

# C<sub>1</sub> CATALYSIS AT IGT

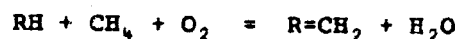
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## OBJECTIVE

Develop catalysts and processes to produce high value chemicals using natural gas directly as a feedstock.

## COUPLING REACTIONS

The oxidative coupling reactions that are considered are illustrated as follows:



If RH is:

methane  
ethane  
propane  
toluene  
xylene

Then R=CH<sub>2</sub> is:

ethylene  
propylene  
butylene  
styrene  
vinyl toluene

The methane-methane and methane-toluene coupling reactions have been reduced to practice at IGT.

## EXPERIMENTAL RESULTS

For methane coupling, the catalyst formulation technology is based on the hypothesis that the higher the basicity of the catalyst, the higher yield of the olefins. We found that when a mixed basic metal oxide is promoted by another metal oxide with a higher oxidation state, there is an increase in catalyst basicity. Sixty different catalyst formulations were tested and some of the representative results are summarized in Table 1. The catalyst with the best performance has an ingredient of Li/B/MgO (U.S. Patent No. 4,826,796). The effect of Boron on the Li/MgO based catalyst is presented in Table 2. Seven other types of promoters were experimented and none was better than the 0.24 weight percent B on Li/MgO catalyst which has a yield of 21% ethylene/ethane per pass.

Table 1. SUMMARY OF CATALYSTS EVALUATED

<u>Compound</u>	<u>Conversion, %</u>	<u>Selection, %</u>	<u>Yield Per Pass, %</u>
MgO	6	58	3
B/MgO	11	35	4
Li/Zr/Al <sub>2</sub> O <sub>3</sub>	11	36	4
Li/SnO <sub>2</sub>	11	48	5
Zr/Al <sub>2</sub> O <sub>3</sub>	2	0	0
Pb/Zr/Al <sub>2</sub> O <sub>3</sub>	2	0	0
Li/TiO <sub>2</sub>	2	0	0
Li/ZnO <sub>2</sub>	4	81	3
Li/V/MgO	7	0	0
Li/ZnO <sub>2</sub>	4	81	3
Li/V/MgO	7	0	0
Mg/LiAlO <sub>4</sub>	5	79	4
Li/SiC	5	0	0
LiTi/MgO	10	33	3
Li/Ti/MgO	12	46	6
Li/Ag/MgO	6	43	3
Li/Ta/MgO	14	67	9

Table 2. EFFECT OF BORON ON Li/MgO CATALYST

<u>Promoter, wt %</u>	<u>Conversion, %</u>	<u>Selectivity, %</u>	<u>Yield per Pass, %</u>
<u>Boron</u>			
0.0	17	74	13
0.12	17	75	13
0.18	21	80	17
0.24	24	86	21
0.35	18	69	12
0.51	17	73	12

Selected catalysts from this group were used in methane-toluene coupling experiments. The boron promoted Li/MgO catalyst was found to have the best performance to date. The results are summarized in Tables 3 and 4. The best yield of styrene/ethyl benzene is 15% per pass.

#### DISCUSSION

None of the published results has reported an ethylene/ethane yield of anywhere near 30% per pass which is the estimated "economic zone" which leads us to suspect, therefore to investigate, the "barrier." Some of our initial findings are:

- Catalysts with deep pores promote deep oxidation.
- Catalyst beds with long after-bed vapor phase zone increases olefin as well as carbon dioxide yields.
- Rapid quenching of products reduces both carbon oxide and olefin yield.
- Small catalyst beds, less than 20 grams of catalyst, prevents accurate direct quantitative measurements.
- Large non-isothermal or pseudo-adiabatic catalyst beds result in high temperature rise.
- The effective yield zone is limited due to rapid temperature rise as shown in Figure 1.

#### RESEARCH NEEDS

- Development of a catalyst with low light-off temperature ( $<600^{\circ}\text{C}$ ).
- Stabilization of catalytic active species at high temperatures ( $>900^{\circ}\text{C}$ ).
- Incorporation of heat removal schemes to provide near isothermal conditions within the catalyst bed.
- Development of vapor phase promoters.
- Development of sulfur-resistant coupling catalysts for using natural gas directly as a feedstock.
- Development of correlations to predict catalyst activity, selectivity, and stability.

Table 3. METHANE + TOLUENE + STYRENE

Small Unit: 10-20 g Catalyst

<u>Catalyst</u>	<u>Conversion, %</u>	<u>Selectivity, %</u>	<u>Carbon Balance, %</u>
Li/B/MgO	12	92	<50
Li/B/MgO	6	83	<50
Li/B/MgO	20	41	81
Li/B/MgO	12	43	78
Li/B/MgO	12	51	89
Li/B/MgO	16	38	78
Li/B/MgO	24	NA	NA
Li/B/MgO	22	18	92
Li/B/MgO	7	28	99
None	70	10	73
None	86	0	76

Table 4. METHANE + TOLUENE + STYRENE

Large Unit: 70-100 g Catalyst

<u>Catalyst</u>	<u>Conversion, %</u>	<u>Selectivity, %</u>	<u>Carbon Balance, %</u>
None	17	14	101
None	23	25	97
Li/B/MgO	15	31	93
Li/B/MgO	50	15	93
Li/B/MgO	19	25	102
Li/B/MgO	17	44	100
None	11	40	100
None	43	35	102

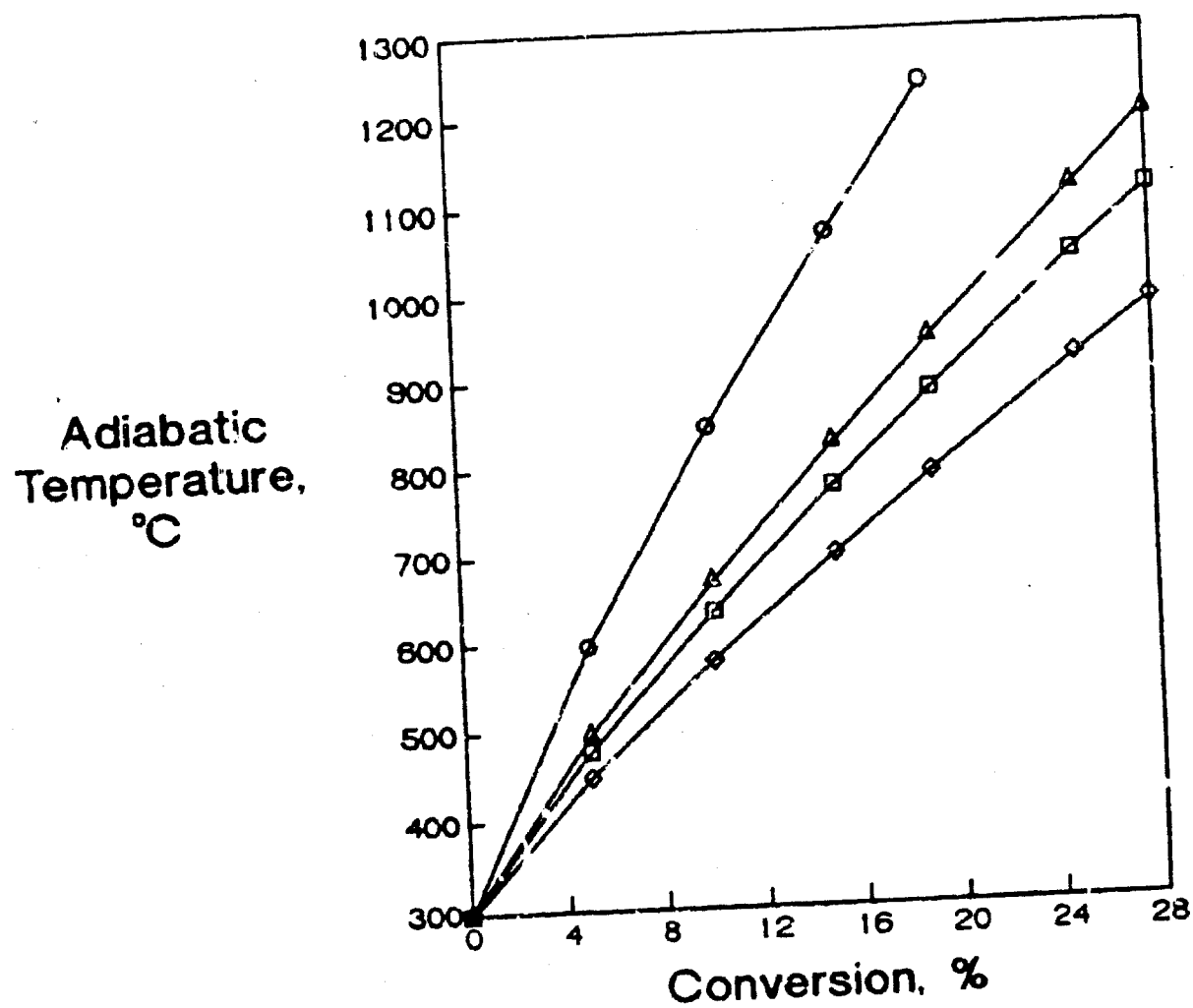


Figure 1. ADIABATIC REACTION TEMPERATURE VERSUS CONVERSION

**ACKNOWLEDGMENT**

This project is supported by the Gas Research Institute and IGV's Sustaining Membership Program. Frequent discussions with Messrs. Irvine Solomon, Howard Meyer, Kermit Woodcock, Vern Hill, Dennis Leppin,, James Semrau and Bob Zahransky were most enlightening. The mere mention of these names is by no means indicative of the degree of appreciation by the authors.

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