

Center for Advanced Materials

CAM

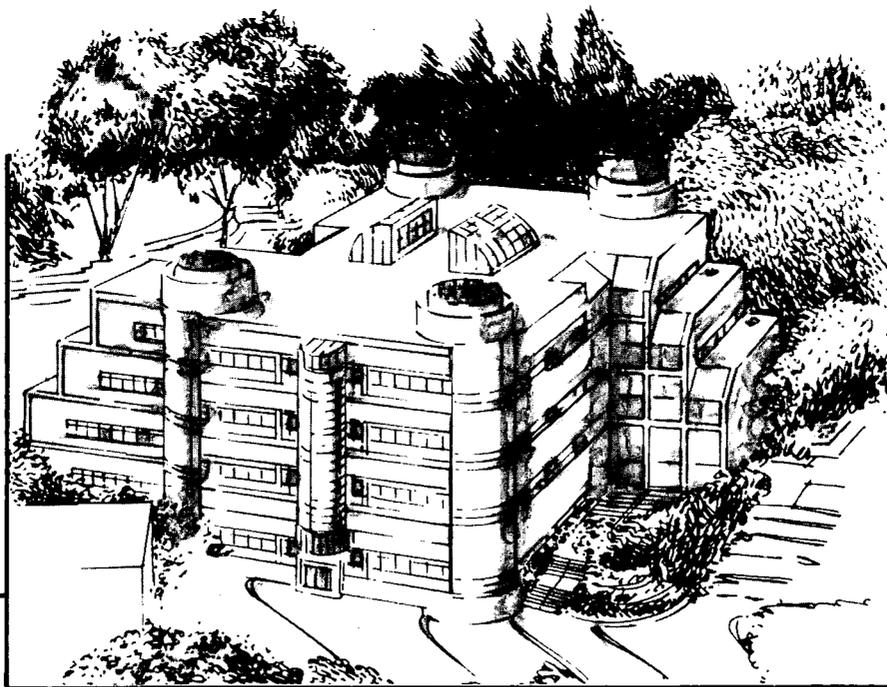
Fundamental Studies of Catalytic Gasification: Quarterly Report, January 1–March 31, 1990

H. Heinemann and G.A. Somorjai

March 1990

For Reference

Not to be taken from this room



Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory • University of California
ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-28710
Bldg. 50 Library

Copy 1

LBL-28710

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

QUARTERLY REPORT

January 1, 1990 - March 31, 1990

FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION

Principal Investigators: Heinz Heinemann
Gabor A. Somorjai

Center for Advanced Materials
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, CA 94720

This work was supported by the Assistant Secretary for Fossil Energy, Office of Technical Coordination, U.S. Department of Energy under Contract DE-AC03-76SF00098, through the Morgantown Energy Technology Center, Morgantown, West Virginia 26505.

TABLE OF CONTENTS

	<u>Page</u>
I Task Description for Fiscal year 1990 .	3
II Introduction.	3
III Highlights.	3
IV Progress of Studies	4
a) Catalyst Preparation	4
b) Catalyst Testing	7

I. Task Description for FY 1990

Our previous work has shown that chars and coal can be gasified with steam in the presence of alkali-transition metal oxide catalysts or alkali-earth alkali catalysts at relatively low temperatures. These studies are to be extended to the investigation of the amounts of catalysts required and whether a throw away catalyst can be used. Fresh versus stored char will be gasified to determine the role of oxidation of the char on gasification rates. Less expensive catalyst materials such as sodium instead of potassium and iron instead of nickel will be explored. Reaction rates will be determined in the presence of nitrogen, CO, and CO₂. Reactions of methane and carbon solids in the presence of an oxidizing agent such as water, oxygen, and/or carbon dioxide will be explored in the presence of similar catalysts. It is expected that hydrocarbon liquids and C₂ plus gases will be produced along with hydrogen. These studies will be performed over a wide range of reaction pressures and reaction temperatures in a flow reactor using a GC-MS detector. Pure paraffinic and cyclic hydrocarbons of high carbon to hydrogen ratio will be gasified to have an indication of the ease of gasification of different carbonaceous materials.

II. Introduction

During the second quarter of FY 1990, work was concentrated on the oxidative coupling of methane over catalysts of the type discovered during coal gasification. A change of personnel during the last month of the quarter caused some delay in experimental work.

III. Highlights

- A novel catalyst (KCaNiO_x) has been discovered that will permit oxidative coupling of methane at close to 100% selectivity to C₂ hydrocarbons at 10% CH₄ conversion. Essentially no CO_x production occurs. Temperatures below 600°C are used.

- The presence of water has been found important for oxidative coupling of C_4 over either $KCaNiO_x$ or $KCaO_x$ catalysts.
- Absence of CO_x in the products from coupling greatly effects economics because of lower oxygen demand, less methane loss and less recycle purification.
- High selectivity to C_2 hydrocarbons was maintained over extended periods of time.
- A large number of potential methane coupling catalysts have been prepared. In general silica or alumina supported catalysts are less active than unsupported bi-or tri-metallic oxides.
- Calcination conditions of the catalysts are important factors in their performance.
- $KCaO_x$ catalysts ex steam gasification of char give highest C_2 yields at the lowest CH_4/O_2 ratios feasible outside explosive limits. Yields of 15-17% are obtained at relatively low temperatures (650-700°C). Occasionally much higher yields are obtained, but these have not yet proven reproducible at will.

I. Progress of Studies

a) Catalyst Preparation

A series of catalysts has been prepared for testing in both steam gasification of coals and oxidative methane coupling. These catalysts were prepared so that they could be used in admixture with coal (in contrast to impregnation of coal) for gasification and in the absence of carbon in methane coupling. In the latter case large enough quantities were

prepared to fill appreciable reactor volume and avoid by-passing of gases. Although several unsupported catalysts were made, their preparation in sufficient quantity is difficult and time consuming and supported catalysts could be supplied easier, at least for laboratory tests. A total of thirty catalysts were prepared and most are listed in Table 1.

Table 1
CATALYSTS PREPARED

Composition	Support	% Active Component	Preparation Method
KCaO _x	none	100	C
KCaNiO _x	none	100	C
KCaO _x	SiO ₂	1;2;3;4;5;6;7;8;9	A
KCaO _x	Al ₂ O ₃	5;12;25	A
KCaNiO _x	Al ₂ O ₃	10;25	A and B
CsBaO _x	Al ₂ O ₃	5	A and B
CsBaO _x	SiO ₂	5	A and B
CsBaNiO _x	Al ₂ O ₃	10	A and B
KCaCoO _x	Al ₂ O ₃	8	A and B
KCaFeO _x	Al ₂ O ₃	8	A and B
CsBaCoO _x	Al ₂ O ₃	10	A and B
CsBaFeO _x	Al ₂ O ₃	10	A and B

- A. Impregnation of support with solution of mixed nitrates, drying and calcining.
- B. Impregnation of support with solution of mixed alkali-earth alkali nitrates, drying and calcining followed by impregnation with transition metal nitrate, drying and calcining.
- C. Evaporating solution of mixed nitrates to dryness then calcining.

Table 2 gives BET surface areas for some of these catalysts. It is apparent that for silica supported catalysts pore plugging occurs with increasing KCaO_x deposition, while on Al₂O₃ supports there is little change in the much higher surface area.

Table 2
CATALYST SURFACE AREAS (BET)

-----Catalyst-----		Preparation	Surface Area,
Composition	Support	Method	m ² /g
K-CaO _x	none	C	3
K-CaNiO _x	none	C	2
1%K-CaO _x	SiO ₂	A	44
2%K-CaO _x	SiO ₂	A	58
3%K-CaO _x	SiO ₂	A	20
4%K-CaO _x	SiO ₂	A	5
5%K-CaO _x	SiO ₂	A	3
6%K-CaO _x	SiO ₂	A	2
7%K-CaO _x	SiO ₂	A	5
8%K-CaO _x	SiO ₂	A	1
9%K-CaO _x	SiO ₂	A	3
5%CsBaO _x	Al ₂ O ₃	A	180
10%CsBaCoO _x	Al ₂ O ₃	A	184
10%CsBaCoO _x	Al ₂ O ₃	B	180
8%KCaCsO _x	Al ₂ O ₃	A	184
8%KCaCoO _x	Al ₂ O ₃	B	183
5%KCaO _x	Al ₂ O ₃	A	185

- A. Impregnation of support with solution of mixed nitrates, drying and calcining.
- B. Impregnation of support with solution of mixed alkali-earth alkali nitrates, drying and calcining followed by impregnation with transition metal nitrate, drying and calcining.
- C. Evaporating solution of mixed nitrates to dryness then calcining.

As will be shown in the section on catalyst testing, the KCaNiO_x catalyst showed exceptional characteristics. This catalyst must be carefully prepared and was found to require calcination in air for 72 hours at 700°C to give high activity. At lower calcination temperature or shorter calcination times the catalyst functions as a steam reforming catalyst, producing H₂ and CO₂, rather than as a methane coupling catalyst. However, insufficient data are available at this time to pinpoint the optimum preparation conditions. The reasons for the criticality of preparation

procedure are also not clear, though they may have to do with the oxidation state of the catalyst.

b) Catalyst Testing

A number of the catalysts prepared (section a) were tested for methane coupling in the presence of oxygen and steam and were found to be essentially inactive. These included the whole series of $\text{KCaO}_x/\text{SiO}_2$ catalysts, the KCaCoO_x and the $\text{CsBaNiO}_x/\text{Al}_2\text{O}_3$ catalysts. In general catalysts supported on silica or on alumina appear to be less active than unsupported catalysts and silica supported catalysts are less active than alumina supported catalysts.

The two most interesting catalysts found thus far are KCaO_x derived from char gasification and unsupported KCaNiO_x .

The effect of methane partial pressure and of water partial pressure was investigated for KCaO_x derived from char gasification. Variations of partial pressure were obtained by using helium, resp. water to keep the total pressure constant.

Table 3 shows data for changes in the CH_4/O_2 ratio obtained by helium addition in the absence of water. Table 4 gives similar information for the case of changing CH_4 partial pressure by steam addition.

Table 3

Total pressure kept constant by He addition;
no steam used; KCaO_x catalyst ex char gasification

Ratio CH_4/O_2	CH_4 Conversion %	Hydrocarbon Select. %	C_2 Yield %
8	9.3	50.94	4.90
7	11.16	52.38	5.85
6	14.77	58.96	8.71
5	19.63	47.13	9.25

Table 4

Total pressure maintained by water addition;
 KCaO_x catalyst ex char gasification

Ratio CH_4/O_2	CH_4 Conversion %	Hydrocarbon Select. %	C_2 Yield %
8	17.34	52.38	9.08
7	18.52	62.72	11.62
6	15.59	76.22	11.88
5	21.84	65.00	14.94

It is apparent that the presence of water increases conversion, selectivity and therefore, yield at 680°C . Lower CH_4/O_2 ratios than 5 could not be used because of the danger of explosions. In all cases conversion increased with decreasing CH_4/O_2 ratio over the range of 8/1 to 5/1, while selectivity appeared highest at a ratio of 6/1 or 7/1. The C_2 yield also increased with lower CH_4/O_2 ratio; the highest C_2 yield obtained in this series was 15%, a yield obtained by other researchers only at 100-150% higher temperature. In occasional runs and quite infrequently, much higher yields (25+%) were obtained, but these have thus far not proven reproducible at will.

The unsupported KCaNiO_x catalyst when operated in the presence of water exhibited exceptional properties. It performed at temperatures as low as 550°C and at 580° gave a yield of C_2 hydrocarbons of 10% at ~10% CH_4 conversion and >99% selectivity. While this is a lower yield than obtained in other experiments, there is essentially no CO or CO_2 production. This means that all oxygen consumed is used for coupling, resulting in only one-fourth of the oxygen consumption compared to converting CH_4 to CO_2 and H_2O . ($2\text{CH}_4 + 1/2 \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$; $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$). Oxygen is the most expensive feedstock in this process. Further, no methane is converted to valueless by-products and the

recycle stream does not have to be purged of CO_2 , the second most expensive item in the process. Thus, a 10% yield under these conditions may be economically attractive. There is at this time no evidence that 10% is the highest yield obtainable at close to 100% selectivity and much further work is needed to define and optimize the reaction and the catalyst.

Fig. 1 shows that low temperature is essential for high hydrocarbon selectivity and very low CO_x production.

A different preparation of the KCaNiO_x catalyst which had been calcined at a lower temperature was less selective. Fig. 2 shows a sequence of oxidative couplings with this catalyst at different temperatures. It is apparent that on return to the initial temperature the conversion and selectivities were the same or slightly better than before. The total time on stream with this catalyst was 38 hours.

A 10% KCaNiO_x catalyst on alumina was found to be much less active than the unsupported catalyst.

The various catalysts described in this section were tested for extensive periods and maintained their conversion and selectivity over long periods (5 days maximum test period).

METHANE COUPLING ON A $KCaNiO_x$ CATALYST USING A MIXTURE
STEAM/OXYGEN AT SEVERAL TEMPERATURES.
WHSV: 213 H^{-1} . $H_2O/O_2=5$

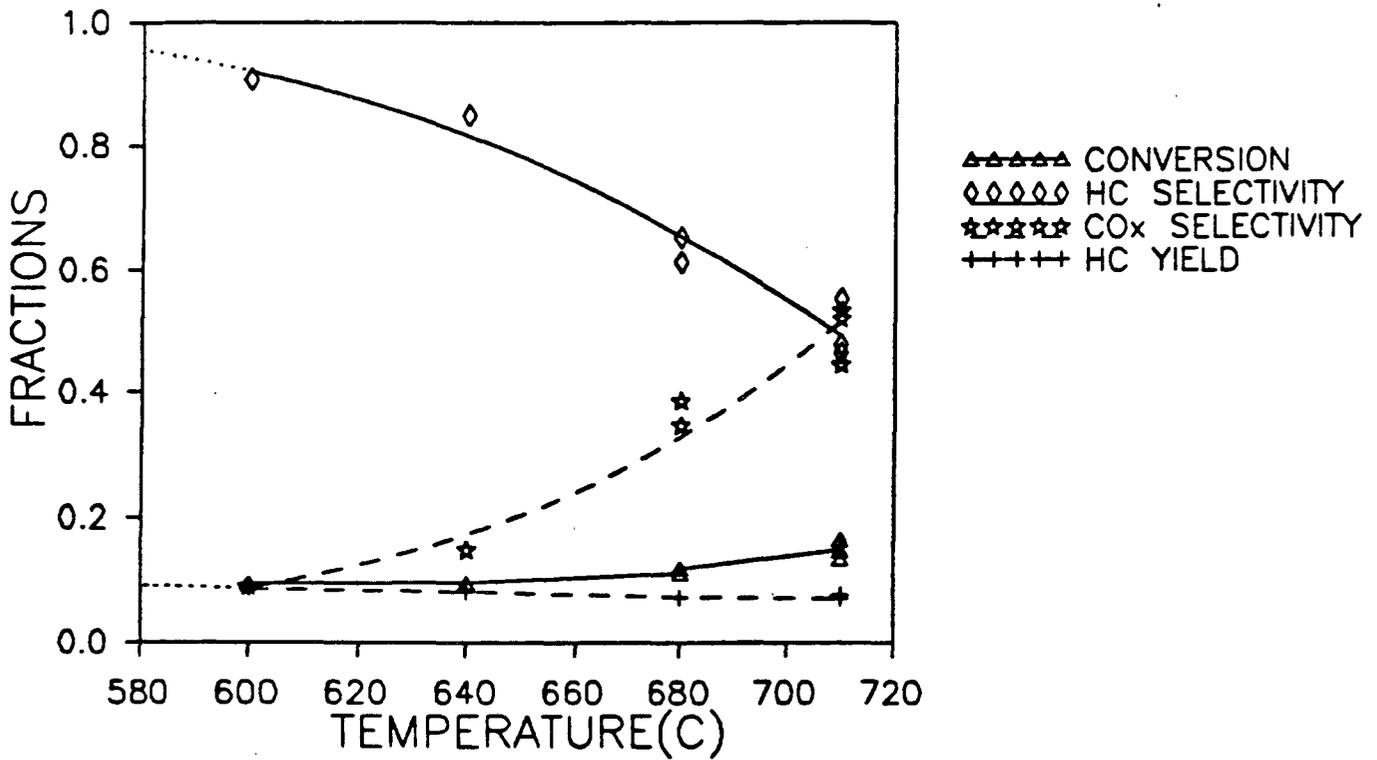


Fig. 1

METHANE COUPLING ON KCaNiO_x USING STEAM/ O_2 MIXTURES. STD. COND.

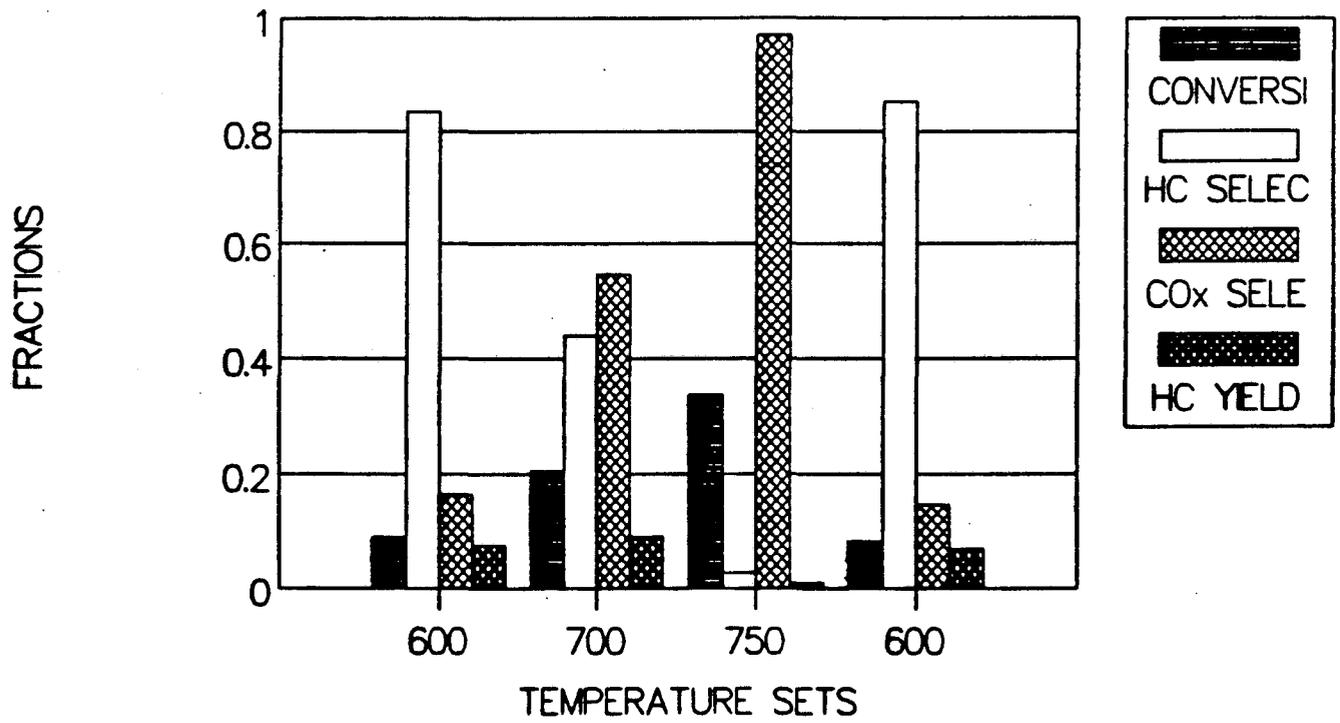


Fig. 2

*LAWRENCE BERKELEY LABORATORY
CENTER FOR ADVANCED MATERIALS
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720*