Catalysis Letters 6 (1990) 255–262

THE CONVERSION OF METHANE TO ETHYLENE AND ETHANE WITH NEAR TOTAL SELECTIVITY BY LOW TEMPERATURE ($< 610\,^{\circ}$C) OXYDEHYDROGENATION OVER A CALCIUM-NICKEL-POTASSIUM OXIDE CATALYST

P. PEREIRA, S.H. LEE, G.A. SOMORJAI and Heinz HEINEMANN

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

Received 10 July 1990; accepted 22 July 1990

Total selectivity in methane conversion, calcium-nickel-potassium oxide catalyst, methane conversion to ethylene and ethane

The catalytic oxidative coupling of methane to C_2, C_3 and C_4 paraffins and olefins has been accomplished with close to 100% selectivity at methane conversions of about 10% per pass. Essentially no carbon oxides are formed and the mechanism appears to be a surface catalyzed reaction. Temperatures of $< 600\,^{\circ}$C are used and the presence of steam is important. The catalyst comprises a ternary mixture of calcium, nickel and potassium oxides. Method of preparation and composition of the catalyst are critical for its performance. Presence of a carbidic carbon on the catalyst surface may be important.

1. Introduction

This letter reports the catalytic oxidative coupling of methane to C_2 hydrocarbons and to small amounts of C_3 hydrocarbons at close to 100% selectivity at about 10% CH_4 conversion/pass. At this high selectivity oxygen consumption is minimized as is the need for purification of recycle methane. Even though the yield of C_2 and C_3 hydrocarbons/pass is relatively low, these factors offer advantages over higher yields at relatively high conversions to carbon oxides.

It appears that the reaction path is catalytic and that there is no evidence for homogeneous gas phase oxidative reaction, in contrast to most of the methane conversion studies reported in the literature [1] that are usually performed at high temperatures (700 °C) and high space velocities.

The reaction of methane with small amounts of oxygen is carried out in the presence of steam typically at ratios of methane : oxygen : water = 3 : 1 : 6.5 at relatively low temperatures $< 600\,^{\circ}$C and at atmospheric pressure. The role of water is under study and it is shown to be essential. In the absence of water much lower selectivities are obtained and substitution of inert gases: e.g. helium, for water to achieve the same partial pressure of the reactants and products results in lower yields of hydrocarbons.

The catalyst used is a calcium-nickel-potassium oxide and care should be taken for catalyst formulation. Slight variations in catalyst preparation have led to materials exhibiting different activities and selectivities.

2. Experimental

The equipment used has been described before [2]. Methane and oxygen were obtained from Mathesson with a purity of better than 99.99%. Steam was produced from distilled water pumped into the reactor by a Harvard syringe pump; the lines from the exit of the syringe up to the inlet of the reactor were heated at 140 ° C.

After the catalyst has been loaded into the reactor, it is oxidized with O_2 at 680 ° C. The flow rate is approximately 2 cc of oxygen per minute. The length of time of oxidation is important as shown in the Results section. The reaction temperature is then raised to the desired value and steam and methane mixed with oxygen are introduced. The range of reaction temperatures explored was 580–750 ° C. The methane space velocity was 4.0 mmol/g cat./hr. There is an induction period as shown in table 1 (which presents a carbon material balance) during which carbon is deposited on the catalyst. (The deposited carbon may play a significant role as an elementary reaction step or for modifying the catalyst.) After this induction period, a 100% ± 2% carbon material balance is obtained for extended periods of time (days).

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

Blank runs were performed over inert ceramic granules and in the absence of catalyst and indicated that in the temperature range of 560–600 ° C, approximately 2–4% conversion of methane to CO_2 was obtained. Since less carbon oxides are obtained during the runs over the catalyst, it is apparent that in the

Table 1
Material balance as a function of operating time

Time (min)	Carbon balance (%)
25	70
50	95
100	98
200	100
400	100

presence of the catalyst, the gas phase reaction leading to CO_2 formation is minimized.

XPS analyses of the catalyst were performed in a PE 5000 ESCA unit. The samples consisted of powdered catalysts compressed between a gold mesh and a gold foil. Charging effects were thus minimized and were corrected for the spectra shown in this work. The standard conditions for the analysis were: angle 45°; acquisition time 5 min; pass energy 35.7 eV; anode: Mg 400 W.

The preparation of the catalyst is of great importance and is very sensitive to the procedure employed. Most catalysts of high activity were prepared from solutions of calcium and nickel nitrates which were dried and decomposed in air at 700°C to the corresponding oxides, then, small amounts of potassium nitrate were added and decomposed in oxygen and further oxidized at 700°C as well. Catalysts of similar performances were obtained by starting with the corresponding hydroxides. The ratio of the components is important and the best catalyst thus far prepared consists of an atomic ratio of calcium to nickel to potassium of 2 : 1 : 0.1. As previously mentioned, oxidation of the finished catalyst is also very important. Studies to elucidate the reasons for this and to find catalyst modifications giving higher yields are underway.

3. Results and discussion

When the methane-steam-oxygen reaction mixture was passed over the best performing calcium-nickel-potassium oxide catalyst at 600°C, conversion of methane was 10% and selectivity to C_2 hydrocarbons was 97 + %. Fig. 1 shows the hydrocarbon selectivity over a 6 hour period for the calcium-nickel-potassium

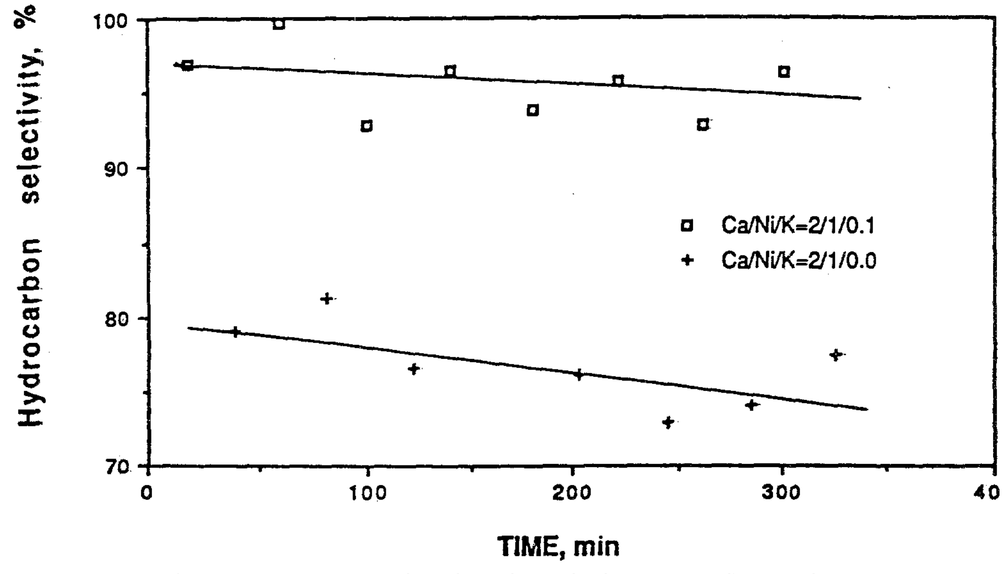

Fig. 1. Effect of potassium on the selectivity to hydrocarbons. Standard conditions.

Table 2
Effect of the in-situ activation of the catalyst on its performance; activation was with oxygen prior to reaction.

Activation time (hours) (O_2 2ml/min)	% conversion of CH_4	% hydrocarbon selectivity	% C_2H_4 selectivity	% C_2H_6 selectivity	% C_3H_6 selectivity	% C_3H_8 selectivity	% C_4^+ selectivity	Total Olef/Paraf.
1	1.8	100	16.0	82.0	0	2.0	0	0.19
18	6.6	100	32.3	57.1	2.7	5.8	2.1	0.56
40	9.5	100	38.1	48.2	5.3	5.6	2.8	0.81

Selectivity was assumed 100% because CO_2 production was always below the blank run values and approximately constant.

oxide catalysts. The 2 : 1 : 0.1 ratio of components gave appreciably better selectivity than the same ratio of calcium and nickel in the absence of potassium. The conversion in both cases was about 10%. The selectivity to C_2 of 95 + % was stable over extended periods (8–10 hours). CO_x was produced in quantities less than in the blank runs ($>$ 3–4%), indicating that most of the conversion to carbon oxides occurred in the preheat zone of the reactor.

The importance of activation of the catalyst in oxygen is indicated in table 2. It clearly shows that conversion of methane increases with activation time and that the selectivity to the olefin content of hydrocarbons also increases. Further, it is interesting to note that with increasing oxidation time, larger amounts of C_3 hydrocarbons are formed and that C_4 hydrocarbons appear.

Fig. 2 shows that variation of the ratio of the components gives catalysts showing greatly different yields of hydrocarbons (product of selectivity and conversion) as well as of stability.

An investigation of the effects of temperature on the yield and selectivity are shown in fig. 3. While methane conversion increased over a 150 ° C range (600–750 ° C), hydrocarbon selectivity declined dramatically with increasing temperature and CO_x formation increased correspondingly. When the temperature was lowered back to 600 ° C from 750 ° C, the earlier results exhibiting near 100% selectivity for hydrocarbons were reproduced. Thus the catalyst is stable in spite of temperature excursions in the 150 ° C range.

The effect of steam is shown in table 3. When steam was replaced with helium (same partial pressure of methane and oxygen) the selectivity to hydrocarbons at 600 ° C dropped from 100% to 75% and rapidly declined further to 15%. When steam was substituted for helium, selectivity and conversion recovered to near the original values. Thus the catalyst is stable in the presence and absence of steam.

XPS analysis was used to compare the surface of an active and a less active form of the catalyst. The active sample (A) was analyzed after reaction during 10 hours. The less active sample (B) was analyzed both before and after reaction and

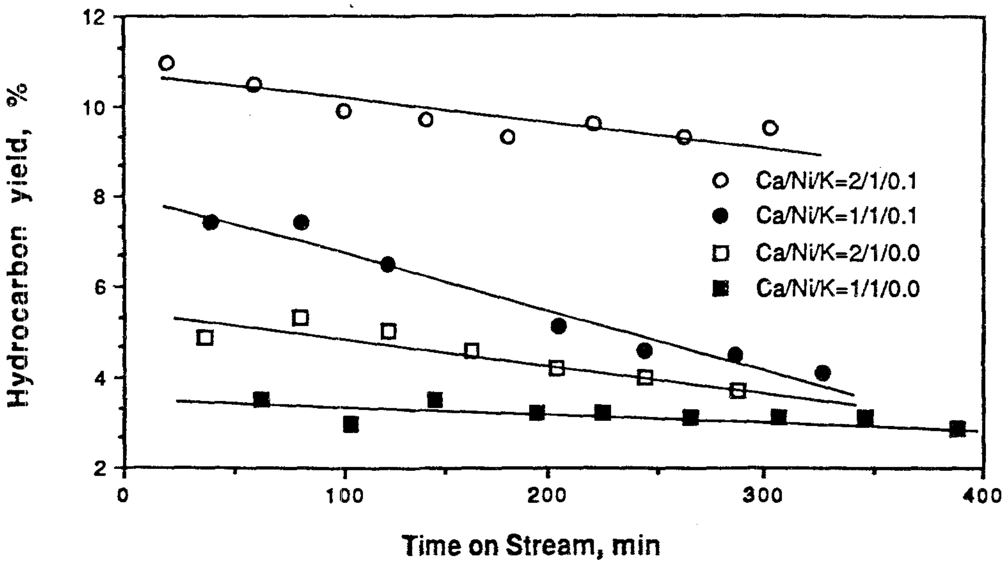

Fig. 2. Effect of catalyst composition on the yield of hydrocarbons at standard conditions.

there were neither qualitative nor quantitative changes in the spectra. In fig. 4 the Ni $2p_{3/2}$ photoemission signals are shown for both samples. Analysis of the Ni $2p_{3/2}$ signal for the inactive sample shows the presence of a shoulder at 854.5 eV that has been assigned in the literature to NiO [9]. In both samples A and B the presence of NiOH at the surface is shown by the peak at 856.4 eV. This value corresponds to the binding energy reported by Kim et al. [9]. There is a third

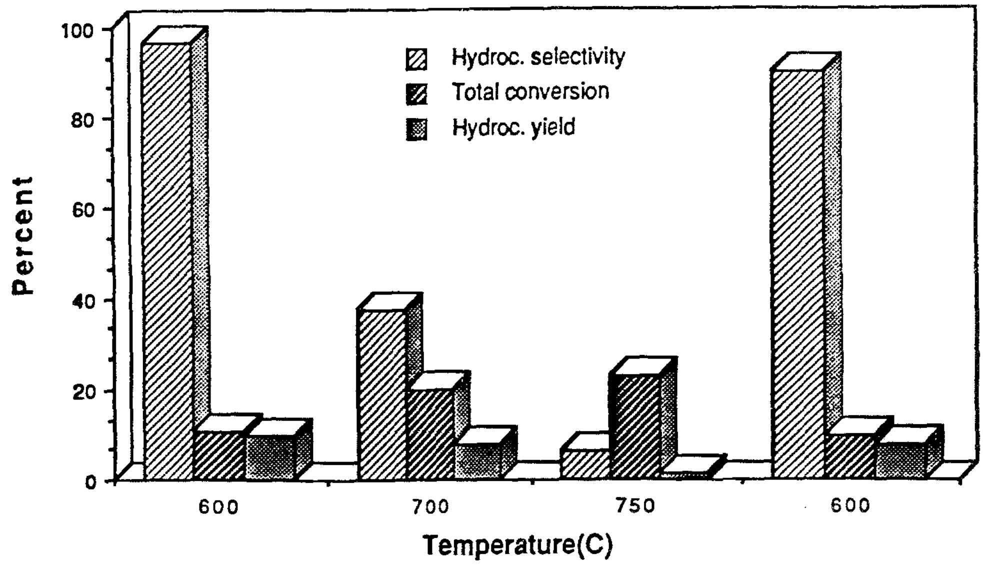

Fig. 3. Effect of temperature cycling on catalyst performance of a Ca/Ni/K-2 : 1 : 0.1 oxide catalyst.

Table 3
The importance of steam in the reaction mixture for methane conversion and hydrocarbon selectivity

Time on stream (min)	Temp. (°C)	Dilutant	Hydrocarbon selectivity	Methane conversion	Hydrocarbon yield
85	600	steam	100	9.5	9.5
200	600	helium	75	5.0	3.8
300	600	helium	15	2.1	0.3
400	600	steam	90	11.0	9.9

(shoulder) peak at higher binding energy (858.01 eV) in the signal for the active catalyst, which must correspond to a higher oxidation state of Ni. This peak does not correspond to values reported in the literature for Ni_2O_3; it could be due either to the formation of a non-stoichiometric oxide or to a calcium nickelate, a species which could be involved in the catalysis of the selective reaction. NiO appears to be the predominant form on the surface of the inactive catalyst. The presence of carbonates in both samples was also confirmed by XPS and X-ray

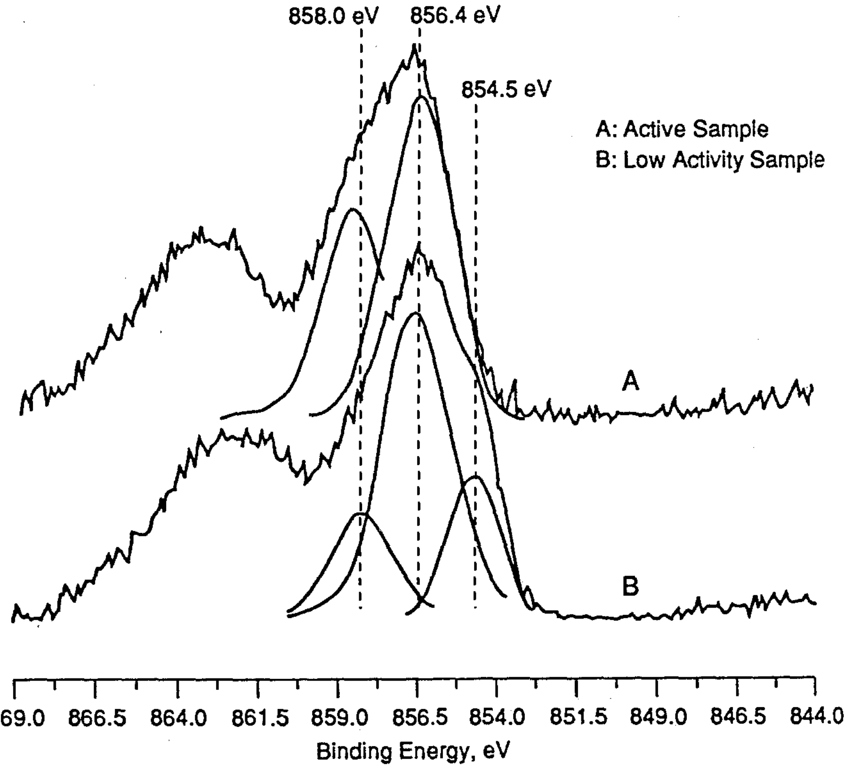

Fig. 4. $Ni_{2p_{3/2}}$ XPS spectra from an active (A) and a low activity (B) Ca/Ni/K-2:1:0.1 oxide catalyst.

diffraction analysis. The formation of calcium carbonate during the reaction could be related to deactivation of the catalyst [3]. However, the analyzed powder (A) was still very active when it was again used for conversion of methane. Potassium seems to be forming an oxidic-hydroxidic mixture in both samples A and B as deduced by XPS and X-ray diffraction. A subsequent paper will comment more specifically on the details concerning oxide states and deactivation of the catalyst.

A surface composition Ca : Ni : K equal to 2 : 1 : 0.1 was obtained for the active catalyst from the ESCA analysis. The use of this formula for the preparation of the catalyst led to the results already shown in fig. 2.

The Ca-oxide-Ni-oxide-K-oxide catalyst exhibits chemical behavior that is very different from other catalysts used for methane coupling; it operates at a significantly lower temperature range and it does not produce carbon oxides, CO or CO_2.

It has been proposed that the mechanism of methane oxidative dimerization in the presence of alkali-earth alkali oxides at high temperatures involves a catalytic activation of methane. The active species is a methyl free radical that consequently reacts, mostly in gas phase [4–6]. Because of the lower temperatures and the fact that the reaction does not occur in the absence of the catalyst, we can rule out the gas phase free radical reaction path.

The formation of carbon oxides constitutes a thermodynamically driven pathway that affects the selectivity when long residence times and high temperatures are used. When methane is activated at high temperatures it is difficult for oxidative dimerization to occur without producing substantial amounts of carbon oxides. Our catalysts, however, produces hydrocarbons with near 100% selectivity and thus CO or CO_2 formation is inhibited.

If an active adsorbed species from methane were to form on the surface of the catalyst and lower temperatures were used, a more selective methane coupling could be achieved. This is what we believe is taking place at the conditions of this work. Low temperatures were used while the longer than usual contact time is such that an amorphous carbon deposit could be continuously formed that apparently plays an important role in the reaction mechanism.

The need for the presence of a partial pressure of water requires further research to be understood. It could be related to the formation of a stable concentration of hydroxyl species on the surface instead of the O^- species that are more likely to produce carbon oxides.

A few results with stable catalysts, high selectivity (95 + %) and using a co-fed reactor system have been reported for the coupling of methane [7]. The relevance of the present finding is highlighted by relatively low oxygen consumption, by low temperature operation with steam and by the ability to recycle methane without scrubbing out CO_2 in the case of 100% selectivity to hydrocarbons.

Work is currently in progress to attempt to increase conversion at 100% selectivity and to change the olefin to paraffin ratio. Studies on the mechanism of this reaction which appears different from those proposed in the literature [8] at different operating conditions are also under way.

Acknowledgement

This work was supported by the Assistant Secretary for Fossil Energy, Office of Management Planning and Technical Coordination, Technical Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, through the Morgantown Energy Technology Center, Morgantown, WV 26505.

References

[1] a) T.A. Garibyan and L. Ya. Margolis, Cat. Rev.-Sci. Eng. 31 (4) (1989–90) 355–384;
b) Y. Amenomiya, V.I. Birrs, M. Goledzinowski, J. Galuszka and A.R. Sanger, Cat. Rev. -Sci. Eng. 32, 3 (1990) 163.
[2] P. Pereira, R. Csencsitz, H. Heinemann and G.A. Somorjai, J. Cat. 123 (1990) 463–476.
[3] W. Fan-Cheng, Z.L. Zhang, L.T. Au and K.R. Tsai, Pacifichem 89, Preprints of 3B Symposium on Methane activation, Conversion, and Utilization, Paper 26 (Dec. 17–20, 1989) p. 2–4.
[4] T. Fang and C.T. Yeh, J. Cat. 69 (1981) 227.
[5] D.J. Driscoll, M. Wilson, Z.-X. Wang and J.H. Lunsford, J. Am. Chem. Soc. 107 (1985) 58.
[6] C.H. Lin, T. Ito, J.-X. Wang and J.H. Lunsford, J. Am. Chem. Soc. 109 (1987) 4808.
[7] B. Yingli, Z. Kaiji, J. Yutao, T. Chiwen and Y. Ziangguong, Appl. Catal. 39 (1988) 185.
[8] J.S. Lee and S.T. Oyama, Cat. Rev. -Sci. Eng. 30 (1988) 249.
[9] K.S. Kim, W.E. Baitinger, J.W. Amy and N. Winograd, J. Elec. Spec. Rel. Phen. 5 (1974) 350.