OST TECHNICAL PROGRESS REPORT TEAM WORK PLAN--FY 1998 RESULTS

TITLE: Gas Conversion Team

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DESCRIPTION: The Gas Conversion Team explores experimental pathways for the conversion of natural gas to higher valued products (e.g., transportation fuels). During FY98 research focused on the upgrading of acetylene (a product of natural gas conversion) and the conversion of natural gas to synthesis gas (syngas).

RESEARCH OBJECTIVES: The objective of these projects is to conduct in-house research on developing and testing new and commercial catalysts for the conversion of natural gas. Acetylene produced from natural gas is not suitable as a transportation fuel. The catalytic conversion of acetylene to higher hydrocarbons provides a non-steam reforming option for the conversion of natural gas into transportation fuels. *The research is conducted in the Methane-to-Liquid Fuels Laboratory*

Syngas is a valuable feedstock for producing transportation fuels (specifically high quality diesel fuel from Fischer-Tropsch (FT) processes), hydrogen, fuel additives and other chemicals. Since production of syngas and the FT process are carried out catalytically, the development of new and novel catalysts is very important for utilization of natural gas, particularly for producing liquid fuels.

LONG TERM GOAL/RELATIONSHIP TO FETC's PRODUCT LINE(S): The production of a "clean" transportation fuel from an abundant natural resource (natural gas) is of great interest. The combination of current DOE research efforts to convert methane to acetylene (a project funded by FETC's Natural Gas Downstream Processing Team at Idaho National Engineering and Environmental Laboratory (INEEL)) and FETC's acetylene conversion technology would produce a method of utilizing remote gas supplies (i.e., North Slope or Gulf gas supplies) to produce transportation fuels.

The primary barrier to the conversion of acetylene is that the two thermodynamically stable conversion products are benzene and coke. While there exists a market for both products, neither one meets the criteria of a suitable transportation fuel.

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fuels. The Down Stream Gas Processing Product Team is working with other DOE agencies in developing a method for the production of "clean" diesel fuels, such as those produced by FT.

Either of these processes would, if successful, reduce U.S. dependence on foreign supplies of transportation fuels and allow utilization of remote gas fields, such as those located on the north slope of Alaska.

SUMMARY ACCOMPLISHMENTS: Dry Reforming of Methane

On the basis of a literature review conducted on catalytic dry reforming of methane to syngas, nickel is the least expensive catalyst and it's performance can be significantly improved using suitable catalysts supports and promoters. More than 15 new and commercial catalysts were tested for dry reforming of methane to syngas at temperatures of 650, 750, 850 and 950°C. Carbide catalysts of molybdenum and tungsten were prepared and tested for dry reforming, these catalysts were irreversibly deactivated after 35 hrs on stream. A new nickel containing catalyst was prepared and tested for 50 hrs, and the results are comparable to the most expensive 1% Rh/alumina catalyst. A methane conversion of 90% was obtained at 750° C compared to 89% for 1% Rh/alumina catalyst. Fresh and spent catalysts were analyzed using x-ray diffraction, semi-quantitative x-ray microanalysis, scanning electron microscopy (SEM), and x-ray photoelectron spectroscopy (XPS). A fixed-bed reactor was refurbished, including mass flow controllers, heaters and a GC for dry reforming studies.

Conversion of Acetylene

A literature survey was conducted on the catalytic conversion of acetylene to higher hydrocarbons. The majority of the literature on acetylene conversion is from the last century. Based on the literature available, a research route was planed for FY98 work. Several catalysts, based on preparations reported in the literature, were synthesized for conversion studies. Conversion studies were also performed on commercial catalysts. A total of 15 different experiments were performed in which the conversions of acetylene and methane, acetylene and methanol, and acetylene alone were investigated. Anticipated reaction products of reaction are propene, 1,1 dimethoxyethane, and a mixture of higher hydrocarbons respectively. The anticipated products were formed in the experiments, but the reactions were plagued by either low reactant conversions (~15%) or large amounts of coke formation.

RESULTS: Dry Reforming of Methane

This project was initiated to develop and test new and commercial catalysts for the conversion of methane to syngas. The task for FY98 was to verify claims made in the literature that group (V)

and (VI) transition metal carbides are active catalysts for reforming of natural gas to syngas. More than 15 catalysts for dry reforming were prepared and tested. Three of the carbide catalysts were prepared at FETC, one was pure tungsten carbide and two were tungsten carbide supported on silica. The catalytic activity of the supported catalysts was very poor, and a methane conversion of less than 41% was obtained at 950°C. Higher activity was obtained with the pure tungsten carbide, and the results are shown in Table I. At 650 and 750°C, methane and CO₂ conversions were less than 15% and H2/CO ratio was about 0.2. A H₂/CO ratio of 1.1 was obtained at 850°C. The reaction was continued at 850°C for about 45 hrs, and the results showed that the catalyst is not as stable as reported earlier and deactivated after 35 hours (Figure 1). The deactivation was irreversible and could not able to regenerated by flowing hydrogen or a mixture of 11.6% ethane in hydrogen overnight. A second tungsten carbide sample was tested, and results were similar to those obtained with the first sample (not shown).

The molybdenum carbide catalysts were prepared at FETC by temperature-programmed reduction of molybdenum oxide with 11.6 vol% methane in hydrogen or 11.6 vol% ethane in hydrogen. The catalyst prepared with methane mixture was tested at 650, 750, 850, and 950°C and the results are shown in Table 1. The catalyst prepared with ethane was also tested at these temperatures and the results are also shown in Table I. The later catalyst was tested for 16 hours. Higher catalytic activity was observed for the catalyst prepared with ethane mixture than the catalyst prepared with methane mixture as shown in Table 1. Molybdenum carbide supported on TiO₂ was prepared by mixing MoO₃ with TiO₂ in an ethyl alcohol solution, and then reacted with 11.6 vol% ethane in hydrogen to form carbide. About 90% of methane and 100% of CO₂ were converted to hydrogen and CO with a ratio of 1.0. This catalyst was tested for 2.5 hrs at 900°C.

For comparison and obtaining base-line data two more expensive Nobel metal catalysts for dry reforming of methane to syngas were tested. The catalysts tested were one and 5 percent rhodium supported on alumina and the results are shown in Tables 2 and 3. Higher catalytic activity was observed with catalyst containing one percent compared to that with 5 percent rhodium. These catalysts were more active and stable than the carbide catalysts at lower temperatures of 750 and 650 °C giving higher H2/CO ratios at these temperatures. The catalyst with one percent rhodium was tested for more than 25 hrs and no significant amount of carbon was deposited on the catalyst. Although these nobel metal catalysts are an acceptable choice for reforming of natural gas, they are very expensive compared to carbide- and nickel-based catalysts.

From the experimental results, it was concluded that the Nobel metal-based catalysts are very expensive and the carbide catalysts are not stable for dry reforming of methane to syngas. However, published literature suggested that the use of alkali or alkaline earth oxides may reduce carbon depositions on the nickel catalyst. Therefore, a nickel-based catalyst was prepared and tested. The results are shown in Table I. This catalyst has also been tested for about 50 hours. The preliminary results indicated that this catalyst performed as well as the more expensive commercial (Rhodium) catalyst at 750°C (Figure 2). The Nobel metal- and nickel-based catalysts are very active catalysts at lower temperatures of 650 and 750°C (Table I) producing H2/CO

ratios of 0.8 and 0.9, respectively. A 750°C a H2/CO ratio of 0.7 was observed for molybdenum carbide and a value of 0.2 for tungsten carbide (Table I).

Catalyst characterization

Fresh and spent catalysts were analyzed using x-ray diffraction, semi-quantitative x-ray microanalysis, scanning electron microscopy (SEM), and x-ray photoelectron spectroscopy (XPS). There are no distinguishable differences between the fresh and spent (deactivated) tungsten carbide catalyst using x-ray diffraction. Amorphous W_2C and WC were observed in both carbide samples. The semi-quantitative x-ray microanalysis of these samples showed that about 3% Cl remained on the fresh carbide sample, and it was removed during catalytic reaction. Less than 1% Fe was also detected on these samples. The SEM photographs clearly show the differences between the fresh and the spent samples of tungsten carbide catalyst. The particles in the fresh sample have very sharp edges whereas the particles in the spent sample have round edges indicating that some of the active sites are destroyed or covered with carbon during the reaction. The XPS analysis of fresh and spent tungsten carbide samples showed a significant amount of carbon deposited on the surfaces of spent catalyst, the ratio of carbon to tungsten was increased from 7.6 to 64.5 during reaction.

Conversion of Acetylene

This project was initiated to develop and test new and commercial catalysts for the conversion of acetylene to transportation fuels. The task for FY98 was to determine if a feasible catalytic process could be found to convert acetylene into transportation fuels. To accomplish this, several catalysts were prepared and tested using various feeds of acetylene, neat or mixed with other hydrocarbons assumed to be present in sufficient quantities at a remote natural gas location (either methanol, from an associated FT plant, or methane). Eight catalysts were prepared and tested for acetylene conversion. The catalysts tested, along with reaction data are listed in Table IV. In general, the catalytic activity of the catalysts was poor. In all instances, the main reaction product was coke.

An extensive literature search was conducted prior to beginning the research and used to select the catalysts investigated. The majority of research in the conversion of acetylene dates to the late nineteenth century. The most promising candidate, conversion of acetylene and methanol over a mercury salt dissolved in boiling sulfuric acid, was deemed too environmentally unfriendly to pursue.

Reactions of acetylene and methane were conducted over eight different catalysts in an effort to produce propene. Propene was identified in the product stream from each catalyst. In all cases, with the exception of the Cu-K-La/SiO₂ catalyst, methane conversion was negative. This is due to the disassociation of acetylene over these catalysts. As conversion of acetylene increased with temperature, production of propene decreased. The major product was coke, in some instances plugging the reactor. The Cu-K-La/SiO₂ catalyst was the only catalyst that exhibited a positive

methane conversion. Conversion of acetylene and methane was relatively stable over the temperature range tested (175 - 340°C). As with the other catalysts, propene production decreased and coke production increased as the temperature increased. The other major product was benzene.

Conversions of acetylene alone over ZSM-5 were also investigated. Conversion of acetylene increased with temperature from ~3% to ~16%. The product slate was similar to the products of methyl chloride or methanol conversions over the same catalyst. Coke was a major product of reaction, increasing in quantity with increasing temperature. Figure 4 shows the gas chromatograms of acetylene, methyl chloride and methanol over ZSM-5.

Reactions of acetylene and methanol were conducted using soda lime as the catalysts. The desired product of reaction, 1-1 dimethoxyethane, can be used as a chemical feedstock or as a cetane booster in diesel fuel. Conversions of both reactants are low with benzene and coke being the major products.

Further studies are planned in FY99 to investigate the conversion of acetylene with other components of remote gas fields.

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	Temperature	$\% CH_4$	% CO ₂	% CO	H ₂ /CO
Catalyst	(°C)	Conversion	Conversion	Yield	ratio
Pure SiC	950	6.2	0.5	0	N/A
Commercial Mo ₂ C mixed with SiC	950	11.2	17.2	34	0.2
Mo ₂ C from MoO ₃	950	43.6	62.1	58.8	0.6
mixed with SiC	850	9.2	24.5	25.5	0.2
Mo ₂ C/Pure MoO ₂	950	92	100	96	1
(methane)	850	18.3	37.3	37.3	0.3
	750	4.7	16.8	16.7	0.2
	650	1.7	12.9	11.5	.01
Mo ₂ C/Pure MoO ₃	850	89.5	99.9	89.4	1.1
(ethane)	750	36.9	59.1	51.6	0.7
Tungsten carbide	850	90.7	100	86.6	1.1
(Pgh-1)	750	5.4	12.1	13.4	0.2
5%RhAl+SiC	650	35.4	44.1	41.5	0.8
Mo ₂ C+TiO ₂	900	94.5	100	92.3	1.1
	850	70.1	88.7	77.8	0.9
	750	69.9	87.1	76.2	0.9
	650	19.1	42.1	35.6	0.5
W_2 C-SiO ₂ (Pgh-2)	950	21.0	36.0	35.6	0.5
HSAWC5 (Pgh-3)	950	40.3	52.4	32.0	0.8
1%Rh-Al	750	89	88	88	1.0
	650	59	65	66	0.9
Ni-Ca	750	90	100	96	0.9
	650	50	63	62	0.8
W ₂ C	750	5	12	13	0.2
-	650	0.7	2	2	0.1

Table I. Preliminary results of dry reforming of methane over catalysts, 0.5 g sample, 42 cc/min total flow, $CH_4/CO_2=1.1$ to 1.2)

Solid Temp (°C), under H_2	650	750	850	850	850
Solid Temp (C), reaction	622	723	817	817	817
Flow (cc/min), CH ₄ -CO ₂	20-22	20-22	20-22	30-35	40-45
CO_2/CH_4 feed ratio	1.1	1.1	1.1	1.2	1.1
H_2/CO ratio	0.9	1	1	1	1
Percent CO yield	65.6	88	95.7	96.1	94.7
Percent CH ₄ conversion	59.2	86.9	97.2	97.2	95.9
Percent CO ₂ conversion	65.2	88.1	97.4	93	92.3

Table II. Reaction of CO₂ with methane over 1% Rhodium supported on alumina, 0.5 g sample

Table III. Reaction of CO₂ with methane over 5% Rhodium supported on alumina, 0.5 g sample

Solid Temp (°C), under H_2	650	752	850
Solid Temp (°C), reaction	626	716	808
Flow (cc/min), CH ₄ -CO ₂	20-22	20-22	20-22
CO_2/CH_4 feed ratio	1.1	1.1	1.1
H_2 /CO ratio	0.6	0.8	1
Percent CO yield	31.7	63.3	93.6
Percent CH ₄ conversion	21.6	54.4	94.6
Percent CO ₂ conversion	29.2	62.9	92.6

	Temperature	$% C_{2}H_{2}$	% CH ₄	% CH ₃ OH
Catalyst	(°C)	Conversion	Conversion	Conversion
Soda Lime	100	7.18	N/A	78.34
	150	29.20	N/A	48.89
WO ₃	250	17.39	3.20	N/A
5	300	10.93	- 1.90 N/A	
	350	74.83	- 37.56	N/A
	400	99.73	- 34.52	N/A
TiO ₂	200	64.37	- 19.03	N/A
-	250	85.35	- 59.43	N/A
	300	87.57	- 62.45	N/A
	350	99.94	-134.92	N/A
Cu-K-La/SiO	175	28.25	17.95	N/A
	200	58.02	13.26	N/A
	250	21.33	16.33	N/A
	300	29.73	17.42	N/A
	340	96.64	12.98	N/A
Cu/TiO ₂	200	6.94	- 2.93	N/A
	250	50.69	- 16.33	N/A
	300	87.21	- 25.57	N/A
	350	96.67	- 20.25	N/A
	400	96.33	- 9.99	N/A
	450	98.90	- 6.95	N/A
Cu/SiO ₂	200	32.49	- 9.01	N/A
	250	96.02	- 25.34	N/A
	300	99.50	- 31.02	N/A
	350	99.26	- 31.08	N/A
SiO ₂	200	7.05	- 2.19	N/A
	250	5.42	- 3.50	N/A
	300	6.30	- 4.30	N/A
	350	11.64	- 5.29	N/A
Al_2O_3	200	2.82	- 5.82	N/A
	250	0.00	- 5.97	N/A
	300	11.05	- 6.41	N/A
	350	0.00	- 6.55	N/A
ZSM-5	200	30.50	- 13.58	N/A
	250	29.83	- 15.36	N/A
	300	38.53	- 16.22	N/A
	350	65.01	- 13.10	N/A
ZSM-5	200	4.72	N/A	N/A
	250	2.93	N/A	N/A
	300	4.05	N/A	N/A
	350	16.09	N/A	N/A

Table IV. Preliminary results of acetylene conversion over catalysts, 1.0 g sample feed ratio, 1/1.







