Conversion of methane to ethylene

B.K. Miremadi, K. Colbow, and S. Roy Morrison

Abstract: A lithium aluminate – MgO catalyst has been found to convert methane to ethylene with a high selectivity. The rate of conversion increased when a MoO_3 co-catalyst was used to remove the poisoning products. It is shown that for optimum conversion and selectivity to ethylene, the oxygen pressure should be at an intermediate value, high enough to provide active sites but low enough to avoid ethylene oxidation. Thus the oxygen should be "bled-in" along the catalyst bed. In demonstration of these concepts we have shown a 28.6% CH_4 conversion with 63.2% ethylene selectivity and 9.8% ethane, producing a C_2 yield of about 21.4%.

Key words: methane oxidation, methane conversion, ethylene production, oxidation catalyst, aluminate catalyst.

Résumé : On a trouvé qu'un catalyseur d'aluminate de lithium – MgO permet de transformer le méthane en éthylène avec une grande sélectivité. La vitesse de conversion augmente lorsqu'on utilise un cocatalyseur de MoO_3, pour éliminer les produits provoquant un empoisonnement. On a démontré que, pour obtenir une conversion et une sélectivité optimales en éthylène, on doit utiliser une pression d'oxygène intermédiaire, suffisamment élevée pour fournir des sites actifs, mais suffisamment basse pour éviter l'oxydation de l'éthylène. On doit donc laisser l'oxygène s'écouler le long du lit du catalyseur. Une conversion à 28,6% du méthane, avec une sélectivité à 63,2% d'éthylène et 9,8% d'éthane correspondant à un rendement en produits en C_2 de 21,4%, permet de démontrer l'applicabilité de ces concepts.

Mots clés : oxydation du méthane, conversion du méthane, production d'éthylène, catalyseur d'oxydation, catalyseur d'aluminate.

[Traduit par la rédaction]

1. Introduction

There has been increasing interest in the possible use of oxidative coupling to convert methane to higher hydrocarbons, preferably ethylene. The concept is based on the fact that an oxidative reaction

[1] $2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$

is exothermic and has been found to occur on many basic oxide catalysts (1–4). The interest in such a reaction is of course that methane is a relatively low-cost gas compared to ethylene, which is more valuable as a petrochemical or as a raw material for oligomerization to higher hydrocarbons.

Part of the problem has been that high C_2H_4 selectivity is usually accompanied by low CH_4 conversion (5). It has been found that the catalyst must be basic (6–8), that the reaction can proceed at temperatures between 700 and 850°C, and that one can best obtain a high selectivity if the CH_4 conversion rate is slow (6). It has been shown (9–12) that the rate-limiting step is the removal of one hydrogen from the methane, producing CH_3, which has been observed in the gas phase. The gas input can be alternated between air and methane (1, 6), but the reaction goes well with a mixture of the gases, and there seems no advantage in switching back and forth between gases. It has been concluded that the dehydrogenation to produce CH_3 occurs on the catalyst, but the remainder of the reaction occurs in the gas phase (2, 13, 14). The most promising catalysts have been based on manganese oxide, samarium oxide, and bismuth oxide (15), with lead oxide (16) or alkali additives as promoters (6, 13, 14).

We observed originally that a lithium aluminate catalyst we were studying for the Fischer–Tropsch reaction at 300–400°C produced a distribution of hydrocarbons in which the ethylene content was relatively high. We found the same kinetic preference to ethylene at the high temperatures for the methane coupling reaction. This was surprising because alumina has been considered a poor support because of its acidity (2, 6, 7), but presumably the high lithium content suppresses this acidity. Studies were initiated to further improve the catalyst. The catalyst was based on an MoS_2–Fe–Al_2O_3 material, featuring alumina platelets (17) obtained by reacting Li at room temperature, or LiOH at high temperature, with porous alumina. We found this lithium aluminate catalyst caused the preference for ethylene. Because of the higher cost of the platelets, we chose to study the catalyst prepared from LiOH.

2. Experimental

The porous alumina was Alcan AA-101 alumina, an activated porous Chi-alumina of 240 m^2/g in area; MoO_3 (98.5%) and LiOH (99%) were from BDH, and $MgCl_2{\cdot}6H_2O$ (98.5%) from Anachem. A model ISI-DS130 scanning electron microscope (SEM) with EG&G ORTEC energy-dispersive X-ray attach-

---

Received June 11, 1996[1].

B.K. Miremadi,[2] K. Colbow, and S. Roy Morrison. Energy Research Institute, Simon Fraser University, Burnaby, BC V5A 1S6, Canada.

[1] Revision received February 20, 1997.

[2] Author to whom correspondence may be addressed. Telephone: (604) 291-4807. Fax: (604) 291-3592. E-mail: miremadi@sfu.ca

Table 1. A comparison of optimized selectivities, conversion, and C_2 yield at 785°C. Total air flow ≈ 140 mL/min. Methane flow ≈ 27.2 mL/min. O_2/CH_4 ≈ 1.

		Reactor		
		Single bed r_1	Double bed in series $r_1 + r_2$	Double bed in series with MoO_3 in addition to 20 mL/min of air injected between r_1 and r_2
% O_2 used		4.13	7.96	8.44
% CH_4 converted		13.33	16.51	28.62
Product[a]	C_2H_4	53.2	51.4	63.6
	C_2H_6	11.4	10.6	9.8
	C_2H_2	1.3	0.9	1.4
	C_3	2.1	1.4	3.4
	CO_2	27.6	34.2	17.3
	CO	0.4	0.6	0.9
	C_4	<0.5	<0.5	<0.5
C-balance[b] %		96.5	99.6	96.9
% H_2 at exit		1.1	1.4	—
C_2 yield[c]		8.8	10.5	21.4

[a] Percent of converted CH_4 appearing as species indicated.
[b] Percent of converted CH_4 appearing as CO_x and C_n (carbon balance).
[c] Percent of CH_4 flow converted to C_2.

ment (EDX) was used to analyze the elemental compositions of the sample. For the analysis of elemental Li, laser ablation was employed.

The lithium aluminate was prepared by slurrying LiOH and the porous alumina with the Li and Al in the approximate atomic ratio 1/7. The slurry was dried, other additives (such as Mg and particularly powdered MoO_3) were mixed in if desired, and the powder was calcined for more than 5 h at 880°C. In most of the work to be reported, we have included $MgCl_2$ in the slurry at a Mg atomic ratio of 15–20%, calcining the alumina with the additives at 880°C for 10 h. This high-temperature treatment ensured that no trace of Cl^- ions remained in the catalyst. Calcination of the catalysts, for example, at 650°C resulted in poor catalytic activity and residual Cl^- ions of less than 0.4 atomic percent as measured by the Kα Auger line. The catalyst composition was in the approximate atomic ratio of Li:Al:Mg = 1:7:2. The as-received alumina had originally a BET area of 237.6 m^2/g. After the heat treatment the surface area was reduced to 156.8 m^2/g. Addition of Li and Mg produced a further reduction in area to 56.3 m^2/g.

The reactor was a single-pass quartz reactor, generally held at an optimum operating temperature of 785°C (±0.7%). The heating system used was limited to a maximum temperature of 825°C. The temperature was measured with a thermocouple placed in a narrow quartz tube inserted into the catalyst bed. At about 800°C most CH_4 was oxidized to CO_2, with poor selectivity for other products. About 0.1 g of catalyst was dispersed as a powder in quartz wool, held between quartz wool plugs, with the catalyst bed about 0.2 cm in length and 0.8 cm^2 in area. For some of our investigations two such identical catalyst beds were mounted in series 50 cm apart with the option of introducing more gas to the mixture before the second bed. Only one reactor was used except where indicated. The air–methane mixture was not preheated before entering the reactor except where so indicated, although the length of the heating zone was about 6 cm, compared to a length of 0.2 cm for the catalyst bed.

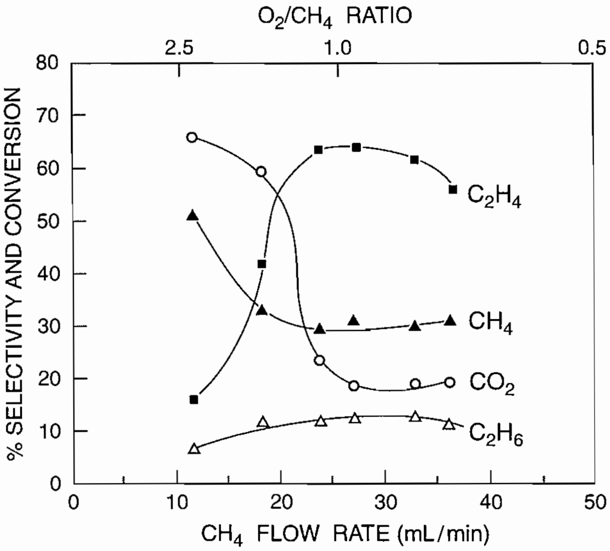
At a pressure of 1 atmosphere (101.3 kPa) the gas mixtures used were air and methane. When the methane flow was reduced, He gas flow was added to keep the total flow rate constant. A Varian gas chromatograph (model 6000), featuring a thermal conductivity and a flame ionization (1) detector, using a 13 X molecular sieve in series with a Porapak-N column was used to sample the gas mixture. The gas flow (air, methane, and helium) was monitored with mass flow meters calibrated against a bubble flow meter installed at the exit of the reactor. Good carbon balance was obtained, as will be noted later in discussion of Table 1. Nitrogen lost in mass balance, $(1 - N_{out}/N_{in})$, was obtained to within 2×10^{-2}. The calibrating gas used to convert the GC data to percent products was from Lil Squirt Ideal Gas Products provided by Varian Corp. It contained a mixture of all possible gases used and produced in our experiments.

3. Results

3.1 Lithium aluminate

Table 1 shows a comparison of selectivities and CH_4 conversion. In this experiment we had two identical quartz reactors r_1 and r_2 in series 50 cm apart. As far as was possible the reactors were held at the same temperature. From the results for a single reactor there was ample partial pressure of methane and air reaching the second reactor. However, we observed that the second reactor did not contribute appreciably to the ethylene production, except for an increase in CH_4 conversion (16.5%), which in turn increased the CO_2 production (34.2%). As will be discussed in the next section, a substantial increase in the conversion was observed by addition of 100 mg MoO_3 co-cat-

Fig. 1. Percent of products as a function of optimized CH_4 flow rate for catalyst and promoter (MoO_3) at 785°C in a double bed reactor with an air flow of 120 mL/min and an injected 20 mL/min of air at the input of the second reactor. At peak conversion methane flow is 27.2 mL/min and $O_2/CH_4 \approx 1$.



alyst powder mixed with the aluminate catalyst in both reactors. MoO_3 oxidizes hydrogen produced in the first reactor (r_1) that was poisoning the second reactor (r_2), thus leading to a further conversion of methane and higher selectivity for ethylene. With addition of MoO3 promoter, at an optimized methane flow rate of 27.2 mL/min and 20 mL/min air injection at the input of the second reactor, the conversion was 28.6%, selectivity was 63.6%, and CO_2 produced reduced to 17.3%. Without addition of MoO_3, the air injection at the input of the second reactor resulted in an increase in both CO_2 and H_2O products.

Figure 1 shows the percent of the products (ethylene and ethane selectivities, methane conversion, and CO_2 produced) of a MoO_3 promoted catalyst against the methane flow rate at a constant air flow of 120 mL/min and with an extra 20 mL/min of air bled-in at the input of the second reactor. The selectivity and conversion peak at a methane flow of 27.2 mL/min, where the oxygen/methane ratio is about 1 and CO_2 produced is a minimum. With high oxygen to methane ratio, conversion is high but most of methane is converted to CO_2. There is evidence of a peak in C_2H_4 conversion at intermediate oxygen-to-methane ratio and low conversion of methane with low oxygen-to-methane ratio.

4. Discussion

4.1 Lithium aluminate catalyst

It was observed that for good conversion of CH_4 and good selectivity to C_2H_4 a high oxygen partial pressure is required, much higher than the stoichiometric ratio (0.5) for

$$[2] \quad 2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$$

This is consistent with the currently accepted model with adsorbed O^- as active sites (12); presumably a significant oxygen pressure is required to maintain a high state density. With ample reactive gases still present in the gas stream, no (or negligible) reaction occurred in the second reactor. This observation suggests strongly that the second reactor is poisoned by the products formed in the first reactor, mainly the hydrogen produced. Possible poisons, such as ethylene, carbon dioxide, water, and hydrogen, are all produced during the reaction. These were tested under our "standard" conditions. Addition of C_2H_4 to the input had no effect on the reaction; the ethylene in the output was simply increased by the extra amount added in the input. H_2O added to the input actually increased the yield and selectivity slightly. Added CO_2 at about 5 mL/min also showed no effect. Hydrogen was awkward to introduce in large quantities because of potential explosion, but a small addition of 5 mL/min Forming gas (5% H_2, 95% N_2) was found to lower the selectivity by 10–15%. Since the hydrogen flow from the Forming gas (0.25 mL/min) was lower than hydrogen produced in the reactors, we concluded H_2 was poisoning the active sites and (or) inducing the back reaction:

$$[3] \quad 2H_2 + C_2H_4 \rightarrow 2CH_4$$

With the consideration that such a back reaction is rather unlikely, our suggested model is based on poisoning the active sites.

4.2 MoO_3 and lithium aluminate – Mg as co-catalysts

A search was made for catalysts to remove the H_2, viz. catalysts that would catalyze the oxidation of 5% H_2 in He but not 5% C_2H_4 in He under our normal reaction conditions at 785°C. Of eight oxides tested (Fe_2O_3, Cr_2O_3, Mn_2O, ZnO, SnO_2, TiO_2, ZrO_2, MoO_3), MoO_3 and ZrO_2 were found to be most effective. With 100 mg commercial MoO_3 powder, 95% of the hydrogen but only 18% of the ethylene was oxidized in one pass through the reactor in a ratio of O_2 to reducing agent of 1:6. For this test the lithium aluminate catalyst was not present.

The activity of MoO_3 alone was also tested as a catalyst under our experimental conditions, which indicated a poor selectivity for ethylene production. In comparison to MgO aluminate catalysts, MoO_3 is a poor oxidation catalyst (18, 19), but together with aluminate catalyst (without additional air injection at the input of reactor r_2) it resulted in a 13% increase in selectivity, while the increase with optimized air injection was close to 23%. There is a good possibility that high-temperature calcination of MoO_3 used in this experiment has converted the oxide to some other phases that have become a part of the catalyst itself. Without addition of MoO_3, the air injection at the input of the second reactor resulted in an increase in both CO_2 and H_2O products. A similar test with ZrO_2 showed an overall increase of only 8%. Thus, both MoO_3 and air injection are equally contributing factors in improving ethylene production.

If hydrogen is the poison, the presence of an oxidation catalyst that selectively removes H_2 should (*a*) increase the conversion, either if the back reaction in eq. [3] occurs, or if hydrogen blocks active sites, and (*b*) permit continuing conversion if, as with the second reactor described above, the H_2

produced at the input to the catalyst bed poisons the rest of the catalyst bed and the second reactor.

4.3 Air injection

The conclusion from the above results is that addition of MoO_3 leads to lower hydrogen concentration and higher methane conversion. For such high conversion of methane it appears one must prevent the back reaction of eq. [1] and (or) the blocking of active sites of hydrogen. It also suggests that one must keep the oxygen pressure up, both to provide active sites and to oxidize the hydrogen. However, if the oxygen pressure is too high, there will be a greater tendency to oxidize the ethylene and the selectivity will drop, in addition to an increase in CO_2 product. This effect was also noticed when 20 mL/min air injection was replaced with 10 mL/min pure oxygen to avoid a substantial increase in the total flow. All this leads to the conclusion that oxygen should be admitted in a controlled manner along the catalyst bed, maintaining the oxygen partial pressure at the optimum value as it is consumed, in agreement with the suggestion by Smith and Galuszka (20). To permit somewhat better adjustment of the oxygen partial pressure in the experiments of Fig. 1, we introduced air not only at the input with CH_4, but also between the two reactors r_1 and r_2.

5. Conclusions

We have presented observations regarding the methane oxidative coupling reaction and a possible explanation of the process for the catalyst used. The observations are that lithium aluminate is an excellent catalyst for the reaction, providing a high yield of ethylene and a high conversion per pass of methane. An oxidation catalyst chosen to oxidize hydrogen but not ethylene under the reaction conditions improves the conversion rate substantially. Introducing oxygen along the length of the catalyst bed to replace that used in the reaction leads to a high conversion of methane with a high selectivity to ethylene.

The model suggested for ethylene generation differs from the standard model where the $CH_3\cdot$radical first dimerizes to C_2H_6 and subsequently the ethane oxidizes to form C_2H_4 + H_2O. A dominant experimental feature suggesting a different role for our catalyst is the low concentration of C_2H_6 as shown in Table 1 and Fig. 1. The poisoning of active sites by hydrogen is the novel result of the analysis. Because the conversion of methane is so strongly limited, it is clear that sites for it must be poisoned, as is observed clearly where the added reactor in series does not affect the product yield, suggesting the sites are poisoned by a product generated in the first reactor.

Considering the confusion in the general behavior of the oxidative methane coupling, it is possible that unnoticed hydrogen poisoned other catalysts as well as ours. The strong effect of MoO_3, which is a comparatively poor catalyst for oxidation of methane (18, 19) as discussed in Sect. 4.2, could be difficult to explain by another model.

It may be possible, by carefully controlled oxygen admission, to further increase CH_4 conversion and the corresponding C_2 products.

Acknowledgments

The authors with to thank T. Cowan and R. Singh for their technical assistance.

References

1. G.E. Keller and M.M. Bhasin. J. Catal. **73**, 9 (1982).
2. J.A. Sofranko, J.J. Leonard, and C. Jones. Catalyst (Philadelphia), **103**, 302 (1987).
3. M.M. Bhasin. *In* Studies in surface science and catalysis. Elsevier, Amsterdam. 1988. pp. 40–65.
4. K. Otsuka, K. Jinno, and A. Morikawa. J. Catal. **100**, 353 (1988).
5. J.S. Lee and S.T. Oyama. Catal. Rev.-Sci. Eng. **30**, 249 (1988).
6. C. Jones, J.J. Leonard, and J.A. Sofranko. J. Catal. **103**, 311 (1987).
7. W. Bytyn and M. Baerns. Appl. Catal. **28**, 199 (1986).
8. K. Asami, S. Hashimoto, S. Shikada, T. Jujimoto and K. Jujimoto. Chem. Lett. 1233 (1986).
9. K.T. Amorebieta and A.J. Colussi. J. Phys. Chem. **92**, 4576 (1988).
10. O.V. Buevskaya, A.I. Suleimanov, S.M. Aliev, and V.D. Sokolovskii. React. Kinet. Catal. Lett. **331**, 223 (1987).
11. N.W. Cant, C.A. Lukey, P.F. Nelson, and R.J. Tyler. Chem. Commun. 766 (1988).
12. K. Otsuka and K. Jinno. Inorg. Chem. Acta, **121**, 237 (1986).
13. C.H. Lin, T. Ito, J.X. Wang, and J.H. Lunsford. J. Am. Chem. Soc. **109**, 4808 (1987).
14. T. Ito, J.X. Wang, C.H. Lin, and J.H. Lunsford. J. Am. Chem. Soc. **107**, 5062 (1985).
15. I.T. Ali-Emesh and Y.J. Amenomiya. J. Phys. Chem. **90**, 4785 (1986).
16. S.K. Agarwal, R.A. Migone, and G. Marcelin. J. Catal. **103**, 302 (1987).
17. B.K. Miremadi and S.R. Morrison. Mater. Res. Bull **25**, 1139 (1990).
18. T.A. Garibyan and L.Ya. Margolis. Cat. Rev.-Sci. Eng. **31**, 355 (1989).
19. J.A. Sofranko, J.J. Leonard, and C.A. Jones. J. Catal. **103**, 302 (1987).
20. K.J. Smith and J.Z. Galuszka. U.S. patent no. 5 132 482 (1992).