coal Sulfur In Ni Catalyst	Ash	System Loss
750	68	Fe_2O_3, 0.017	11.9	740	20.9	81.0	-1.9
752	58	Fe_2O_3, 0.017	9.0	880	7.9	92.9	-0.1
756	66	Fe_2O_3, 0.032	9.4	970	6.2	92.4	1.4
763	70	Fe_2O_3, 0.024	10.3	900	14.3	85.1	0.6
764	66	Fe_2O_3, 0.042	10.8	910	7.1	92.6	0.3
761	68	Fe_2O_3, 0.048	9.2	900	7.0	94.9	-1.9
765	64	Fe_2O_3, 0.063	10.0	920	20.4	77.3	2.3
753	73	ZnO, 0.021	7.7	890	6.3	98.4	-4.7
755	72	ZnO, 0.042	8.6	940	9.3	91.9	-1.2
757	68	PbO, 0.010	10.2	960	3.2	98.6	-1.8

sulfur escaping in the product gas, metallic sulfides were formed on the walls of the stainless steel reactor.

Runs 734, 737 and 738 were at 112 psia while the rest of the tabulated runs were at 32 psia. Although the per cent coal conversion was essentially the same for both low and high pressure runs, a significant difference in the original sulfur was observed. The elevated pressure increased the distribution of the coal's amount of sulfur deposited on the nickel catalyst and decreased the amount in the ash and that lost to the system. Experimentally there was essentially no difference in the sulfur distribution of the low pressure results for Consol lignite and Glenrock coal.

Roughly between 30 and 60% of the coal's sulfur was deposited on the nickel catalyst in the low pressure runs. In some of the runs the form of nickel sulfide was identified by x-ray diffraction to be Ni_3S_2, presumably formed by the following reaction.

$$H_2S + 3/2Ni = 1/2Ni_3S_2 + H_2 \qquad (13)$$

The presence of the sulfide instead of the sulfate is in agreement with the reducing atmosphere within the system. This has been supported by qualitative analysis performed on the catalyst. In view of the large amounts of nickel catalysts employed in the experiments, no decrease in its activity was observed for the batch charge runs.

The nature of sulfur compounds in the ash containing alkali carbonate was not determined by x-ray diffraction. There was no evidence to support sulfate formations by the alkali carbonate. Some wet analytical results have indicated that in the neighborhood of 70% of the sulfur remaining in the Glenrock ash under these conversion conditions is in the sulfate form. This represents a considerable increase in this form since the Glenrock coal initially contained only about 0.05% sulfate. Of the remaining 0.75% sulfur in this coal, 0.3% is organic and 0.5% pyritic. Although there have been no intensive attempts to identify the sulfate compounds in the Glenrock ash, the coal is known to contain considerable amounts of Ca, Mg, Fe and Al, all of which could potentially form sulfates.

By employing an average value of 45% of the coal's sulfur combining with the nickel catalyst in the above low pressure runs, one can estimate the amount of coal required to completely sulfide the methanation catalyst (35% Ni) by using Eq. 13. This value is 35.4g coal per g nickel catalyst or 54.9 lb catalyst per ton of coal. In view of the price of nickel methanation catalysts and provided the data extrapolation is valid, such a high catalyst usage would be economically infeasible without some means of catalyst regeneration. In view of this situation, some preliminary efforts have been directed at this problem.

Tentative Solutions to Sulfur Problems

Four general approaches to coping with catalyst poisoning in the multiple catalyst direct conversion process have been considered. These include:

1. Employing sulfur scavengers in the system
2. Devising some means of catalyst regeneration
3. Searching for active, more sulfur resistant catalysts and
4. Sulfur removal from coal prior to gasification.

Sulfur Scavengers.-Although several techniques for the clean up of sour gas are commercially available, the direct use of sulfur scavengers in a coal gasifier has received considerably less attention. The approach in the direct conversion process was to mix inorganic materials with the catalysts and coal so that they could compete with the nickel catalyst for the gaseous compounds produced during the gasification. These sulfur scavengers were selected on the basis of their thermodynamic suitability for sulfide formation and relative cost.

Sulfur scavenger results with Fe_2O_3, ZnO and PbO are contained in Table IV. The powdered inorganic scavengers were dry mixed with the coal. The variance in the results of the sulfur retained in the ash is analogous to the results with no scavengers present. Here again this is attributed to the sensitivity to experimental conditions and difficulty in obtaining homogeneous samples. Nevertheless, when these scavenging results are compared to the non-scavenging results it is clear that the scavengers have played a definite role. Only 6-20% of the coal's original sulfur was deposited on the nickel catalyst in the iron scavenger runs and 3-10% for PbO and ZnO scavenger runs. These values may be compared to 30-60% of the coal's sulfur reacting with the nickel catalyst in the absence of the scavengers. Based on this data, the use of scavengers could provide as much as an order of magnitude improvement in the nickel catalyst life.

The tabulated sulfur scavenger results with Fe_2O_3 indicated that the method of contacting the scavenger and coal is more important than its concentration over the investigated concentration range. Although the ZnO and PbO were not investigated as extensively as the Fe_2O_3 scavenger, they appear to function as well, if not better, than the hematite. Although the first three tabulated iron runs (750, 752, 756) were at 112 psia, the sulfur scavenging results were essentially the same as later runs with iron at 32 psia.

Some of the ash samples from the sulfur scavenger runs were examined by x-ray diffraction. The only sulfide defintely identified was ZnS in the case of the zinc scavenger runs. The failure to observe the metallic sulfides in the iron runs may have been due to insufficient concentrations or formation of amorphorous compounds.

It is interesting to note that the ash from the iron scavenger experiments failed to show the presence of hematite (Fe_2O_3) but the reduced form, magnitite (Fe_3O_4) was observed. This is not surprising in view of the reducing atmosphere present in the system. The reduction is probably due to a combination of the following reactions.

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \qquad (14)$$

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O \qquad (15)$$

Another effect of such reactions is to increase the CO_2-free heating value of the product gas, since the low heating value constituents H_2 and CO are removed by these redox reactions. This is in agreement with the observed heating values for the scavenger runs being somewhat higher than the non-scavenger runs.

Catalyst Regeneration.-For the sake of completness, it is informative to examine the Ni-H_2S equilibrium. Under conversion conditions in the integrated system, the nickel sulfide formation (Ni_3S_2) according to Eq. 13 is predicted from the phase diagram (9). The equilibrium temperature dependence of this reaction has been investigated by Kirkpatric (10) and Badger (11). Figure 3 is an extrapolation of this data. Clearly, if the H_2S/H_2 ratio at any designated temperature should exceed the equilibrium value at that temperature, then Ni_3S_2 would form according to Eq. 13. On the other hand, if the H_2S/H_2 ratio should fall below the equilibrium value at a given temperature sulfur would be removed from the nickel catalyst. Furthermore, it is apparent that as the temperature is increased a larger concentration of H_2S can be tolerated without Ni_3S_2 formation.

This information suggests an approach to catalyst regeneration, namely the use of essentially sulfur-free hydrogen or synthesis gas at elevated temperatures to remove sulfur from the nickel catalyst according to Eq. 13. This approach has been employed for sulfur removal from a sulfided form of the nickel methanation catalyst. The experiment was carried out in the previously described 1/2" adiabatic flow reactor using a sulfur-free synthesis gas composed of 28.4% CO, 71.3% H_2 and 0.3% CO_2. Regeneration conditions were 690°C, 117 psia and 10,500 hr^{-1} space velocity. The results are tabulated in Table V. Although the run continued over a 17-hour period, the most rapid improvement in the catalyst activity was in the first

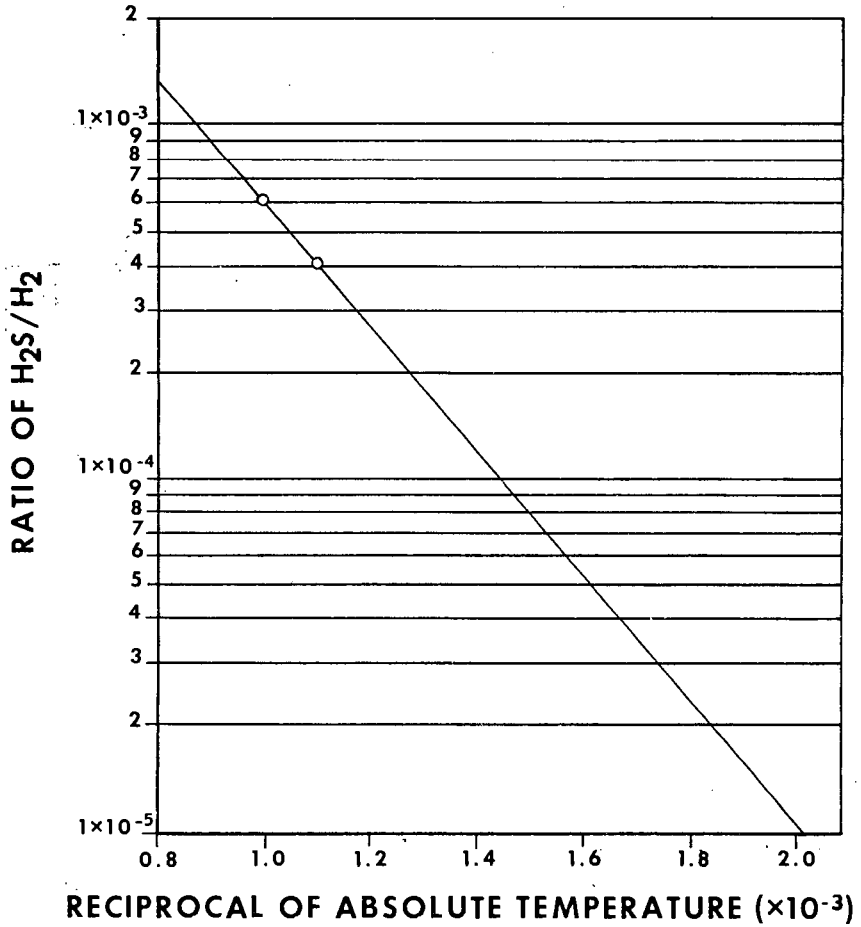

FIGURE 3 THE Ni-H_2S EQUILIBRIUM. $1/2\ Ni_3S_2 + H_2 = 3/2\ Ni + H_2S$

Table V. Catalyst Regeneration Data

	Initial Catalyst	Final Catalyst
Total Sulfur (wt. %)	9.4	0.4
Sulfide Sulfur	7.4	0.3
Sulfate Sulfur	2.0	0.1
Regeneration Conditions		
Pressure (psia)	117	117
Temperature (°C)	690	695
Space velocity (hr^{-1})	12,000	10,500
Product Gas Composition (mole %)		
H_2	68	54
CO	26	13
CH_4	4	26
CO_2	1	6

5 hours where the methane in the product increased from 4% to about 18%. During this time there was a detectable oder of H_2S in the product gas. Even though a significant improvement in the methanability of the sulfur poisoned nickel catalyst was achieved by the regeneration, it was still found to be less active than the non-sulfided catalyst since the product composition from the latter at H_2/CO = 2.86, 667°C, 120 psia and 213,000 hr^{-1} space velocity was 41.2% H_2, 2.4% CO, 49.0% CH_4 and 7.2% CO_2. Aside from the Ni_3S_2 formation, additional deactivations of the catalyst are implicated. This would appear to be caused either during the sulfiding of the catalyst with H_2S or during its regeneration with sulfur-free synthesis gas.

Two additional, less successful means of sulfur removal were briefly considered. One method was to use air or oxygen to oxidize the sulfur to SO_2 according to the following reaction.

$$Ni_3S_2 + 7/2O_2 \rightarrow 3NiO + 2SO_2 \qquad (16)$$

This approach suffered the competing reaction for nickel sulfate formation. Consequently, about half of the sulfur was expelled as SO_2 while the remainder was retained by the catalyst as nickel sulfate. The other approach was the use of aqueous solutions of acids for sulfur removal as H_2S. Although, the sulfur was readily liberated, the acidic solutions badly degradated the catalysts' physical structure. Some success in sulfur removal was realized by employing dilute aqueous solutions of hydrogen peroxide to liberate the sulfide as SO_2. No activity tests have been made to date in these latter two instances.

Alternate Catalysts.-Since nickel methanation catalysts are susceptible to deactivation in the presence of small concentrations of sulfur gases produced during coal gasification, alternate catalyst possibilities have been considered. Alternatives that have been suggested are either active more sulfur resistant catalysts or active sulfided catalysts.

In view of the generally favorable thermodynamics of metallic sulfide formation from metallic catalysts it would appear that the search for active sulfided forms of catalysts would be the most profitable. Furthermore, there are a number of different sulfided catalysts that are currently used for hydrotreating in the hydrocarbon processing industry that show hydrogeneration activity. In this regard a completely sulfided form of the nickel methanation catalyst used in the single-step conversion process was prepared and tested for its methanation activity in the 1/2" adiabatic flow reactor. A comparison between the activity of this sulfided catalyst (14.2%S) and its nonsulfided (0.06%S) form are presented in Figure 4. It is apparent that the sulfided form of the catalyst shows considerable methanation activity although it is still inferior to the nonsulfided catalyst. The thermal conversion is an order of magnitude less than that for the sulfided catalyst. In view of these results it would appear that further investigations of sulfided catalysts for high temperature methanation are warranted. In this respect a number of sulfided catalysts of various transition metals are commercially available.

A Prior Sulfur Removal.-The removal of a portion of the coal's sulfur prior to its utilization would reduce the extent of catalyst sulfidation. Prior sulfur removal schemes have recently been reported (12,13,14) and this appears to be an area in which considerable future research will be directed. Although these prior sulfur removal techniques are not particularly economically attractive that does not preclude significant breakthroughs in the area with intensified research. In regard to the single-step conversion, a prior sulfur removal would conceivably be combined with one or more of the preceding remedies to help alleviate the sulfur poisoning problem.

CONCLUSIONS

A qualitative description of the chemical processes involved in the single-step catalytic production of high Btu gas from coal-steam reactions has been presented. The role of the catalysts in the conversion and thermodynamic justifications were also presented. Using this direct approach for the production of SNG from coal, several

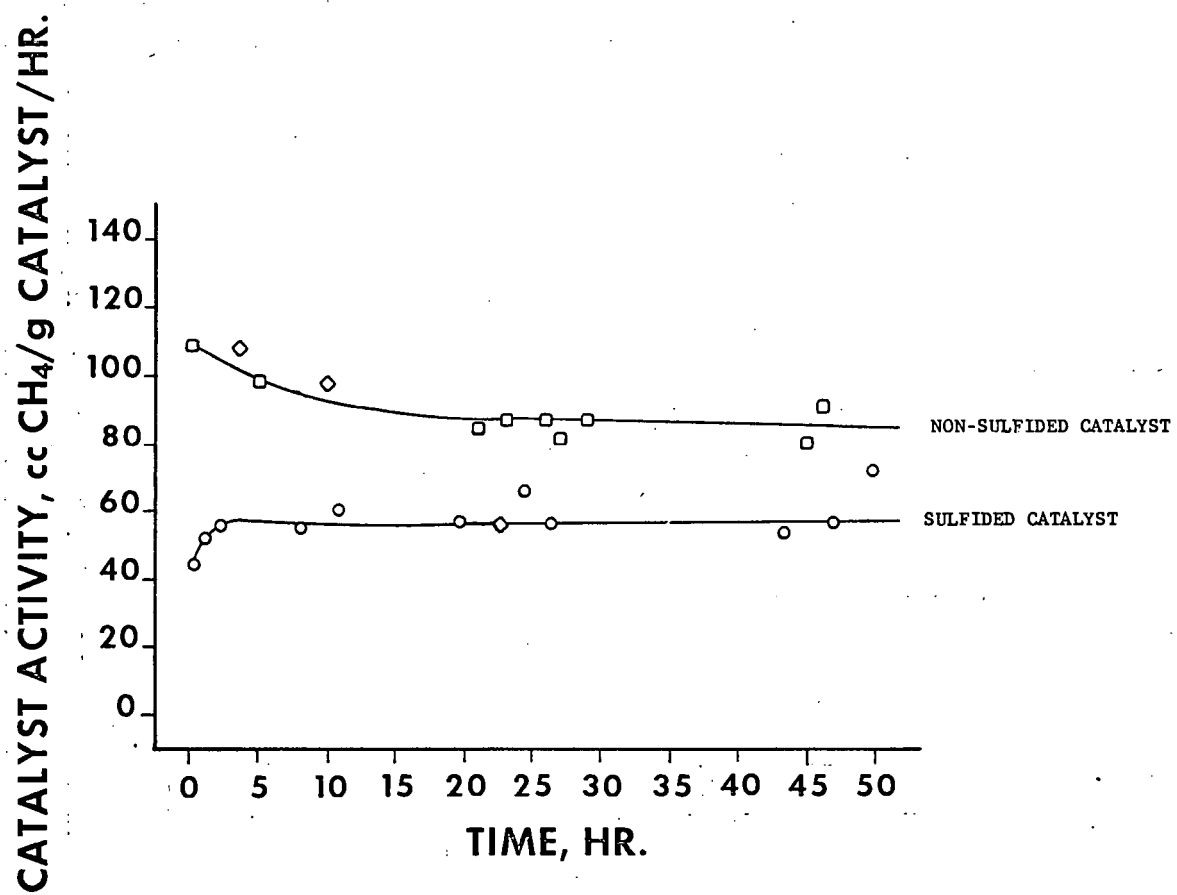

FIGURE 4. COMPARATIVE CATALYST ACTIVITY $3H_2/1CO$ at 25 psia, 675°C and 1000 hr^{-1} space velocity.

processing steps could potentially be eliminated and the thermal efficiency of the overall conversion increased. However, problematic areas concerning the poisoning of nickel catalysts used in the single-step conversion remain unanswered.

Although several approaches to coping with catalyst poisoning by sulfur compounds in the direct conversion process have been presented, no clear cut solution to date is indicated. Instead, a proper combination of the use of sulfur scavengers, catalyst regeneration, more sulfur resistant catalysts and a prior sulfur removal could be the final solution. Although, the experimental results of using sulfur scavengers, catalyst regeneration and sulfided catalysts have been encouraging, neither of these methods have proven to date to be completely satisfactory. Nevertheless, the potential reward to be derived from the direct single-step production of SNG from coal is of such magnitude that continued efforts in this area are necessary.

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