

Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century

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Abstract

The very large reserves of methane, which often are found in remote regions, could serve as a feedstock for the production of chemicals and as a source of energy well into the 21st century. Although methane currently is being used in such important applications as the heating of homes and the generation of hydrogen for ammonia synthesis, its potential for the production of ethylene or liquid hydrocarbon fuels has not been fully realized. A number of strategies are being explored at levels that range from fundamental science to engineering technology. These include: (a) stream and carbon dioxide reforming or partial oxidation of methane to form carbon monoxide and hydrogen, followed by Fischer–Tropsch chemistry, (b) the direct oxidation of methane to methanol and formaldehyde, (c) oxidative coupling of methane to ethylene, and (d) direct conversion to aromatics and hydrogen in the absence of oxygen. Each alternative has its own set of limitations; however, economical separation is common to all with the most important issues being the separation of oxygen from air and the separation of hydrogen or hydrocarbons from dilute product streams. Extensive utilization of methane for the production of fuels and chemicals appears to be near, but current economic uncertainties limit the amount of research activity and the implementation of emerging technologies. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic conversion; Methane; Fischer–Tropsch synthesis

1. Introduction

Methane, which is the principal component of most natural gas reserves is currently being used for home and industrial heating as well as for the generation of electrical power. In many respects, methane is an ideal fuel for these purposes because of its availability in most populated centers, its ease of purification to remove sulfur compounds and the fact that among the hydrocarbons, it has the largest heat of combustion relative to the amount of CO₂ formed. On the other hand, methane is a greatly underutilized resource for chemicals and liquid fuels. The known reserves are enormous and rival those of liquid petroleum, as shown in

Fig. 1 [1]. Moreover, the reserves are increasing more rapidly than those of liquid petroleum, and it is anticipated that this trend will extend well into the 21st century.

The geographical distribution of methane (natural gas) is given in Fig. 2 [1]. Much of the methane is found in regions that are far removed from industrial complexes and often it is produced off shore. Pipelines may not be available for transporting this remote gas to potential markets and liquefaction for shipping by ocean-going vessels is expensive. Approximately 11% of this gas is reinjected, and unfortunately, another 4% is flared or vented [2], which is a waste of a hydrocarbon resource. Both methane itself and carbon dioxide derived from methane are greenhouse gases.

Strategies for the use of methane depend on its price and location, the demand for products, construc-

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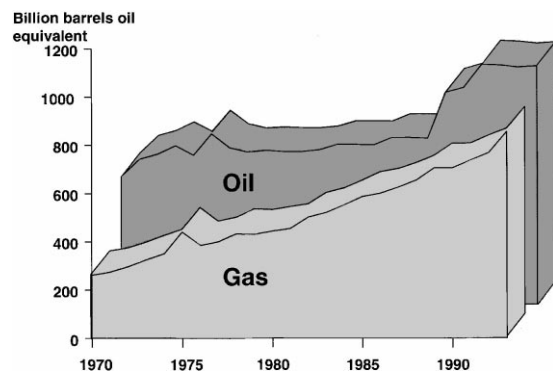


Fig. 1. Proven world oil and gas reserves [1].

tion costs, the economic and political stability of a region, and many other factors. Methane (natural gas) frequently is produced along with liquid petroleum and some contracts require that the producer takes the gas along with the oil. Because of this arrangement, the methane may actually have “negative value”, i.e., it is a liability to the producer. In such cases, the methane is essentially free for the taking, but, of course, the capital and operating costs necessary to utilize this methane may be prohibitively high. Consideration should also be given to the very large amount of methane that is present in certain reservoirs. Extensive

utilization of this methane would require its conversion either to a transportation fuel or to a limited number of high volume chemicals such as methanol or ethylene.

Three examples will illustrate the challenges, and in some cases the solutions that have been adopted. (1) On the North Slope of Alaska, the natural gas reserves exceed the liquid petroleum reserves. There is a pipeline for the transportation of liquids to a port in the southern part of Alaska, but the gas is reinjected into the reservoir. As the oil becomes depleted, an increasing amount of gas will be recycled per barrel of oil produced. (2) In Western Australia, a large liquefaction facility has been constructed to utilize the methane. The liquefied gas is shipped to Japan. (3) In Malaysia, Shell has built a Fischer–Tropsch (F–T) plant to produce a variety of fuels, as well as waxes. This plant has been shut down for a number of months because of an explosion, but it is scheduled to be in operation sometime during 2000 [3]. In a free market economy, the profitability of these facilities will depend on the selling price of the product and the cost of alternative technologies, both of which may fluctuate significantly over a relatively short period. At the time of this writing, crude oil is selling for ca. \$25 per barrel, which makes the production of high grade fuels from methane more attractive.

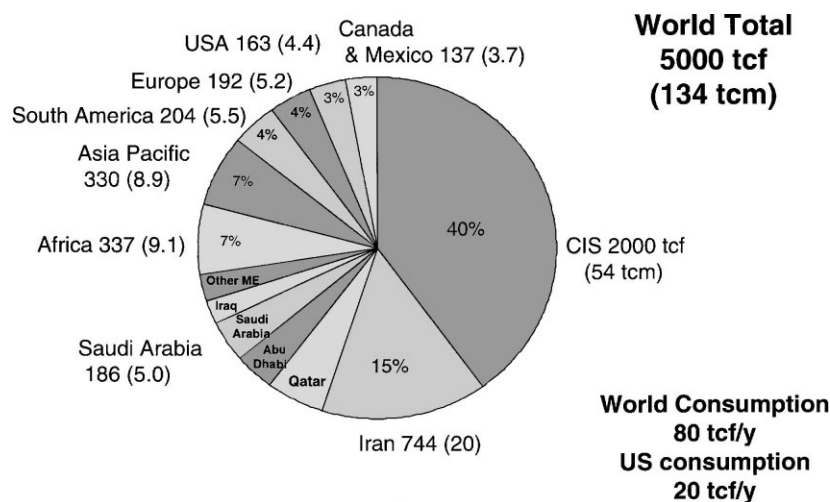


Fig. 2. Geographical distribution of proven natural gas reserves [1].

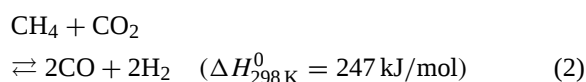
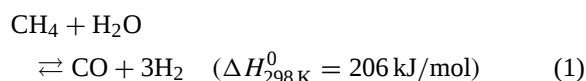
2. Indirect methods for methane utilization

2.1. Synthesis gas production

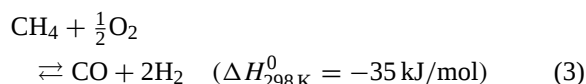
All indirect methods for the utilization of methane require carbon monoxide and hydrogen synthesis gas. Here, we are not considering the use of only H₂ as needed for fuel cells and ammonia synthesis. The production of CO and H₂ in the appropriate ratios is achieved through three principal processes or combinations thereof:

1. Steam reforming,
2. Carbon dioxide (or dry) reforming, and
3. Partial oxidation.

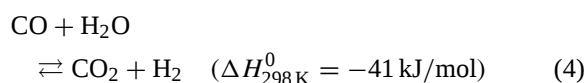
Each of these processes has advantages and disadvantages, although the trend has been to partial oxidation. Methane reforming reactions [2]



are highly endothermic and require extensive heat transfer equipment. By contrast, partial oxidation



is slightly exothermic, but requires oxygen or air. At a mechanistic level, over most catalysts, partial oxidation involves total combustion of part of the CH₄, followed by reforming of the remaining CH₄ with CO₂ and H₂O [4,5]. These two steps (total combustion and reforming) may be formally separated in a process known as autothermal reforming. As a complement to these three methods for synthesis gas formation, the water gas shift reaction



may be used to adjust the H₂/CO ratio. Again, at a fundamental level, the water gas shift reaction occurs simultaneously with reactions (1) and (3).

Steam reforming is a mature technology and is widely used to generate syngas for the production

of methanol. The process, however, requires elevated temperatures and high pressures of steam in order to favor H₂ and CO at equilibrium. Moreover, the nickel catalyst is subject to coke formation. Catalytic partial oxidation, with the use of nearly pure O₂, circumvents the coking problem, but requires the separation of oxygen from air and involves the hazards of handling large quantities of undiluted oxygen, as well as O₂/CH₄ mixtures. The explosion at the Shell F-T plant occurred in the oxygen separation facility [3]. Heat management issues are common to both processes; with steam reforming, large quantities of heat must be supplied, whereas, with catalytic partial oxidation, a large amount of heat is released during the front end of the catalyst bed as the CH₄ undergoes total oxidation. There are reports that over certain catalysts such as Ru/TiO₂ the partial oxidation reaction occurs directly, i.e., without the initial formation of CO₂ and H₂O [6]. From the standpoint of heat removal, these catalysts would provide a definite advantage for the partial oxidation of methane, assuming that coke formation did not become a problem.

2.2. Synthesis of methanol: a route to dimethyl ether (DME), gasoline and ethylene

A major advance in methanol synthesis occurred in 1966 when ICI introduced a lower pressure process that was based on a more active copper/zinc oxide/alumina catalyst. The mechanism for the reaction and the active phase of the catalyst have been reviewed by Chinchin et al. [7]. Surprisingly, methanol is actually formed from CO₂ that is produced during the water gas shift reaction. Under normal operating conditions, CO₂ is added to the feed gas. Although there appear to be limited opportunities for further development of the copper-based catalyst, other more robust and sulfur tolerant catalysts may utilize supported palladium as the active component. Palladium on several basic oxide supports, including La₂O₃ [8] and lithium-promoted palladium on SiO₂ [9,10], is an active and selective catalyst for methanol synthesis that could find application in slurry reactors.

With respect to methane utilization, the major advance has been in the scale of methanol synthesis plants which are consistent with the production of fuels (see below). According to Vora et al. [11], “a single-train methanol plant with a capacity in the range

of 5000–10,000 metric tons per day is possible”. Large scale methanol synthesis plants have recently been constructed to meet the demand for methyl *t*-butyl ether (MTBE), which is a fuel additive, but recent environmental concerns make the continued use of MTBE unlikely. As a consequence, there is a large oversupply of methanol from which alternative fuels could be produced.

One such conceivable process is the conversion of methanol to DME, which has been touted by Amoco as “a fuel for the 21st century” [12]. DME has several properties that make it attractive as a fuel for diesel engines, including no sulfur and very low particulate emission. In addition, DME is one of the best fuels with respect to greenhouse gas emissions. The low boiling point (-25°C) is both an advantage with respect to combustion and a disadvantage with respect to storage. As with any alternative transportation fuel, the vehicles and the distribution system would have to be modified.

The only commercial methanol-to-fuel process was carried out for a period of several years in New Zealand as a response to the energy crises in the early 1970s. Mobil developed a methanol-to-gasoline (MTG) process that utilized an H-ZSM-5 zeolite catalyst [13]. The MTG process yields high octane gasoline that is rich in aromatics, which would make it unsuitable for use under current regulations in many countries. The initial steps of the reaction mechanism are similar to those described below for SAPO-34, but the stronger acidity of the H-ZSM-5 catalyst promotes extensive aromatization. Because deactivation is relatively slow, it is possible to use a fixed bed-reactor with an excess of catalyst. The facility at Motonui, New Zealand, performed quite well; however, the cost of the product eventually became noncompetitive with that of gasoline produced at conventional refineries, and the facility was eventually modified to produce only methanol. Nevertheless, the technical success demonstrates that methane can be converted to fuels and chemicals (aromatics) via methanol on a commercial scale.

Two other potential large scale chemical products from methane, via methanol, are ethylene and propylene. Methanol may be converted to these chemicals over a moderately acidic SAPO-34 molecular sieve, and a methanol-to-olefin (MTO) process has been developed by UOP [14]. Ethylene, which is the pri-

mary product, oligomerizes and cracks to propylene. The catalyst deactivates rapidly and regeneration is required. This is achieved in a fluidized bed-reactor which is similar to those employed in conventional catalytic cracking. Utilization of this technology probably will occur in integrated petrochemical complexes (e.g., in Saudi Arabia) rather than in remote locations.

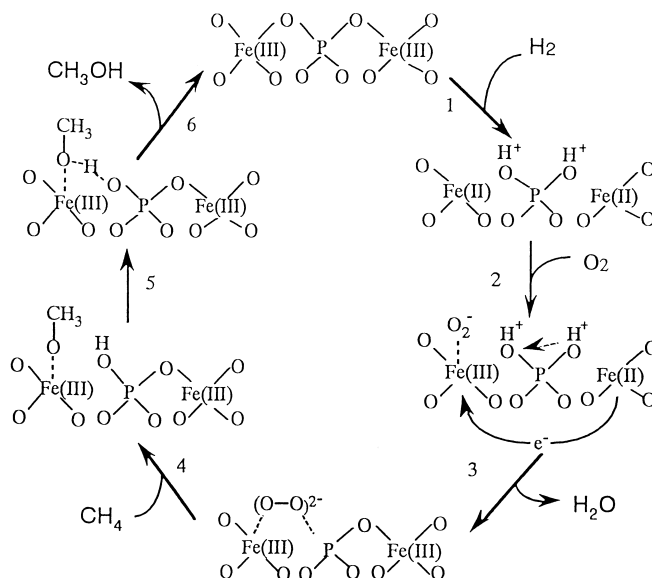
2.3. *F–T synthesis*

F–T synthesis for the production of hydrocarbons and higher alcohols has a rich history that dates back to the early 1920s. A brief overview of the process has recently been given by Schulz [15]. Originally, coal was considered as the primary source of carbon for the synthesis gas, but currently, increased attention is being given to methane for the reasons described above. The catalysts employed are based on cobalt or iron with the addition of ruthenium to improve the yield of waxes. Through catalyst improvement and process modification, alpha values of 0.9 have been achieved, which means that the products will contain a significant fraction of hydrocarbons having a high carbon number ($>\text{C}_{20}$).

The Shell middle distillate synthesis (SMDS) process, which operated on a commercial scale of 12,000 bbl per day for over 4 years, yielded both high quality fuels and chemicals such as waxes and solvents [16]. In addition to the F–T component, the plant includes a hydrocracker that forms the middle distillate products. As a refinery, the facility is quite small, but as a chemical plant, it is very large. This venture by Shell illustrates both the pitfalls and the opportunities that await us in the 21st century as methane becomes more widely employed for the production of fuels and chemicals. It should also be noted that Sasol in South Africa is a leader in F–T technologies, although their commercial process is based on coal gasification [17]. Nevertheless, the slurry reactors that they have developed could also be used with natural gas as the feedstock.

3. Direct methods for methane utilization

Direct methods for the conversion of methane to the desired products circumvent the expensive syngas step; however, in two of the examples described here,

Scheme 1. Proposed catalytic cycle for the conversion of CH_4 to CH_3OH [18].

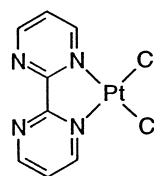
oxygen separation from air is still required. Conceptually, direct methods should have a distinct economic advantage over indirect methods, but to date, no direct processes have progressed to a commercial stage. Product yields are generally small while operating in a single-pass mode, which makes separations difficult and costly.

3.1. Synthesis of methanol and formaldehyde

Perhaps, the greatest potential for a major advance in methane conversion technology is in the discovery of a direct route for the formation of the oxygenates methanol and formaldehyde. The methane mono-oxygenase (MMO) enzyme, which is able to convert methane to methanol at ambient conditions, is an enticing example of what could be achieved. The enzyme activates O_2 at iron centers with the aid of a reductant known as NADH. Using this example, Otsuka et al. [18] have shown that FePO_4 is an interesting model catalyst for the production of CH_3OH and HCHO when H_2 is added to the CH_4 and O_2 reagents. Presumably H_2 reacts with O_2 to form a surface peroxide species, which is responsible for the activation of CH_4 as shown in Scheme 1. Methanol and formaldehyde selectivities of 23 and 45%, re-

spectively, have been achieved, but only at a methane conversion level of about 0.6%. Formaldehyde is commercially produced by the oxidation of methanol over iron molybdate catalysts; therefore, one would expect that it would be formed as a secondary product during the oxidation of methane at elevated temperatures.

Partial success in the conversion of methane to methanol has been achieved by Periana et al. [19], who used a bipyrimidyl platinum (II) complex



in concentrated H_2SO_4 . At 220°C , $\sim 90\%$ of the methane reacted with H_2SO_4 in a catalytic manner to form methyl bisulfate at 81% selectivity. It is expected that the methyl bisulfate could be hydrolyzed to methanol, although this was not demonstrated. A complete cycle would require the regeneration of the concentrated H_2SO_4 .

The high temperature oxidation of CH_4 to HCHO may be carried out over pure SiO_2 and $\text{V}_2\text{O}_5/\text{SiO}_5$. In

the single-pass mode, the HCHO yields do not exceed 3–4%; however, respectable space–time–yields (STY) of about 1200 g/kg cat h at 30% selectivity have been achieved over a 2% V_2O_5/SiO_2 catalyst at 600°C [20]. Parmaliana et al. [21] have used a recycle reactor with continuous removal of HCHO to determine the yields that could be achieved over a precipitated silica catalyst. At 690°C with a recycle ratio of 64, a formaldehyde yield of 24.5% was attained. In this case, the STY was 150 g/kg cat h.

An earlier study using N_2O as an oxidant with MoO_3/SiO_2 as the catalyst indicated that methoxide ions resulted from the reaction of methyl radicals with the metal oxide [22]. These methoxide ions could either react with water to form methanol or they could decompose to form formaldehyde. In a separate study, $CH_3\cdot$ radicals derived from the decomposition of azomethane, $CH_3N=NCH_3$, were allowed to react with MoO_3/SiO_2 , V_2O_5/SiO_2 and V_2O_5 [23,24]. The results of Fig. 3 show the selective conversion of surface methoxide species to CH_3OH at temperatures as low as 200°C and to HCHO at temperatures as low as 350°C. If water is present, CH_3OH is favored over HCHO at the lower temperatures. Clearly, these oxygenates could be produced in high yields by the activation of methane at low temperatures (<300°C). This is indeed a challenging problem because of the strength of the C–H bond in CH_4 (431 kJ/mol), but an iron peroxide species, such as shown in Scheme 1, may be able to activate methane. Following this approach, however, one still has the problem of reducing the Fe(III) to Fe(II), and it is desirable that this be achieved with CH_4 rather than H_2 . Furthermore, the reduction step itself should result in a methoxide ion.

3.2. Oxidative coupling

In the oxidative coupling reaction, CH_4 and O_2 react over a catalyst at elevated temperatures to form C_2H_6 as a primary product and C_2H_4 as a secondary product. Unfortunately, both the CH_4 and the C_2H_4 may be converted to CO_2 , and the single-pass combined yield of C_2H_4 and C_2H_6 (C_2 products) is limited to about 25%. Over the better catalysts, which include SrO/La_2O_3 [25] and $Mn/Na_2WO_4/SiO_2$ [26,27], a C_2 selectivity of about 80% can be achieved at a CH_4 conversion of 20%. About half of the C_2 is C_2H_4

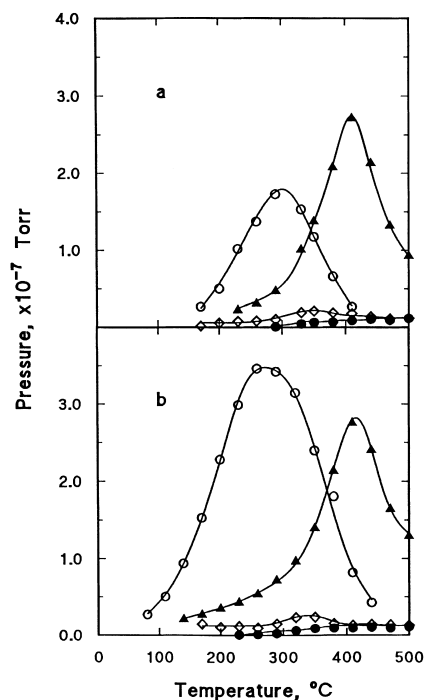


Fig. 3. Temperature-programmed surface reaction results after reaction of 3 mTorr $CH_3\cdot$ radicals with 5.1% V_2O_5/SiO_2 for 30 min at 150°C followed by cooling to 50°C: (a) sample heated in vacuo; (b) sample heated in 7 mTorr H_2O : (○) CH_3OH , (▲) HCHO, (◇) CO, (●) CO_2 [24].

and half is C_2H_6 , although the C_2H_4/C_2H_6 ratio can be enhanced by using a second catalyst. The high C_2 selectivities are almost always achieved under oxygen limiting conditions; thus, the specific activity of the catalyst is not a factor. Because the overall reaction is exothermic, a zone within the catalyst bed may be 150–300°C hotter than the external temperature [28,45]. Heat management, therefore, is a serious engineering problem. This is complicated by the fact that metals normally used for construction of reactors catalyze the total combustion of methane.

The reaction network is interesting from a fundamental perspective because it is an example of a heterogeneous–homogeneous system. Methyl radicals that are formed at the surface of the catalyst enter the gas phase where they couple to form ethane. At atmospheric pressure, this coupling occurs mainly in the void space between catalyst particles, but by two techniques, the methyl radicals have been detected in

the gas phase after they exit the catalyst bed [29,30]. In addition to coupling, the gas phase radicals may enter into chain reactions that result in the formation of CO and subsequently CO₂. Isotopic labeling experiments have demonstrated that at small conversion levels most of the CO₂ is derived from CH₄, but at commercially significant conversion levels, C₂H₄ would be the dominant source of CO₂ [27]. Additional experiments have shown that this occurs mainly via a heterogeneous reaction. One of the challenges in catalyst development is to modify a material so that the secondary reaction of C₂H₄ will be inhibited while the activation of CH₄ will still occur. There is no inherent reason that these two reactions should take place on the same types of sites.

In order to avoid the cost associated with the use of pure O₂ in the feed gas, attempts were made by ARCO to use the catalyst for oxygen storage. A NaMnO₄/MgO catalyst was found to be suitable for this purpose in that separate pulses of air and methane resulted in favorable C₂ selectivities [31]. But the oxygen storage capacity was limited so that a very large mass of catalyst would have to be used to achieve a reasonable amount of C₂ products. The fact that the conversions and selectivities obtained in the sequential pulse mode were comparable to those observed in the cofeed mode substantiates the claim that the nonselective reactions are mainly heterogeneous in nature.

By operating in a recycle mode with continuous removal of ethylene, a considerable improvement in the ethylene yield can be achieved. Vayenas and co-workers [32] demonstrated this concept by using a closed-loop recycle system with continuous removal of C₂₊ olefins. The olefins were adsorbed in a 5 Å molecular sieve at 30°C and subsequently desorbed in an inert gas stream by heating the sieve to 400°C. The resulting ethylene yield was 85%. We developed a recycle system in which olefins were continuously removed as an aqueous silver ion complex via a membrane contactor [33]. The aqueous solution was circulated through a regeneration column, where, upon boiling, it released the olefins (mainly C₂H₄) into the gas phase. Olefin product yields greater than 70% were obtained during continuous operation, but the olefin productivity was approximately 2 ml (STP)/min. The rate of olefin recovery was limited by the transport rate through the membrane.

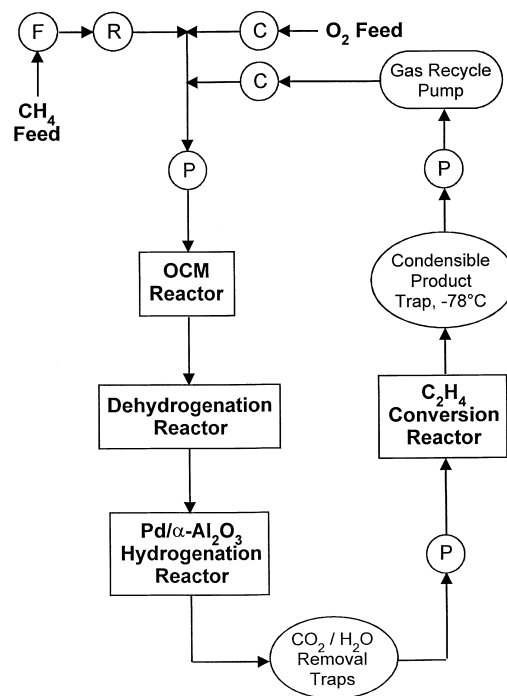


Fig. 4. Schematic diagram of integrated recycle system for conversion of methane to aromatics. C: mass flow controller; F: flowmeter; P: gas sampling port; R: pressure regulator [34].

As a variation of this recycle system, the membrane contactor was replaced by a Ga/H-ZSM-5 zeolite catalyst that operated at 520°C. This zeolite catalyst effectively converted the C₂H₄ from the OCM reactor mainly to benzene and toluene, which were continuously removed by an in-line trap [34]. A scheme of the system is given in Fig. 4. The aromatic product yield as a function of the O₂ flow rate is given in Fig. 5. Again, product (aromatic) yields in excess of 70% could be achieved. To attain these yields, the conversion of the recycled C₂H₆ to C₂H₄ must be highly selective. In this case, the productivity could be increased simply by increasing the amounts of the catalysts, the flow rates and the efficiencies of the traps, thus scale up would be easier with the Ga/H-ZSM-5 catalyst than with the membrane contactor.

3.3. Conversion to aromatics without an oxidant

Many of the processes described about, whether direct or indirect, require the use of oxygen, which has

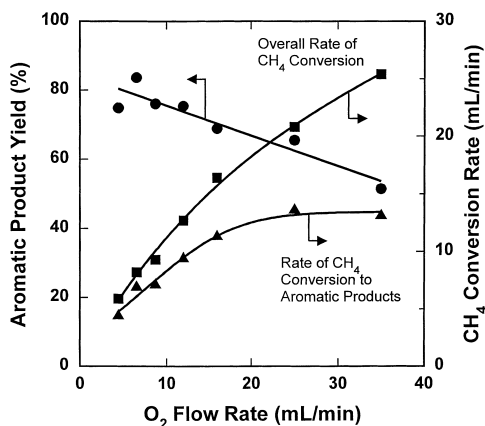


Fig. 5. Effect of O_2 flow rate on CH_4 conversion rates and aromatic product yield at a CH_4 recycle flow rate of 120 ml/min; OCM temperature = $800^\circ C$; dehydrogenator temperature = $800^\circ C$; Pd/Al_2O_3 hydrogenator temperature = $80^\circ C$; C_2H_4 conversion temperature = $520^\circ C$ [34].

a cost that is either equivalent to or greater than the cost of methane. The formation of oxygen-containing products provides a thermodynamic driving force so that the reaction has a negative free energy. But with the kinetically controlled direct oxidation reactions, the formation of the undesirable product CO_2 severely limits the yields that may be achieved. There are, however, a limited number of methane conversion reactions that result in hydrocarbon products but do not require an oxidant. The theoretical yield, of course, is limited by thermodynamic considerations. One such example is the catalytic conversion of methane to benzene, toluene and naphthalene. The equilibrium for a C–H system at 1 atm is shown in Fig. 6. At $700^\circ C$, e.g., the equilibrium conversion of CH_4 would be about 12%, with about half the CH_4 going to benzene and half to naphthalene. The other major product is H_2 , which also has significant value. At $800^\circ C$, the equilibrium conversion would be about 24%.

Several bifunctional catalysts are known to promote this reaction, with the most thoroughly studied being a Mo/H-ZSM-5 zeolite [35–38]. The subject has been reviewed by Xu and Lin [39]. Representative results, reported by Wang et al. [40], are shown in Figs. 7 and 8. One of the objectives of this study was to demonstrate that the active state of molybdenum was Mo_2C , which may be formed by initially exposing the catalyst to CH_4/H_2 mixtures. Several observations can be made

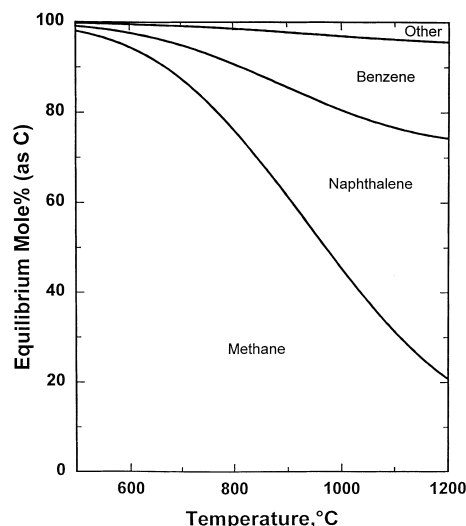


Fig. 6. Effect of temperature on the thermodynamic equilibrium composition of the C–H system (excluding graphite and polycyclic aromatic molecules except naphthalene) at 1 atm pressure [40].

from these results. First, during the time when benzene is being formed, the methane conversion never reaches the equilibrium limit of 12%, although other investigators have reported conversions of about 11%

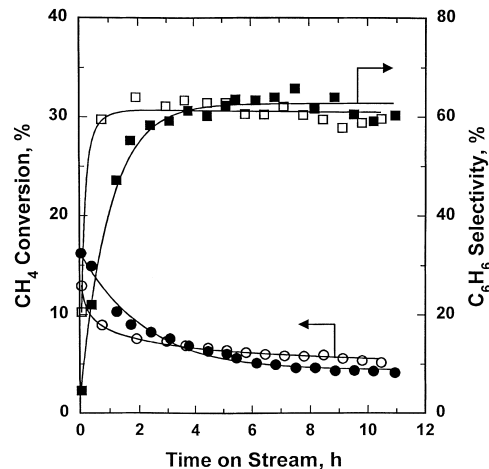


Fig. 7. Methane conversion and benzene selectivity for CH_4 reaction over 2 wt.% Mo/H-ZSM-5 at $700^\circ C$, 1 atm and $GHSV = 800\ h^{-1}$: (●), (■) catalyst pretreated in O_2 at $700^\circ C$; (○), (□) catalyst pretreated in 20% CH_4/H_2 and then in 10% CH_4/H_2 at $700^\circ C$, following treatment in O_2 at $700^\circ C$ for 0.5 h [40].

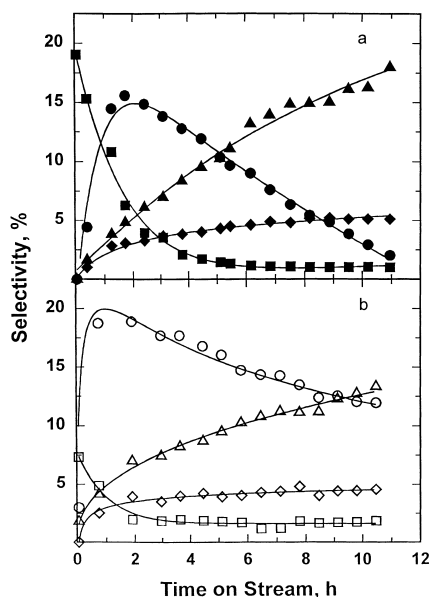


Fig. 8. Selectivity results for CH_4 reaction over 2 wt.% Mo/H-ZSM-5 at 700°C , 1 atm and $\text{GHSV} = 800 \text{ h}^{-1}$: (●), (○) naphthalene; (◆), (◇) $\text{C}_2 + \text{C}_3$; (▲), (△) toluene; (■), (□) CO. (a) Pretreated in O_2 at 700°C for 0.5 h; (b) pretreated in 20% CH_4/H_2 for 12 h and then in 10% CH_4/H_2 for 4 h at 700°C , followed by treatment in O_2 at 700°C for 0.5 h [40].

at 700°C and 18% at 750°C [41]. Second, after an initial rapid decline in activity, the rate of decline after ca. 4 h on stream is slow. Third, a nearly constant benzene selectivity of about 60% is achieved, but the naphthalene selectivity goes through a maximum after 1–2 h on stream. Meanwhile, the toluene selectivity continuously increases. The maximum in the naphthalene selectivity has been attributed to shape selectivity which is more pronounced as the zeolite channels become partially coked. Ichikawa and co-workers [42] have shown that the addition of small amounts of CO or CO_2 to the feed inhibits the deactivation of the catalyst.

Two fundamental issues continue to be discussed in literature; namely, (i) the state and location of the active form of molybdenum, and (ii) the mechanism of the reaction. Most investigators agree that molybdenum carbide or oxycarbide is responsible for the conversion of CH_4 to C_2H_4 and that the C_2H_4 is converted to aromatic products over the acidic sites within the channels of the zeolite. Other metals including W and Fe are effective for promoting this reaction, and

there is evidence that these metals are active as suboxides, rather than as carbides [37]. A W, Zn/H-ZSM-5 catalyst, prepared by Zhang and co-workers [38] via a controlled impregnation technique, is of particular interest because a CH_4 conversion of 23% at 850°C , with high benzene selectivity, has been observed. This conversion is approaching the level that might be commercially attractive for the production of aromatics from methane.

4. Separation technology

Improvements in separation technology are essential for the practical utilization of all of the processes described above. In particular, there is a need for less expensive O_2 to be used in the partial oxidation of methane and the oxidative coupling reaction. Likewise, there is a need for new or improved methods to separate methanol, olefins or aromatics from dilute streams. Such separations would find application not only in CH_4 conversion processes, but also in refinery operations. Removal of H_2 , perhaps by membrane separation [43], would shift the equilibrium in the direct methane-to-aromatics process, and would allow larger conversions to be achieved.

5. Conclusions

A number of strategies are being explored and developed for the conversion of methane to more useful chemicals and fuels. These may be broadly divided into two groups, which are described as indirect and direct. The indirect processes rely upon the formation of synthesis gas (CO and H_2) either by reforming reactions or by partial oxidation. In the direct processes, methane may be converted to methanol, formaldehyde, ethylene or aromatics. The stage of development of the several processes varies greatly, with the indirect ones being more advanced than the direct ones. For example, steam reforming of methane, with subsequent methanol synthesis, is a mature technology, while the indirect conversion of methane to methanol is at the level of fundamental discovery. Each of the alternatives has its own limitations; however, economical separation is common to all, with the most important issues being the separation of oxygen from air and the

separation of hydrogen or hydrocarbons from dilute product streams. Catalyst development has played a crucial role in the advances that have occurred; nevertheless, there remains a need for catalysts that promote higher selectivity to the desired product and have a longer life.

There are many parallels between the challenge of ammonia synthesis at the beginning of the 20th century and the effective utilization of methane at the beginning of the 21st century. A successful ammonia synthesis process depended not only on persistent catalyst development, but also on major advances in process engineering which resulted in high purity reagents and reactors that withstood both elevated temperatures and high pressures [44]. Similarly, successful methane conversion will require catalyst innovations and novel engineering developments. Moreover, there is a need for industrial leadership such as that provided by BASF for the ammonia synthesis process.

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