

LOW TEMPERATURE STEAM-COAL GASIFICATION CATALYSTS

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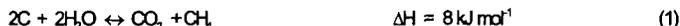
INTRODUCTION

Shrinking domestic supplies and larger dependence on foreign sources have made an assortment of fossil fuels attractive as possible energy sources. The high sulfur and mineral coals of Illinois would be an ideal candidate as possible gasification feedstock.

Large reserves of coal as fossil fuel source and a projected shortage of natural gas (methane) in the US, have made development of technology for commercial production of high Btu pipeline gases from coal of interest. Several coal gasification processes exist, but incentives remain for the development of processes that would significantly increase efficiency and lower cost. A major problem in coal/char gasification is the heat required which make the process energy intensive. Hence, there is a need for an efficient and thermally neutral gasification process.

At the present time, natural gas (methane) reserves are sufficient to meet the demands but projections indicate a dwindling supply in the future. There is a need to develop an economical process for production of methane to ensure a steady supply. Direct methanation of high sulfur and mineral coals would not only utilize this important fossil fuel feedstock but would also be inexpensive as compared to other energy intensive gasification processes. Direct formation of methane in the gasifier would also increase the efficiency of the combined cycle power generation plant over that of an integrated gasification combined cycle (IGCC) process, producing CO and H₂ only.

Catalytic steam methanation of coal is an almost thermoneutral process:



The role of the catalyst in coal/carbon gasification has been to reduce the reaction temperature and increase the rate of reaction. The main objective of these studies has been to improve the production of water gas, producer gas, or hydrogen as sources for ammonia production. Most of these works were carried out at lower pressures and have little qualitative value in assessing the catalytic effects on coal/char gasification for methane production.

Catalytic gasification of coal/carbon has attracted much attention recently. A majority of the elements in the periodic table have been tested as potential gasification catalysts and a number of leading candidates have been identified. Catalyst that are active at low temperatures would favor the process of direct gasification for methane production, since low temperature and high pressure favors the formation of methane.

Various oxides, halides and carbonates of both alkali and alkaline earth metals, along with transition metals have been surveyed as possible char gasification catalysts. Some of the general conclusions drawn are as follows:

- (1) Catalytic effect decreases with increasing temperature;
- (2) Catalysts are more effective in gasification processes if steam is present in the gasification gases;
- (3) There usually is an optimum catalyst loading, beyond which either negligible or negative effects are observed;
- (4) Relative effects of catalysts can differ under different reaction conditions;
- (5) Gasification reactivity can be effected significantly by the method /condition of catalyst impregnation; and
- (6) Catalyst impregnation is more effective than physical mixing with the carbon.

Methane cannot be produced by the reaction of C(H)₂ complex with hydrogen, if no catalyst is present. Therefore, incentives exist to explore the thermoneutral catalytic steam methanation (reaction 1) of coals to produce methane economically and in a single reaction.

Catalytic effects on gasification of carbon materials have been studied for last several decades. The mechanisms of catalytic gasification are still not completely understood and are not the same for all catalysts systems and reactions. In general, reactivity of catalyzed carbons is at least one order of magnitude higher than those of uncatalyzed carbons. A majority of the elements in the periodic table have been tested as potential gasification catalysts. The main objective of these studies have been to improve the process for production of water gas or producer gas. Outside of the work at Exxon, these work, have little qualitative value in assessing the catalytic effects on coal/char gasification for production of methane from steam.

Thermodynamically, high pressure and low temperature shift the reaction towards methane formation. It was the aim of this research to study the catalytic steam gasification of high sulfur, high mineral, agglomerating coals at elevated pressures and lower temperatures for production of methane. This research focused mainly on prevention of catalyst deactivation and coal char agglomeration. A study of pure catalysts was performed at various temperatures (773 to 973 K) and pressures (0.1 to 3.5 MPa). These catalysts were also used in various combinations to determine any synergistic effects on the methanation reaction. At High pressures alkali metals such as potassium, kept transition metal catalyst(s) reduced, mobile, and activated for longer time periods. The alkali metals and Mo also helped in the penetration of transition metals and thus provided a better contact with the carbon matrix.

The ultimate goal of this research was to develop a low temperature sulfur resistant catalyst system that would not only be efficient and economic but would also produce methane in a single step. The single-reaction process would eliminate the cost of separation, compression and recycling of hydrogen gas. Developing a low temperature catalyst system should also help reduce catalyst recycle costs. At low temperature operations, interaction of catalyst with the coal mineral phases are less likely.

BACKGROUND

The mechanism of gasification is not the same for all the catalysts systems and reactions. The catalyst basically works through a redox cycle, and dissociates molecular oxygen into atomic oxygen much faster than the uncatalyzed carbon surface. It is these mobile oxygen atoms that migrate to the carbon surface, thereby, generating oxides of carbon (CO and CO₂). This effect is called the *Spill-over effect*.

Recently it has been established that oxygen transfer plays a major role in catalysis. For transition metal salts (e.g. Fe, Ni) the catalyst oscillates between two oxidation states, on the other hand alkali metal salts (e.g. Na, K) during catalysis involve a carboxylic, phenolic or a completely reduced structure.

The catalytic effects of a catalyst system depends on; (i) activation of the catalyst, (ii) intrinsic activity of the active species, and (iii) inactivation of the active species [1]. During activation of the catalyst the metal salt reacts and decomposes to the elemental state or any other intermediate state that is catalytic. The dispersion and adhesion of such species on the carbon surface is extremely important. The catalyst loses its activity due to agglomeration, volatilization, inclusion in micropores, poisoning or interaction with the mineral matter of the coal. Catalyst mobility is important for its effectiveness. If the catalyst is in the molten phase, diffusion will depend on the temperature difference between the melting point and gasification temperature [2-5].

Single catalyst (one metal element) gasification has several limitations: (i) the rate of gas production is very slow, (ii) reduced active surface area by pore blockage, (iii) rapid deactivation of the catalyst by poisoning and sintering, (iv) low gas production, (v) loss of contact of catalyst and reactant, and (vi) volatilization of catalyst, and catalyst encapsulation by carbon deposition [6-12].

Exxon catalytic gasification process produces substitute natural gas (SNG) by catalytic steam gasification of coal [13]. The process operates at 700°C and 3.5 MPa and uses potassium carbonate as the catalyst. The catalyst plays three important roles:

- (1) It enhances the rate of gasification and lowers the reaction temperature thereby favoring methane production.
- (2) Favors gas phase methanation equilibrium.
- (3) Inhibition of swelling and caking of coals.

In this process calcium performed better at lower loadings because it does not interact

preferentially with the mineral matter. Since calcium is not as mobile as potassium its impregnation was very critical.

Iron is one of the desired catalysts for steam gasification of coal. The cheap availability of iron and its salts (mainly sulfate) make it even a more promising catalyst than the alkali metals. Commercially, it is one of the best catalysts for about 10 wt.% char conversion. The problem in using iron is that it deactivates (oxidizes) very rapidly. Nickel is another good catalyst, but it also deactivates fast and the gas production stops after about 10% graphite conversion [14]. Calcium deactivates because of sintering as a result of particle growth but remains active for longer burnoff times than iron and nickel. Abel et al. [2] found that reaction rate falls as a result of pore blockage by the catalyst which results in the reduction of accessible surface area. The catalytic activity of iron has been described by various mechanisms: electron transfer, oxygen transfer, carbide mechanism [15-17].

Bimetallic catalysts have addressed some of the limitations of single catalyst gasification. Gas production increases with the use of bimetallic catalyst. The catalyst remains active for a longer duration and is more resistant to poisoning. A catalyst that is not deactivated by sulfur would enable the gasification of high sulfur coals. Synergistic effects have been observed by the use of bimetallic catalysts [18].

Bimetallic catalysts not only increase the activity and selectivity towards desired products, but are also more resistant towards catalyst deactivation by poisoning or carbon deposition. Researchers have performed both experimental and theoretical analysis for bimetallic catalyst systems and have found significant differences in the surface and bulk compositions, as a result of one component of the catalyst system segregating preferentially to the surface. Also, an adjuvant gas can influence the segregation process [19-20].

EXPERIMENT

The coal used in this study was IL. No. 6 coal. This coal was selected because of its high sulfur content. Both the raw and demineralized coal samples were gasified in this study. Gasification of all samples was conducted in an electric furnace. The reactor, was a stainless steel tube, mounted vertically in the furnace. A high pressure pump was employed to pump water at the rates of 30 ml hr⁻¹ gm⁻¹ of coal. All the experiments were performed at 500 and 700°C and 500 and 1000 psig. Samples were placed in the reactor in a wire mesh bucket. The glass wool at the top of the reactor was used to trap any tarry material that might tend to escape. The system was purged with argon and pressurized with steam. Gas samples were collected at regular time intervals (5, 15, 30, and 60, min.) in gas bags and gas chromatography was performed on each gas bag. Product gas composition and concentration were monitored by gas chromatography. From the gas yield and composition, the carbon conversion in each interval and the accumulated carbon conversion were calculated. The experiments were terminated when the rate of gas production diminished significantly.

RESULTS AND DISCUSSION

At 500°C and both 500 and 1000 psig, negligible amount of raw coal was gasified. This suggested that the activation energy barrier cannot be crossed at 500°C for the raw coal alone. The unreacted steam would condense at the bottom of the reactor. Even when the flow rate of water was reduced to 0.25 ml min⁻¹ similar problems were encountered. At 700°C there was a substantial increase in the amount of coal gasified. Almost 36-39 wt.% (assuming 100% carbon) coal was gasified at 500 psig. At 5 minutes the analysis of the gas at 500 psig showed CO₂ as the main gas (77%), there was significant amount of CH₄ (18%) and minute quantities of CO and H₂. Gas production was observed till 15 minutes but at this time CO₂ was the primary gas (89%). No gas production was observed at 30 minutes. At 700°C and 1000 psig there was a slight increase in the amount of coal gasified (43 wt.%). The gas analysis at 5 min showed 61% CO₂, 28% CH₄, 5% H₂, and 6% CO. At 15 min the gas composition was 79% CO₂, 16% CH₄, 3% H₂, and 2% CO. Once again no gas production was observed at 30 min. This high jump in coal conversion at 700°C suggested that at this temperature the energy was sufficient to clear the activation barrier and a portion of the char formed was also gasified. Demineralized coal gasified almost like raw coal with 38 wt.% conversion at 700°C and 500 psig. The gas analysis at 5 min showed 88% CO₂, 0% CH₄, 6% H₂, and 6% CO. At 15 min the gas composition was 96% CO₂, 0% CH₄,

4% H₂, and 0% CO. Once again no gas production was observed at 30 min. Conversion numbers and gas analyses are presented in Table 1.

In presence of the catalyst significant gasification was observed at 500°C and 500 psig. Both the raw and demineralized coal samples were gasified in presence of the catalyst. Catalysts studied thus far are salts of potassium, iron, nickel, and molybdenum. For the single catalyst experiments of potassium salts (hydroxide and carbonate) increasing the catalyst loading from 5 to 10% had little effect on coal conversion. For KOH catalyzed raw coal experiments the coal conversion was around 28-35 wt.%. Similarly increase in temperature had very little effect on conversion. Gas production was observed till 30 min. Increase in pressure resulted in increased methane formation. For 10% potassium loading (KOH) the gas analysis at 5 min showed 55% CO₂, 32% CH₄, 7% H₂, and 6% CO. At 15 min the gas composition was 61% CO₂, 29% CH₄, 6% H₂, and 4% CO. At 30 min the gas composition was 66% CO₂, 26% CH₄, 5% H₂, and 3% CO. No gas production was observed at 45 min. For potassium carbonate, however, the conversion went down from 40 to 33% with increase in the loading from 5 to 10%. This could be due to interaction of potassium carbonate with the mineral of coal at higher loadings. The gas analyses were comparable to the KOH experiments. Conversion numbers and gas analyses are presented in Table 1.

Salts of transition metals behaved like potassium salts. The conversion numbers were comparable but the methane concentration was slightly lower. In some cases the gas production stopped after 15 min. At 500°C and 500 psig almost 30% conversion was achieved with 10% loading of iron chloride. The gas analysis at 5 min showed 64% CO₂, 27% CH₄, 5% H₂, and 4% CO. At 15 min the gas composition was 68% CO₂, 26% CH₄, 5% H₂, and 1% CO. At 30 min the gas composition was 74% CO₂, 23% CH₄, 3% H₂, and 0% CO. No gas production was observed at 45 min. At the same conditions 37% conversion was achieved with nickel hydroxide. The gas analysis at 5 min showed 59% CO₂, 30% CH₄, 7% H₂, and 4% CO. At 15 min the gas composition was 67% CO₂, 26% CH₄, 5% H₂, and 2% CO. At 30 min the gas composition was 72% CO₂, 24% CH₄, 4% H₂, and 0% CO. No gas production was observed at 45 min. Conversion with molybdenum oxide was lower (22%) under same conditions. No gas production was observed after 15 min. The conversion numbers and the gas analyses for the demineralized coal samples were comparable to the raw coal conversions. Conversion numbers and gas analyses are presented in Table 1.

When potassium hydroxide was used with transition metals significant increases in the conversions were obtained and also the concentration of the methane in the product gas increased substantially. As shown in Table 1 at 500°C and 500 psig when iron chloride and potassium hydroxide are used together at 5% each loading the conversion increased to 42% with an increase in methane concentration in the product gas. The gas analysis at 5 min showed 56% CO₂, 35% CH₄, 7% H₂, and 2% CO. At 15 min the gas composition was 59% CO₂, 34% CH₄, 6% H₂, and 1% CO. At 30 min the gas composition was 69% CO₂, 27% CH₄, 4% H₂, and 0% CO. No gas production was observed at 45 min. At 10% each loading the conversion went up to 53%. The gas analysis at 5 min showed 47% CO₂, 39% CH₄, 9% H₂, and 5% CO. At 15 min the gas composition was 52% CO₂, 37% CH₄, 7% H₂, and 4% CO. At 30 min the gas composition was 58% CO₂, 33% CH₄, 6% H₂, and 3% CO. No significant gas production was observed at 45 min. This shows some synergistic effects. Possibly potassium helps keep iron reduced for longer duration and thus the conversion and methane formations are increased. Conversion numbers and gas analyses are presented in Table 1.

When nickel hydroxide and potassium hydroxide are used together at 500°C and 500 psig and at 5% each loading the conversion was 39%. The gas analysis at 5 min showed 60% CO₂, 33% CH₄, 5% H₂, and 2% CO. At 15 min the gas composition was 69% CO₂, 27% CH₄, 3% H₂, and 4% CO. No significant gas production was observed at 30 min. At 10% each loading the conversion went up to 55%. The gas analysis at 5 min showed 58% CO₂, 35% CH₄, 7% H₂, and 0% CO. At 15 min the gas composition was 67% CO₂, 28% CH₄, 5% H₂, and 0% CO. At 30 min the gas composition was 76% CO₂, 21% CH₄, 3% H₂, and 0% CO. No significant gas production was observed at 45 min. At 700°C and 1000 psig and 5% each loading of nickel and potassium a conversion of 74% was achieved. The gas had increased concentration of carbon monoxide and lower methane production. Experiments performed with demineralized coal samples resulted in slightly lower conversions but similar gas analyses.

CONCLUSIONS

1. Significant amounts of hydrogen can be produced at moderate gasification conditions.
2. Low to negligible CO concentrations and ratios of H₂/CO is at synthesis gas stoichiometry.
3. Steam reforming of methane is avoided at 3-6 MPa range.
4. The combination of alkali and transition metals gave significant synergistic effects.

Table 1.
Carbon Conversion and Gas Analyses of Various Steam-Coal Gasification Experiments

Run	Temp (°C)	Pres (psig)	Catalyst	Loading (Wt.%)	Conv. %	H ₂ /CO ₂ /CH ₄ /CO 5 Min	H ₂ /CO ₂ /CH ₄ /CO 15 Min	H ₂ /CO ₂ /CH ₄ /CO 30 Min
Raw	700	500	None	None	37	2/77/18/3	1/89/8/2	-----
Raw	700	500	None	None	39	2/76/18/4	0/91/7/2	-----
Raw	700	500	None	None	36			
Raw	700	1000	None	None	43	5/61/28/6	3/79/16/2	-----
Demin	700	500	None	None	38	6/88/0/6	4/96/0/0	-----
Raw	700	500	K ₂ CO ₃	5	36.4			
Raw	700	1000	K ₂ CO ₃	5	39.9	6/53/35/6	5/59/32/4	4/68/26/2
Raw	700	1000	K ₂ CO ₃	10	33.1	7/54/32/7	5/66/26/3	-----
Raw	500	500	KOH	10	28.4	7/55/32/6	6/61/29/4	5/66/26/3
Raw	500	1000	KOH	10	36.4	6/52/35/7	5/59/31/5	4/64/28/4
Raw	700	750	OH	5	34.6	7/54/33/6	5/60/30/5	5/65/26/4
Raw	500	500	KOH	10	28.4	7/55/32/6	6/61/29/4	5/66/26/3
Raw	500	500	FeCl ₂	10	29.7	5/64/27/4	5/68/26/1	3/74/23/0
Raw	500	500	KOH/FeCl ₂	5 each	42.16	7/56/35/2	6/59/34/1	4/69/27/0
Raw	500	500	KOH/FeCl ₂	10 each	53	9/47/39/5	7/52/37/4	6/58/33/3
Raw	500	1000	NiOH	10	37	7/59/30/4	5/67/26/2	4/72/24/0
Raw	700	1000	KOH/NiOH	5 each	74	8/53/32/7	4/82/11/3	4/72/24/0
Raw	500	500	KOH/NiOH	10 each	55	7/58/35/0	5/67/28/0	3/76/21/0
Raw	500	500	KOH/NiOH	5 each	39	5/60/33/2	3/69/27/1	-----
Raw	500	500	MoO ₃	10	22	1/71/28/0	0/83/17/0	-----

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