THE CATALYTIC LOW TEMPERATURE OXYDEHYDROGENATION OF METHANE. TEMPERATURE DEPENDENCE, CARBON BALANCE AND EFFECTS OF CATALYST COMPOSITION

J. RASKÓ, P. PEREIRA *, G.A. SOMORJAI and H. HEINEMANN

Materials Science Division, Center for Advanced Materials, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, U.S.A.

In an earlier publication [1] it has been claimed that oxidative coupling of methane to higher hydrocarbons had been obtained with close to 100% selectivity at 600°C and atmospheric pressure in the presence of steam over a CaNiK oxide catalyst. These results have been confirmed in longer runs. Artifacts, such as carbonate formation on the catalyst, have been excluded. The reaction is slightly exothermic. An Arrhenius plot shows that methane oxidation to CO_2 predominates at temperatures above 600°C and oxidative methane coupling at lower temperatures. The importance of exact catalyst composition is demonstrated.

Keywords: Oxydehydrogenation of methane, catalytic methane conversion

1. Introduction

We have reported on the catalytic oxydehydrogenation of methane to ethane and ethylene in the presence of excess steam as 600°C over a CaNiK-oxide catalyst with a composition of 2:1:0.1 [1]. The selectivity to C_2 hydrocarbons was nearly 100% and the conversion was 10–12% under our conditions of the experiments. In this paper we present more data obtained by the continued characterization of the catalyst. Temperature dependent studies revealed that the overall activation energy is 83 kJ/mole for producing about 60% ethane and 40% ethylene and this reaction predominates below 600°C as compared to methane steam reforming and CO_2 formation which becomes dominant at higher temperatures. We obtained a carbon balance of 100% under various experimental conditions on the active catalysts. We also varied the Ca:Ni:K ratio over a wide range and report here the effects of catalyst composition on the reaction activity and on the catalyst deactivation properties. The oxide catalyst with a composition of $Ca_{2-4}Ni_1K_{0.1}$ appears to be the most active and selective under our conditions of the methane coupling reaction.

* INTEVEP, S.A.; Apartado 76343, Caracas 1070A, Venezuela.

2. Experimental

Catalyst preparation started with mixing of appropriate amounts of $Ca(NO_3)_2$ $\times 4H_2O$(Mallinckrodt), $Ni(NO_3)_2 \times 6H_2O$(Fischer Scientific Co.) and KNO_3 (Mallinckrodt). The well-homogenized nitrate mixture was heated in air at $120°C$ for about 14 hours. The mixture melted and gradually lost its water content. The dried mixture was heated stepwise at $350°C$ for 2 hours, at $550°C$ for 2 hours and was finally decomposed under flowing air (flow rate: 2 cc/min) at $700°C$ for 18 hours.

The apparatus used is shown in fig. 1. Methane and oxygen were obtained from Matheson (their purities were better than 99.99%). A Harvard syringe pump was used for pumping distilled water to the reactor through a pipe which was heated at $140°C$.

The catalyst was oxidized in the reactor with flowing oxygen (flow rate: 2 cc/min) at $680°C$ for 18 hours before starting experiments. The methane-oxygen-steam gas mixture molar ratio of $CH_4 : O_2 : H_2O = 3 : 1 : 6.5$) was introduced to the reactor at $580–750°C$. The methane space velocity was 4.0 mmol/g catalyst/hr.

Products of the reaction were analyzed by gas chromatography using FID, TCD and mass spectrometer detectors.

Gases on input and output side were controlled and measured by control valves and mass flow meters.
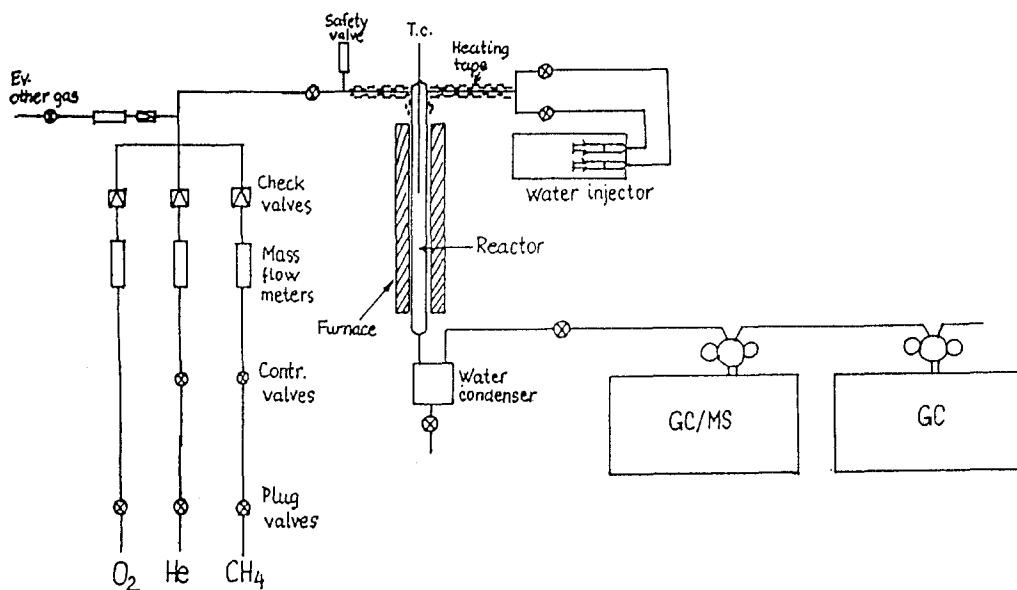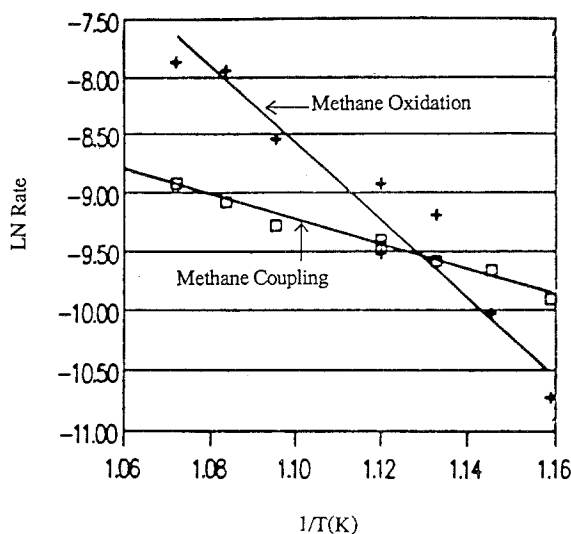

Fig. 1. Flow reactor scheme.

Fig. 2. Arrhenius plot (580–660 ° C) for methane oxydehydrogenation and methane oxidation.

A. The activation energy and thermodynamic consideration for methane conversion

Fig. 2 shows the conversion log rate vs. temperature for producing ethane and ethylene. The activation energy is 83 kJ/mole. The same figure also shows the activation energy found for methane steam reforming under our conditions of the experiment. It appears that below 600 °C the oxidative coupling reaction dominates. Only above this temperature does CO_2 formation which has a much higher activation energy of 263 kJ/mole become significant. In fig. 3 we compare the heats of reaction for five different reactions of methane as a function of temperature. The oxydehydrogenation reactions to produce ethane and ethylene are somewhat exothermic as compared to the highly endothermic steam reforming or the highly exothermic combustion reactions. We find that by using both steam and oxygen we could inhibit both steam reforming and combustion over our catalyst which then is capable of producing ethane and ethylene.

B. The carbon balance during the catalytic conversion of methane to ethane and ethylene

A careful carbon balance was performed to insure that analytical results would not be influenced by a potential absorption of CO_2 produced by the catalyst with formation of calcium carbonate. Carbon input (as methane) and carbon output (as methane, higher hydrocarbons and CO_x) were metered and analyzed. Table 1 shows the carbon balance for two runs, one at high selectivity and the other at relatively poor selectivity. A blank run with an empty reactor at the same conditions gave 0.8 to 1.0% conversion to CO_2. This corresponds exactly to the CO_2 selectivities obtained with catalyst in the reactor (8–10% at 10% conversion, table 1), and indicates that CO_2 was formed thermally and none was absorbed on
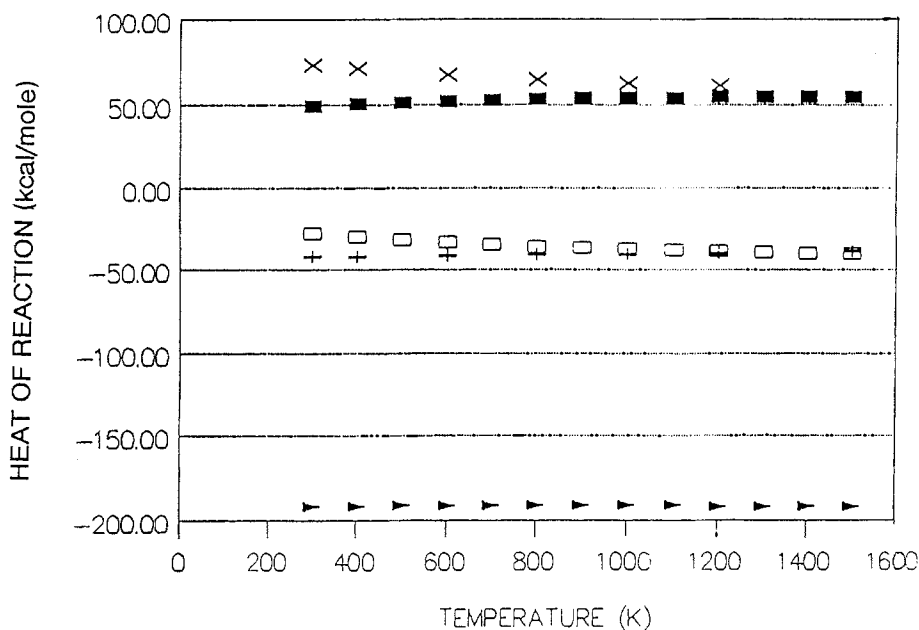
Fig. 3. Heat of reaction at different temperatures: combustion ▶, ethane dehydrogenation ×, steam reforming ■, oxydehydrogenation to ethane +, and ethylene □.

the catalyst. Excellent balances were obtained. An oxygen balance is difficult to obtain because water formed during oxidative coupling is a small fraction of the water used as steam.

C. The effects of variations of composition on the activity, selectivity and deactivation of the CaNiK-oxide catalysts.

CaO, $CaK_{0.1}O_x$, Ca_3NiO_x, $NiK_{0.1}O_x$ and $Ca_3NiK_{0.1}O_x$ catalysts were tested at the same reaction conditions ($600°C$, $CH_4 : O_2 : H_2$) = 3 : 1 : 6.5). The results obtained are shown in table 2.

Table 1
Carbon balance for two runs at different conversion and selectivity values $Ca_3Ni_1K_{0.1}$ catalyst C_{output}/C_{input}

Catalyst	Time (min)	Conversion (%)	Hydrocarbon selectivity (%)	CO_x sel (%)	Carbon balance
A	60	10	93	7	99.8
A	120	10	92	8	100.1
B	50	4	80.3	20	101.8
B	130	5	48.3	52	104.7
B	165	3	83.3	17	101.3
B	205	4	56.9	43	101.3
B	245	3	78.9	21	98.6

Table 2

Methane oxidative coupling run. Conversion and selectivities $Ca_4Ni_1K_{0.1}$ catalyst $600\,^\circ C$; $CH_4 : O_2 : H_2O = 3 : 1 : 6$; atm. pressure

Time (min)	CH_4 conv. (%)	Hyd. sel. (%)	CO_x sel. (%)
95	10.6	91	9
153	9.3	92	8
212	9.2	92	7
271	10.0	93	7
329	8.8	88	11
388	9.3	92	8

CaO alone produced mainly CO_2 and CO (82.0–77.2% and 7.0–11.0%, resp.); only 9.0–11.4% selectivity for hydrocarbons was found at a conversion of 4.8–2.3%. Introducing a small amount of potassium onto CaO, the hydrocarbon selectivity increased up to 80% at a conversion of 4.7–4.6%. The presence of potassium suppressed CO_2 and CO formation. This is also reflected in the results obtained on Ca_3NiO_x (without potassium) where the starting value of hydrocarbon selectivity (43.7%) decreased considerably with time on stream, while CO_2 formation became dominant. On $NiK_{0.1}O_x$ a relatively high conversion (16.9–15.6%) was observed; the main reaction product was CO_2 (i.e., total oxidation was dominant). The most active and selective catalyst proved to be $Ca_3NiK_{0.1}O_x$.

It is interesting to note that in the presence of potassium (see $CaK_{0.1}O_x$) a small amount of CO was observed. It can be inferred that steam reforming of CH_4 occurs on $CaK_{0.1}O_x$. The absence of CO among the reaction products in the presence of Ni may indicate the ability of Ni to oxidize CO to CO_2 in the presence of oxygen.

D. The conversion of CH_4 to higher hydrocarbons

Table 3 presents results from a typical run at $600\,^\circ C$ during 6.5 hours. Conversion was quite steady as was selectivity at $\approx 92\%$. It is important to point

Table 3

Methane oxidative coupling run; product distribution $Ca_4Ni_1K_{0.1}$ catalyst $600\,^\circ C$; $CH_4 : O_2 : H_2O = 3 : 1 : 6$; atm. pressure

Time (min)	C_2H_4 sel (%)	C_2H_6 sel (%)	C_3H_6 sel (%)	C_3H_8 sel (%)	C_4 sel (%)	Par/Ol ratio
95	42	40	3	4	2	0.98
153	40	41	4	4	3	1.0
212	40	41	5	4	3	1.0
271	39	42	5	4	3	1.1
329	44	33	5	4	2	0.8
388	41	40	5	3	3	1.0

Table 4
Characteristic data of CH_4 coupling on different catalysts 600 °C; $CH_4 : O_2 : H_2O = 3 : 1 : 6.5$; atm. pressure

Catalyst	Conversion	HC sel.	CO_2 sel.	CO sel.	CO_x sel.
CaO (8.5%)	4.8– 2.3%	9.0–11.4%	83.0–77.5%	7.0–11.0%	90.0–
$CaK_{0.1}$ (20%)	4.7– 4.6%	81.5–79.9%	16.6–17.5%	1.8–2.5%	18.5–
Ca_3Ni	3.1– 6.7%	43.7–11.0%	56.2–88.9%	0	
$NiK_{0.1}$	16.9–15.6%	2.1– 2.3%	97.8–97.6%	0	
$Ca_3NiK_{0.1}$	9.9– 9.0%	93.7–91.1%	6.3– 8.9%	0	

out that blank runs with an empty reactor at the same conditions gave 0.7–1.0% conversion of CH_4 to CO_2. This amount of CO_2 would correspond to 7–10% CO_2 selectivity at 10% conversion or about what is observed in runs with a catalyst.

Table 4 gives a product distribution of the same run as in table 3. Again all selectivities were steady. Small amounts of C_3 and C_4 hydrocarbons were formed and the olefin/paraffin ratio was about 1.0.

The longest run thus far made lasted about 19 hours. It showed only a small decline in activity and selectivity, probably due to a unit upset after 10 hrs.

3. Discussion

The activation energy for producing ethane is low compared to the ΔE^* for steam reforming. The coupling reaction appears to dominate at low temperatures below 600 °C. It is interesting to note that the activation energy is similar to that found for methanation or for the formation of low molecular weight hydro- carbons from CO and H_2. In that reaction the dominant mechanism appears to be the dissociation of CO by the Boudouard reaction ($2CO \rightarrow C + CO_2$) and the subsequent hydrogenation of the surface carbon to CH_x species that may fully hydrogenate to methane or couple to produce C_2, C_3 ... hydrocarbons. Although we do not have enough kinetic information to verify the mechanisms of CH_x-cou- pling, it is possible that methane is both the source of CH_x intermediates and of H atoms on the surface. The former may couple to produce C_yH_x species by a mechanism similar to that in the Fischer-Tropsch reaction while the surface hydrogen produces water. It would be interesting to extend the range of reaction and to lower the temperature and explore other catalyst compositions in order to obtain products other than C_2 just as in the case of Fischer-Tropsch reactions. In any case the breaking of the first C–H bond in CH_4 does not appear to need the high temperature (> 650 °C) as was originally thought [2]. It appears that by the simultaneous use of both oxygen and water both the combustion and the steam reforming reactions, one highly exothermic, the other highly endothermic can be

inhibited. In this circumstance the oxidative coupling of methane can be the dominant reaction path over the $Ca_{2-4}Ni_1K_{0.1}O_x$ catalyst.

The carbon balance of nearly 100% within the experimental error clearly indicates that the reaction is catalytic and the catalyst does not behave as a possible reactant. This was important to determine since the formation of carbonates could be blamed for the lack of CO_2 formation. This, however, is not the case. Another indication of the non-absorption of CO_2 on the catalyst is the fact that $CaCO_3$ is stable up to $900°C$. A catalyst prepared from $CaCO_3$ was essentially inactive after calcination at $750°C$ but became active after $900°C$ calcination. When the $Ca_3NiK_{0.1}$ catalyst loses activity, it can readily be re-activated by O_2 treatment at $700°C$. The fact that CO_2 production is the same from an empty reactor and from a catalytic run shows that essentially no CO_2 is produced over the catalyst and that selectivity to hydrocarbons is at or close to 100%.

The most active catalyst composition for the selective coupling of methane is $Ca_{2-4}Ni_1K_{0.1}O_x$ as shown by our experiments. However, $Ca_3K_{0.1}O_x$ exhibits significant activity and selectivity that indicates that the surface chemistry leading to C_2 hydrocarbons from methane does not need the presence of nickel which acts as a promoter.

CaO alone is a poor catalyst and NiO and KO_x do not produce C_2 hydro-carbons. Further studies will explore the mechanism of this reaction with $Ca_{2-4}Ni_1K_{0.1}O_x$ and the promoter action of other transition metal oxides on the selectivity and activity of this catalyst. It should be noted that $CaKO_x$ is also an outstanding catalyst for the steam gasification of graphite and char at relatively low temperatures to H_2 and CO_2 [3].

Acknowledgement

References

[1] P. Pereira, S.H. Lee, G.A. Somorjai and H. Heinemann, Catal. Lett. 6 (1990) 255.
[2] Y. Amenomiya, V.I. Birss, M. Goledzinowski, J. Galuszka and A.R. Sanger, Catal. Rev. Sci-Eng. 32 (1990) 163.
[3] P. Pereira, R. Csencsits, G.A. Somorjai and H. Heinemann, J. Catal. 123 (1990) 463.