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A review of C-1 conversion chemistry

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Abstract

Recent progress is reported on C-1 conversion chemistry with emphasis on the direct formation of methanol, hydrocarbon liquids and CO_2 reforming. Aspects of the thermal diffusion column (TDC) reactor are described.

1. Introduction

During the past 20 years the valorization of natural gas has become a highly developed and mature research field. Many reviews have appeared [1–10] and the subject has branched out into various directions.

Natural gas production, which until recently was rising rapidly (4% per year), has now dropped to an apparent steady slower rate of 1.8% per year. The amount of vented or flared gas (see Fig. 1) is still a considerable fraction and this review is addressed to the possible utilization of this wasted gas.

The review is divided into two parts; (A) those processes which can achieve a valuable liquid end product in one reaction step, and (B) those processes in which the final liquid product requires at least two separate reaction steps. Some often neglected or ignored reactions are presented for further possible consideration.

2. Part A: One step reaction processes

Methanol is an attractive valuable liquid which is normally produced from natural gas in two steps. Its annual production and demand is shown in Fig. 2.

The one step partial oxidation of natural gas to methanol and formaldehyde has been studied for many years. However, only in the last recent 15 years has a reasonable understanding of the system been achieved. Several reviews of the reaction have appeared [1,2,11–14]. Though some catalytic systems have been reported [15–17] or patented [18,19] the ''best'' results are achieved in a homogeneous non-catalytic system at high pressures. Gesser and Hunter [14] reported achieving a methanol selectivity of 78% and a conversion of 7% at 4% O_2, 65 atm, 409°C, and a residence time, τ, of 5 min. Higher methanol selectivity of 83% and methane conversions of 12% at 50 atm, 5% air, 330°C and a residence time of 4 min was obtained by Feng et al. [20]. The following additional conditions contributed to the ''better'' results: (1) upward flow, (2) preheater, (3) reaction exit quenched to 250°C, and (4) complete consumption of O_2. They also showed that at a total pressure of 10 atm, the addition of 30 atm of CO_2 increased the selectivity of methanol from 40% to 70%. This inert gas effect was attributed to third body effects. Gesser and Hunter have shown [21] that ethane and dimethyl ether are produced in the partial oxidation of methane when all the oxygen has been consumed implying that

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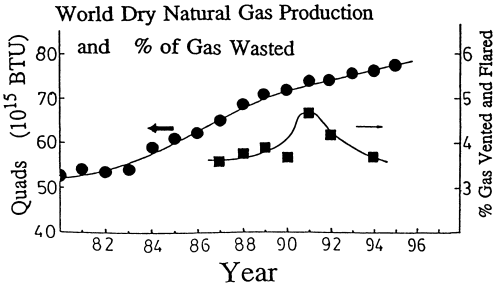

Fig. 1. The total world production of dry natural gas (●), at various years and the percentage of gas vented and flared (■).

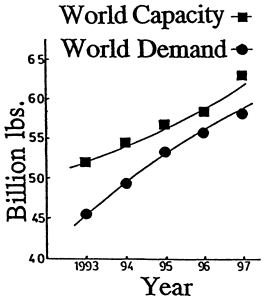

Fig. 2. The world total capacity for methanol production and the world demand.

the recombination of free radicals such as CH_3 and CH_3O occurs. It is also believed that the recombination reaction

$$CH_3 + OH + M \rightarrow CH_3OH + M \quad (1)$$

also becomes important at high pressures though this reaction is not included in modeling or sensitivity studies [22–24].

Similarly the falloff in methanol formation with increase in pressure which has been observed in several studies [25–27] has not been accounted for in modeling studies [22–24]. The proposed "cage" effect [14] which has been well characterized in other systems [28] can open new channels for the destruction of methanol and its precursors such as CH_3O and CH_3OOH.

This is illustrated by the following reactions:

$$CH_3O \rightleftharpoons CH_2O + H \dashrightarrow CHO + H_2 \quad (2)$$

$$CH_3OOH \rightleftharpoons CH_3O + OH \dashrightarrow CH_2O + H_2O \quad (3)$$

$$CH_3O + CH_4 \rightleftharpoons CH_3OH$$
$$+CH_3 \dashrightarrow CH_2OH + CH_4 \quad (4)$$

$$CH_3OO + CH_4 \rightleftharpoons CH_3OOH$$
$$+CH_3 \dashrightarrow CH_2OOH + CH_4 \quad (5)$$

where ----► refers to reactions which can occur in the cage. The detection of ethanol at 100 atm is consistent with the occurrence of reaction (4).

One of the main problems concerning the homogeneous reaction is the long residence times required. Packing the reactor with various metal beads resulted in a slight reduction in selectivity (74–67%) and a decrease in residence times from 50 to 30 s [29]. Assuming a close packing of the reactor beads can, at best, reduce τ by a factor of 4, which may not be sufficient to make a significant improvement. Catalysts [30–32] could show promise in this regard where perhaps lower temperatures, pressures, and higher oxygen levels could be maintained and still be outside the explosion region. The direct conversion of methane to methanol has been initiated by laser [33] as well as by a heated filament [34]. An evaluation has been conducted on the effect of various surfaces on the reactions involved in the partial oxidation of CH_4 to CH_3OH [35]. Gold appears to be the metal of choice for methanol formation.

The oxidation of methane to methanol has also been studied in supercritical water [36,37]. The yields are however low (less than 1%) with CH_4 conversion up to 6%. Though the results are interesting, the system has little practical value except for its application in the destruction of toxic substances.

A more promising non-thermal approach to methanol formation is the use of the silent discharge tube [38–40] at atmospheric pressure or microwave, R.F., or plasma discharge [41,42] at reduced pressures. At 25% O_2 in CH_4 high conversions and significant yields of oxygenates were obtained (30% of the liquids) from a pulsed barrier discharge reactor [40]. The discharge through pure methane leads to acetylene [41,42] and C_2 with minimal quantities of higher hydrocarbons.

An interesting, and as yet unconfirmed, reaction patented in 1941 by Leprestre [43] concerns the direct conversion of natural gas with steam at up to 1000 atm and 540–600°C over an iron oxide catalyst. It was claimed that the product is a gasoline/oil. The addition of CO is intended to consume the excess hydrogen

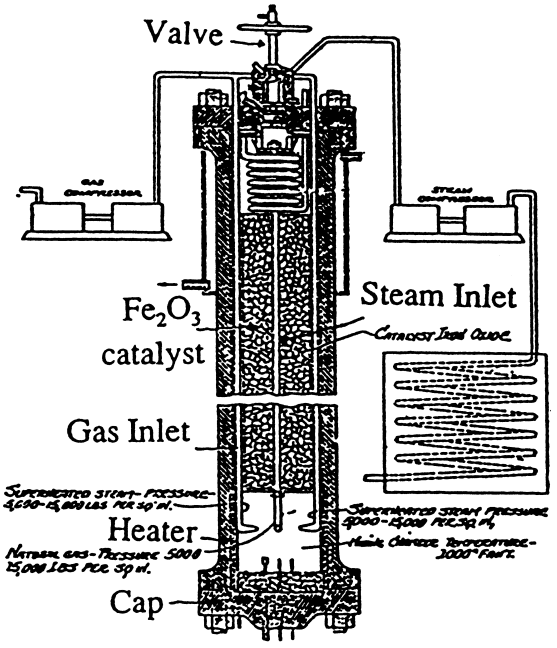

Fig. 3. Diagram of the Leprestre reactor.

forming a high octane rated fuel. A diagram of the apparatus is shown in Fig. 3.

The aromatization of methane has been effected by the oxidation of CH_4 over HZSM-5 zeolite catalyst [44]. The reaction has been studied in detail [45] and the initial formation of methanol and its subsequent aromatization was not excluded as a possible mechanism. This type of conversion was reported by Gesser and Hunter [46] who reacted natural gas homogeneously with oxygen in a reactor (upper part) where some HZSM-5 catalyst was heated downstream (lower part). The products formed (water and aromatics) were similar to those obtained in the Mobil process [47]. The efficiency of the process was not determined and its optimization would be difficult because of the different pressure requirements for the two processes.

The dehydroaromatization of methane under oxygen free conditions has been reported [48,49] with enhanced activity when molybdenum is added to the HZSM-5 catalyst.

The thermodynamics of CH_4 conversion is shown in Fig. 4. Coke formation by reaction (1) in (Fig. 4) is most favorable, and though considered as a catalyst in early studies [50], it can become one of the steps whereby supported noble metal catalysts can be inactivated.

Table 1
Standard thermodynamic quantities for TDC reactions

		ΔH^0 (kJ)	$\Delta H^0/H_2$ (kJ)
1	$6CH_4 \rightarrow C_6H_6 + 9H_2$	530	59
2	$7CH_4 \rightarrow C_6H_5CH_3 + 10H_2$	572	57
3	$8CH_4 \rightarrow C_6H_4(CH_3)_2 + 11H_2$	614	56
4	$10CH_4 \rightarrow C_{10}H_8 + 16H_2$	823	51

Fuel cell: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ (l), $\Delta G^0 = -237$ (kJ).

A novel method of using a Clausius–Dickel thermal diffusion column (TDC) as a reactor was first reported by Hirota in 1941 [51]. A GC/MS analysis of the oil products [52] showed the presence of unsaturated compounds up to C_{18} as well as polynuclear aromatics. This was confirmed [53] with benzene being shown to be the major product. The thermodynamics of the reaction is given in Table 1 and indicates that the H_2 produced can, in principle, be used in a fuel cell to generate the current required to maintain the reaction. Unfortunately, the efficiency of the reaction is only about 2%. However, it was shown by Yamaguchi and co-workers [54] that a reflector or a stainless steel reactor tube can improve the efficiency of the TDC reactor system up to 6% which is still far removed from a required 50% efficiency for the TDC and for the fuel cell. An interesting report [55] has shown that the inclined TDC can improve isotopic separation efficiency. This could also improve the efficiency of the TDC as a reactor since it relies on non-equilibrium thermodynamic characteristics due to the temperature gradient and the molar mass differences between the products. The separation of the hydrogen by means of a thin palladium membrane for the wall could further improve the thermal efficiency [56].

3. Part B: Multi-step reactions

A reaction which has been studied in great detail is the partial oxidation of methane to C_2 hydrocarbons, or the oxidative coupling of methane (OCM) reaction. The final desired product, ethylene, is invariably accompanied by ethane

$$CH_4 + O_2 \rightarrow C_2H_4 + C_2H_6 + H_2O \quad (6)$$

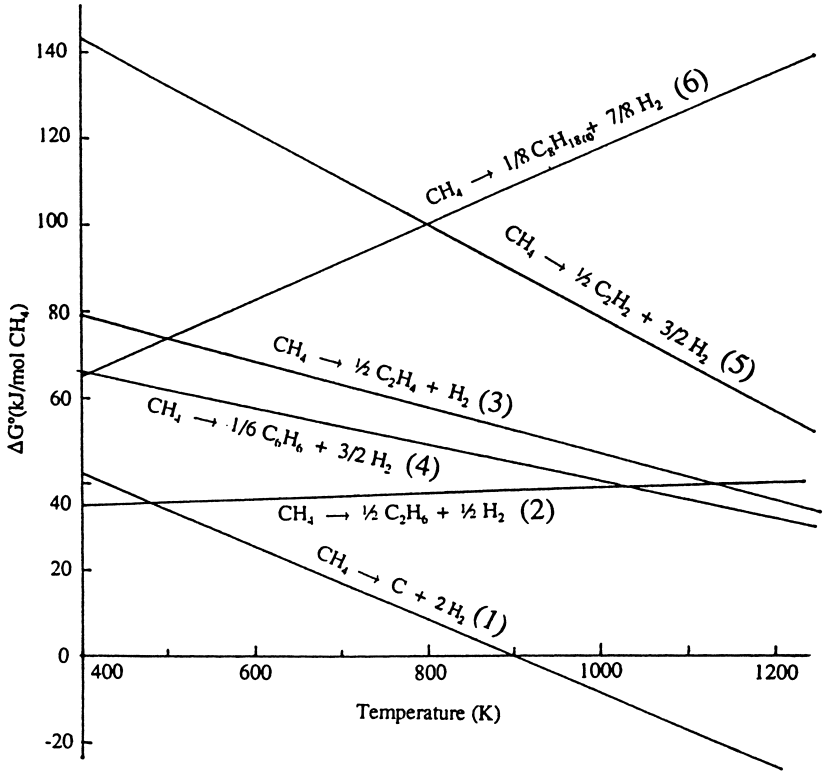

Fig. 4. Thermodynamics of some CH_4 conversion reactions.

Much progress has been made since the pioneering paper by Keller and Bhasin [57] in 1982. The ultimate goal is the oligomerization of the ethylene to long chain hydrocarbons, viz, gasoline and diesel fuel. The OCM reaction is usually conducted at 600–700°C over a variety of mixed oxide catalysts. Recent reviews on this subject [5–7,10,58] have essentially indicated the limits of the process. The presence of surplus ethane from natural gas presents an alternate route to ethylene.

The higher reactivity of O_2 with C_2H_4 as compared to CH_4 has been avoided by the simulated counter current moving bed chromatographic reactor [59]. This system is now being evaluated for the direct methane to methanol reaction [60]. Preliminary results under non-optimum conditions have shown that at 430°C, 70 atm, CH_4/O_2=25, τ=1 min, 10–20% reactants in He gave 68% selectivity of CH_3OH and 8% conversion of CH_4.

In a cyclic process using a silver electrocatalyst, Vayenas and co-workers [61] have achieved 85% selectivity to ethylene with conversions of CH_4 up to 97%. Scale-up of such a cyclic process normally presents problems. High yields of aromatics and higher hydrocarbons were reported by Choudhary et al. [62] for the reaction of CH_4 with lower alkenes and alkanes over HGaAl MFI zeolite at the lower temperatures of 400–600°C.

The dehydrogenative coupling of CH_4 on a TDC reactor was first reported by Yamaguchi and Saito [63] who showed that the downward flow of CH_4 produces C_2 and H_2. Typical results [85] as a function of linear velocity and temperature in a tubular reactor (2 cm i.d.) with a 0.5 mm diameter tungsten wire are shown in Figs. 5 and 6. An increase in conversion is achieved when part of the H_2 is removed through a porous segment of the reactor tube [64] or when argon is added to the feed [65]. The low energy efficiency of 2% is increased to over 6% when the glass reactor is replaced by a stainless steel reactor [54,66]. Other heaters such as Nichrome wire, silicon carbide or carbon rod, and reactor shapes [67] have

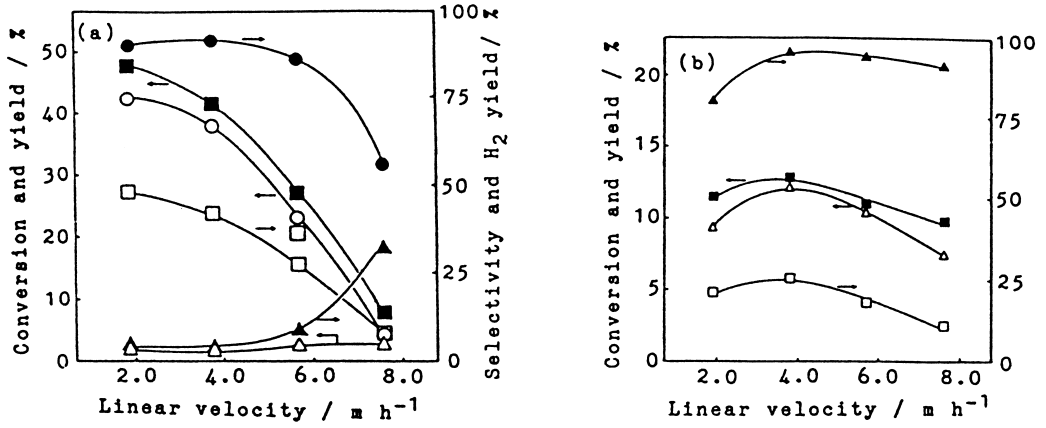

Fig. 5. Dependence of yields and selectivities on the flow rate in a TDC reactor [85] (A): upward flow at 1200°C, and (B) downward flow at 1300°C. (■) Methane conversion; (●) oil selectivity; (○) oil yield; (▲) C_2 selectivity; (△) C_2 yield; (□) H_2 yield.

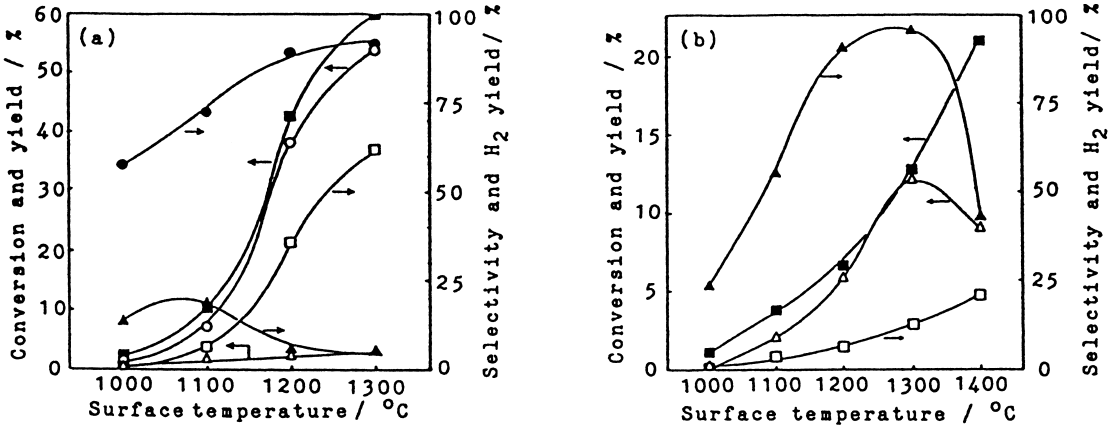

Fig. 6. Dependence of yields and selectivities on the surface wire temperature in a TDC reactor [85] (A): upward flow of 3.8 m h^{-1}, and (B) downward flow of 3.8 m h^{-1}. (■) Methane conversion; (●) oil selectivity; (○) oil yield; (▲) C_2 selectivity; (△) C_2 yield; (□) H_2 yield.

been examined. Recent reviews of this work [68,69] have included economic evaluations of the processes.

Synthesis gas, usually produced by the reforming of CH_4 or coal with steam, is the energy intensive step in producing useful liquid products:

$$CH_4 + H_2O_{(g)} \rightarrow CO + 3H_2, \quad \Delta H^0 = 206.1\,\text{kJ} \tag{7}$$

In contrast, the recently studied partial oxidation reaction

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2, \quad \Delta H = -35.7\,\text{kJ} \tag{8}$$

can achieve high conversion and high yield. However, the formation of carbon deposits tend to poison the noble metal catalysts [70]. Coke formation was reduced to $\frac{1}{3}$–$\frac{1}{6}$ by the addition of cobalt to a nickel catalyst [71].

The reaction of CH_4 with CuO in a fluidized bed to form syngas was reported in 1949 [72]. High conversion (about 95%) and selectivity (of 90%) was achieved.

The use of metal coated ceramic monoliths [73] at high temperatures (up to 1150°C) and short contact time (5 ms) and a single pass with air has made the production of syngas a viable commercial process [74].

The CO_2 reforming of CH_4 to syngas over supported noble metal catalysts has been patented [75]. The catalyst for the reaction

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \quad \Delta H^0 = 247\,\text{kJ} \qquad (9)$$

is poisoned by carbon deposition due to reaction (1) in Fig. 4 as well as by

$$2CO \rightarrow C + CO_2,$$
$$\Delta G^0 = -120\,\text{kJ},\ \Delta S^0 = -23.5\,\text{J K}^{-1} \qquad (10)$$

Supported nickel catalysts have also been shown to be effective [76,86].

We have shown that reaction (9) can be conducted in a TDC reactor with tungsten wire at over 1000°C in an upward flow [77]. The detailed comparison of the thermodynamics and experimental results shows the TDC reactor to be a non-equilibrium system because of the H_2/CO separation due to density differences [78,86].

We have also shown that about 30% conversion for CH_4 can be obtained for reaction (9) on a single pass through a silent discharge reactor [78,79]. A second pass doubled the conversion. Higher wattages could increase the conversion further.

4. Evaluation

Several reports have been published on the economics of natural gas conversion and comparative processes [80–82]. The most recent analysis [83] has concluded that based on work at Amoco [84] the direct formation of methanol would be the most promising process if better yields could be obtained. Such yields have already been realized [14,20].

Nevertheless a packed reactor in the partial oxidation of CH_4 to CH_3OH could reduce the danger of explosions and improve thermal conduction, an important aspect of exothermic reactions.

References

[1] E.Y. Garcia, D.G. Löffler, Lat. Am. J. Chem. Eng. Appl. Chem. 14 (1984) 267.
[2] H.D. Gesser, N.R. Hunter, C.B. Prakash, Chem. Rev. 85 (1985) 235.
[3] M.Y. Sinev, V.N. Korshak, O.V. Krycov, Russ. Chem. Rev. 58 (1989) 38.
[4] M.J. Brown, N.D. Parkyns, Catal. Today 8 (1991) 305.
[5] O.V. Krylov, Catal. Today 18 (1993) 209.
[6] I. Amenomiya, V.I. Birss, M. Goledzzinowski, J. Galuszka, A.R. Sanger, Catal. Rev. Sci. Eng. 32 (1990) 162.
[7] J.C. Mackie, Catal. Rev. Sci. Eng. 33 (1991) 169.
[8] E.E. Wolf (Ed.), Methane Conversion by Oxidative Process, Fundamental and Engineering Aspects, Van Nostrand Reinhold, New York, 1992.
[9] M.M. Bhasin, D.W. Slocum (Eds.), Methane and Alkane Conversion Chemistry, Plenum Press, New York, 1996.
[10] E.N. Voskresenskaya, V.G. Roguleva, A.G. Anshits, Catal. Rev.-Sci. Eng. 37 (1995) 101.
[11] N.R. Foster, Appl. Catal. 19 (1985) 1.
[12] V.S. Arutyunov, V.Y. Basevich, V.I. Vedeneev, Uspekhi Khimii 65 (1996) 211.
[13] V.S. Arutyunov, V.Y. Basevich, V.I. Vedeneev, Y.V. Parfenov, O.V. Sokolov, Russian Chem. Bull. 45 (1996) 45.
[14] H.D. Gesser, N.R. Hunter, The direct conversion of methane to methanol (DMTM), in: E.E. Wolf (Ed.), Methane Conversion by Oxidative Process, Fundamental and Engineering Aspects, Van Nostrand Reinhold, New York, 1992, p. 403.
[15] Y. Wang, K. Otsuka, J. Catal. 155 (1995) 256.
[16] L.-B. Han, S. Tsubota, T. Kobayashi, M. Haruta, J. Chem. Soc., Chem. Commun. 93 (1995).
[17] J.W. Chun, R.G. Anthony, Ind. Eng. Chem. Res. 32 (1993) 259.
[18] V.A. Durante, US Patent No. 5 132 472, 21 July 1992.
[19] V.A. Durante et al., US Patent No. 5 414 157, 9 May 1995.
[20] W.Y. Feng, F.C. Knopf, K.M. Dooley, Energy and Fuels 8 (1994) 815.
[21] P.S. Yarlagadda, L.A. Morton, N.R. Hunter, H.D. Gesser, Ind. Eng. Chem. Res. 27 (1988) 252.
[22] R. Lodeng, O.A. Lindvag, P. Soraker, P.T. Roterud, O.T. Onsager, Ind. Eng. Chem. Res. 34 (1995) 1044.
[23] V.S. Arutyrinov, V.Y. Basevich, V.I. Vedeneer, Russ. Chem. Rev. 65 (1996) 197.
[24] D.J. Thomas, R. Willi, A. Baiker, Ind. Eng. Chem. Res. 31 (1992) 2272.
[25] E.H. Boomer, V. Thomas, Can. J. Res. B 15 (1937) 414.
[26] N.R. Hunter, H.D. Gesser, L.A. Morton, C.B. Prakash, Proceedings of the VI International Symposium on Alcohol Fuel Technology, Ottawa, 21–25 May 1984.
[27] V.S. Arutyunov, V.Y. Basevich, V.I. Vedeneev, Ind. Eng. Chem. Res. 34 (1995) 4238.
[28] J.C. Dutoit, J.M. Zellweger, H. Van den Bergh, J. Chem. Phys. 78 (1983) 1825.
[29] L.A. Morton, H.D. Gesser, N.R. Hunter, Fuel Sci. Technol. Int. 9 (1991) 913.
[30] N.R. Hunter, H.D. Gesser, L.A. Morton, P.S. Yarlagadda, Appl. Catal. 57 (1990) 45.
[31] R.A. Pereana et al., Science 259 (1993) 340.
[32] L.B. Han, S. Tsubota, T. Kobayashi, M. Haruta, J. Chem. Soc., Chem. Commun. 93 (1995).
[33] S.L. Boughcum et al., SPIE Proceedings of the 669 Laser Applications in Chemistry, 1986.

[34] Y. Sekine, K. Fujimote, Low temperature direct conversion of methane to methanol with filament wire initiation, International Chemical Congress of Pacific Basin Society, 17–22 December 1995.
[35] P.P. Olivera, E.M. Patrito, H. Sellers, Surf. Sci. 327 (1995) 330.
[36] P.E. Savage, R. Li, J.T. Santini Jr., J. Supercrit. Fluids 7 (1994) 135.
[37] J.H. Lee, N.R. Foster, J. Supercrit. Fluids 9 (1996) 99.
[38] S. Shepelev, H.D. Gesser, N.R. Hunter, Plasma Chem. Plasma Process. 13 (1993) 479.
[39] R. Bhatnagar, R.G. Mallinson, in: M.M. Bhasin, D.W. Slocum (Eds.), Methane and Alkane Conversion Chemistry, Plenum Press, New York, 1996, p. 249.
[40] S.P. Bugaev, A.V. Kozyrev, V.A. Kuvshinov, N.S. Sochugov, P.A. Khryapov, Plasmochemical conversion of lowest alkanes with stimulated condensation of incomplete oxidation products, Plasma Chem. Plasma Process., in press.
[41] M.S. Ioffe, S.D. Pollington, J.K.S. Wan, J. Catal. 151 (1995) 349.
[42] K. Onoe et al., Fuel 76 (1997) 281.
[43] R. Leprestre, US Patent No. 2 253 511, 7 October 1941.
[44] S.S. Shepelev, K.G. Ione, React. Kinet. Catal. Lett. 23 (1983) 323.
[45] S. Han et al., J. Catal. 136 (1992) 578.
[46] P.S. Yarlagadda, L.A. Morton, N.R. Hunter, H.D. Gesser, Fuel Sci. Technol. Int. 5 (1987) 169.
[47] C.D. Chang, Catal. Rev.-Sci. Eng. 26 (1984) 323.
[48] Y. Xu et al., Appl. Catal. A 136 (1996) 7.
[49] A. Szoeke, F. Solymosi, Appl. Catal. A 142 (1996) 361.
[50] D.S. Chamberlin, E.B. Bloon, Ind. Eng. Chem. 21 (1929) 945.
[51] K. Hirota, Bull. Chem. Soc. Jpn. 16 (1941) 274.
[52] H.D. Gesser, L.A. Morton, Catal. Lett. 11 (1991) 357.
[53] A.N. Shigapov, H.D. Gesser, Catal. Today 24 (1995) 289.
[54] S. Suzuki, K. Onoe, T. Yamaguchi, Report No. 44, Chiba Institute of Technology, 1997.
[55] H.M. Yeh, Can. J. Chem. Eng. 72 (1994) 815.
[56] E. Kikuchi, Cattech (March) (1997) 67.
[57] G.E. Keller, M.M. Bhasin, J. Catal. 73 (1982) 9.
[58] G.J. Hutchings, M.S. Scurrell, J.R. Woodhouse, Chem. Soc. Rev. 18 (1989) 251.
[59] A.L. Tonkovich, R.W. Carr, R. Aris, Science 262 (1993) 221.
[60] M. Bjorklund, Private communication.
[61] Y. Jiang, I.V. Yentekakis, C.G. Vayenas, Science 264 (1994) 1563.
[62] V.R. Choudhary, A.K. Kinage, T.V. Choudhary, Science 275 (1997) 1286.
[63] T. Yamaguchi, C. Saito, Bull. Chem. Soc. Jpn. 61 (1988) 2649.
[64] T. Yamaguchi, C. Xianghao, G. Zhiming, Sekiyu Gakkaishi 35 (1992) 292.
[65] S. Suzuki, Y. Tsuchida, S. Ohara, K. Onoe, T. Yamaguchi, Nippon Kagahu Kaishi 513 (1996).
[66] T. Yamaguchi, S. Suzuki, Proceedings of RUJAS'93, First Russia Japan Joint Symposium on Petroleum, Natural Gas and Petrochemistry, Yuzhno-Sakholinsk, 1993, pp.105–108.
[67] S. Iwaki, T. Yamaguchi, Chem. Express 6 (1991) 293.
[68] S. Suzuki, K. Onoe, T. Yamaguchi, Report No. 43, Chiba Institute of Technology, 1996.
[69] S. Suzuki, K. Onoe, T. Yamaguchi, Report No. 42, Chiba Institute of Technology, 1995.
[70] A.T. Ashcroft et al., Nature 344 (1990) 319.
[71] V.R. Choudhary, V.H. Rane, A.M. Rajput, Appl. Catal. A, in press.
[72] W.K. Lewis, E.R. Gilliland, W.A. Reid, Ind. Eng. Chem. 41 (1949) 1227.
[73] D.A. Hickman, L.D. Schmidt, Science 259 (1992) 343.
[74] S.S. Bharadwaj, L.D. Schmidt, Fuel Process. Technol. 42 (1995) 109.
[75] B.L. Gustafson, J.V. Walden, US Patent No. 5 068 057, 26 November 1991.
[76] Z.L. Zhang, X.E. Verykios, Catal. Today 21 (1994) 589.
[77] H.D. Gesser, N.R. Hunter, A.N. Shigapov, V. Januate, Energy and Fuel 8 (1994) 1123.
[78] D. Prabawono, M.Sc. Thesis, University of Indonesia, Jakarta, 1995.
[79] H.D. Gesser, N.R. Hunter, D. Prabawono, Plasma Chem. Plasma Process., in press.
[80] J.W.M.H. Geerts, J.H.T.J. Hoebink, K. vander Wiele, Catal. Today 6 (1990) 613.
[81] J.M. Fox III, Chem. Eng. Prog. (April) (1990) 42.
[82] J.M. Fox III, Catal. Rev. Sci. Eng. 35 (1993) 169.
[83] M.J. Gradassi, N.W. Green, Fuel Process. Technol. 42 (1995) 65.
[84] M.J. Foral, R.D. Kaplan, Final Report, Direct conversion of light hydrocarbon gases to liquid fuel No. 33 US–DOE Contract No. DE-AC22-89PC90866, Amoco Oil Co., Naperville, IL.
[85] T. Yamaguchi, A. Kadata, C. Saito, Chem. Lett. Chem. Soc. Jpn. (1988) 681.
[86] N.R. Hunter, D. Prabawono, H.D. Gesser, Catal. Today 42 (1998) 653.