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Various routes to methane utilization—SAPO-34 catalysis offers the best option[☆]

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ABSTRACT

At the time when demand for energy is rapidly increasing, the reserves of crude oil are rapidly declining. At the same time an increasing number of new natural gas reserves have been discovered, however, most of them are far away from industrial users and population centers. Because of these large reserves in remote locations, gas transport to user locations is more difficult and expensive. It is more advantageous to convert the natural gas to the useful products and transport the end product to users. Technologies for the production of a number of products from natural gas, via synthesis gas, have been well established. However, production of synthesis gas requires a very large investment and is less energy efficient. With recent sustained oil price above $80/barrel for the crude oil, increasing focus is being given to direct conversion of methane as well as to the conversion of methane to petrochemicals. This paper examines various options of methane conversion.

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1. Introduction

Methane, as the key component of natural gas, is an abundant natural resource. The known reserves of 180 trillion cubic meters are nearly equal to that of known crude oil reserves. Despite the dramatic growth of natural gas use for the electric power generation over the last few decades, methane is underutilized as a feedstock for the production of chemicals or liquid fuels. Actual use of natural gas represents only a fraction of the proven reserves.

Indirect conversion of methane via synthesis gas to basic chemicals such as methanol and ammonia has been in commercial use for a long time, as has production of liquefied natural gas (LNG), but these markets are limited. Gas-to-liquids (GTL) technology has been promoted for many years by various companies and technology providers. Specific processing steps among these technologies may vary, but the goal is the same: to convert natural gas into a more transportable liquid fuel. The market for liquid fuels is large. However, due to high capital investment required in synthesis gas generation as well in Fischer–Tropsch process and product upgrading, margins are small. The growth in GTL technology implementation is relatively slow despite recent technological improvements in GTL technology. Thus, producers are seeking alternative economical methods to facilitate the conversion of natural gas into higher value products that could lead to increased utilization of gas reserves.

Several institutions have reported results of direct conversion of methane to various fuel and petrochemical products, but none have progressed to the commercial stage. This presentation gives a review of options for methane conversion. The authors conclude that, considering the difficulty of selective activation of methane to higher hydrocarbons (that is, for maximizing carbon efficiency), indirect conversion of natural gas to liquid fuels or chemicals via synthesis gas remains the best option at the present time.

In this regard, methanol can play an important role. Methanol is one of the simplest organic molecules that can be used as building block for many products. World methanol production has increased from 15.9 million metric tons (MTA) in 1983 to 32 million MTA in 2006. As some of these natural gas reserves are stranded because of their remote locations, conversion to methanol provides an opportunity to get this stranded natural gas to market. There it can be economically converted to ethylene and propylene, two largest volume petrochemical feedstocks, or used as a liquid fuel, either directly or in the form of DME. Silicoaluminophosphate (SAPO-34)-based catalysis is the key enabler for the indirect methane to light olefins conversion route.

2. Natural gas reserves and its uses

In 2006, proven gas reserves were estimated to be at 180×10^{12} (trillion) cubic meters [1]. At an annual production of about 3 trillion cubic meters, the current reserves will last more than 60

[☆] This forms part of the plenary lecture delivered in the symposium.

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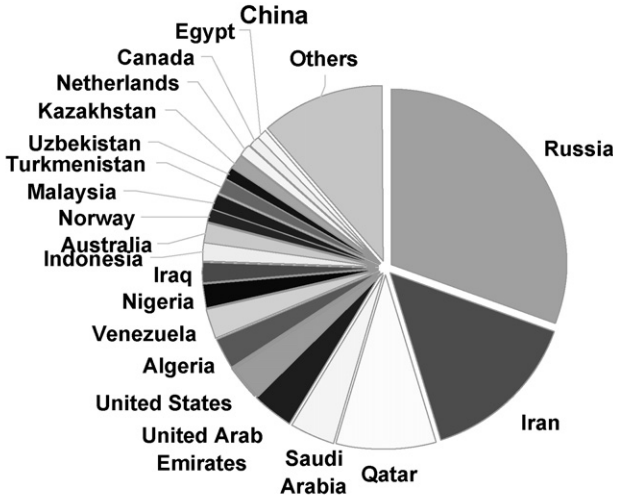


Fig. 1. World natural gas resources.

years. Fig. 1 shows geographic distribution of the gas reserves. The abundance of such gas reserves continues to draw the attention and interest of the international community in how best to use them.

Use of natural gas for electrical power generation, directly or via LNG, and for the production of basic chemicals via synthesis gas, such as ammonia, methanol is well established.

Because some of the gas reserves are far from a major industrial or population center, their direct use as fuel or for the production of electric power is limited. Transportation of the gas between supply and demand centers is a critical factor. Another important factor is the size of the given gas reserve. Because of the large investment required, the LNG or GTL plants are only economical at a very large scale. Hence, to make the project economically feasible, the gas reserve needs to be of sufficient size to supply feed for over an extended period of 25–30 years. Of the 589 gas fields worldwide identified [1], only 86 gas fields are large enough to support mega LNG or GTL plants. Therefore, in addition to GTL and LNG, gas conversion options that producers should consider are to methanol and ammonia, and to petrochemical intermediates or end petrochemical products, such as polyethylene and polypropylene.

3. Natural gas conversion technologies

3.1. Direct conversion

A number of approaches for the direct natural gas conversion to higher hydrocarbons have been studied for more than 50 years [2–6].

- Oxidative coupling
- Oxyhalogenation
- Aromatization
- Selective oxidation to methanol

Of these methods, oxidative coupling has received significant attention. Fig. 2 summarizes a number of different catalyst systems studied by scientists at universities and industrial research centers. The best result to date approaches 30% conversion of methane and about 80% selectivity to C_{2+} hydrocarbon products. If the differential values between the ethane and heavier hydrocarbon products and the natural gas feed are considered, justifying an economical plant is difficult at a per-pass yield of less than 25%.

$$\underset{\text{Methane}}{n\mathrm{CH_4}} + \underset{\text{Oxygen}}{(n/2)\mathrm{O_2}} \rightarrow \underset{\text{Hydrocarbons}}{(-\mathrm{CH_2}-)_n} + \underset{\text{Water}}{n\mathrm{H_2O}}$$

The use of lanthanum-based catalysts for the oxychlorination of methane with HCl and O_2 to methyl chloride has been recently reported [7]. Methyl chloride can be converted to higher hydrocarbons in a separate step with the co-production of HCl which can be recycled to the methane activation step. Direct halogenation followed by a hydrocarbon synthesis step has also been considered [8–12]. It is reported that methyl chloride or bromide are easily converted to olefins or higher hydrocarbon which is analogous to methanol to gasoline (MTG) or methanol to olefins (MTO) [13]. Kaiser in conjunction with their work on methanol to olefins with SAPO catalysts, also disclosed methylhalide as a possible source of the feed in place of methanol [14].

$$\underset{\text{Methane}}{n\mathrm{CH_4}} + \underset{\text{Chlorine}}{n\mathrm{Cl_2}} \rightarrow \underset{\text{Methyl chloride}}{n\mathrm{CH_3Cl}} + \underset{\text{Hydrogen chloride}}{n\mathrm{HCl}}$$

$$\underset{\text{Methyl chloride}}{n\mathrm{CH_3Cl}} \rightarrow \underset{\text{Hydrocarbons}}{(-\mathrm{CH_2}-)_n} + \underset{\text{Hydrogen chloride}}{n\mathrm{HCl}}$$

Methane to aromatics conversion in the range of 6–20% has been reported by various investigators with benzene selectivity of 80–

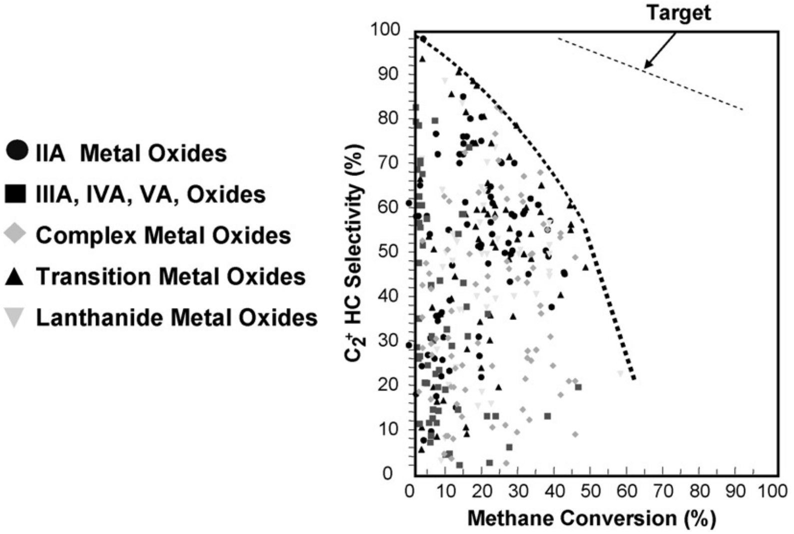


Fig. 2. Direct methane conversion.

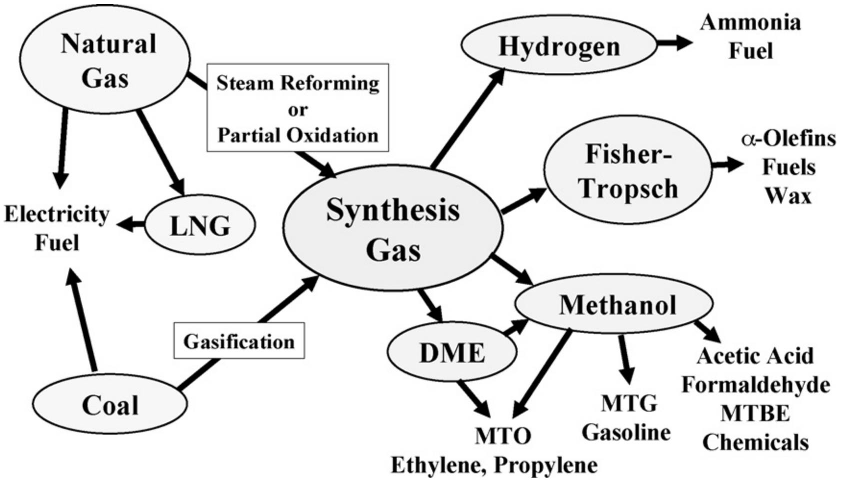


Fig. 3. Synthesis gas: key to indirect methane conversion.

90% at 700–800 °C and 1 atm [15–17]. However, benzene is not an interesting product today.

Several researchers have reported data for liquid phase oxidation in sulfuric acid medium via methyl bisulfate of methane to methanol, as well as gas phase oxidation of methane to methanol [18,19]. Gang et al. reported iodine as a catalyst in sulfuric acid medium for direct oxidation of methane to methanol [20]. Other approaches, such as plasma and photochemical conversion, are also being investigated.

3.2. Indirect conversion

Indirect conversion of methane via synthesis gas shows many promising options. Fig. 3 shows a number of possible uses of natural gas. The technologies for the production of synthesis gas are widely used and well established. Steam reforming to partial oxidation and most recently, autothermal reactor systems have been used commercially. The natural gas conversion options via synthesis gas that are of interest are gas to liquids (GTL), gas to methanol and ammonia, and gas to olefins (GTO). Market volumes of most chemicals are relatively small compared to the natural gas reserves. Therefore, to make a significant impact on the utilization of natural gas reserves, large volume applications, such as transportation fuel, LNG for electricity or a large chemicals market such as ethylene and propylene are needed.

Fig. 4 shows the equivalent value of methane if it were converted to various products using typical conversion efficiencies. The quantity of natural gas equivalent to 1 million British thermal units (MM BTU) corresponds to approximately 21 kg of gas, calculated as pure methane. Based on recent product values for a Middle East location, the $1.00 paid for the natural gas is converted to $12 for low-density polyethylene or polypropylene. By contrast, the value of petroleum products is two to three times less as compared to the value of polyolefins.

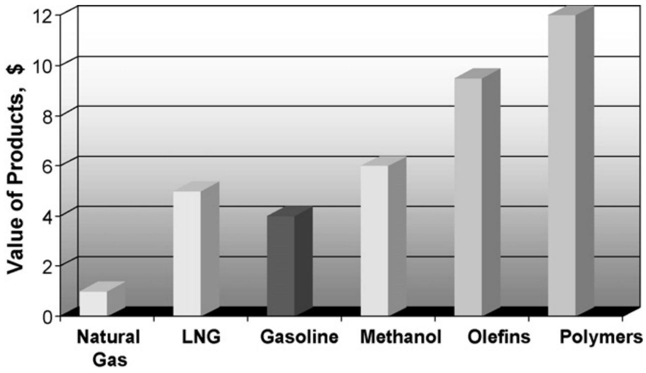


Fig. 4. Value of products produced from 1 MM BTU of natural gas.

3.3. Methanol and ammonia

The conversion of natural gas to methanol and ammonia via synthesis gas is used in many parts of the world, and several commercial processes are available for their production [21–25]. Today, there are more than 50 operating plants ranging in capacity from 100,000 to about 1.7 million metric tons per year (MM MTA) of methanol production. Annual worldwide methanol production of about 30 million metric tons roughly consumes 25 billion cubic meter of natural gas per year. This is a relatively small consumption compared with the available reserves. However, if methanol to olefins technology is used to produce ethylene and propylene, the two largest volume petrochemical raw materials, significantly more methanol can be used.

3.4. Synthesis gas to liquids

During World War II, several small plants were built in Germany to convert coal gas to liquid fuels used a Fischer–Tropsch (F–T) process to support the war efforts. The combined production of these plants was greater than 1 MM MTA.

In 1955, Sasol, in South Africa, commissioned Sasol-I, the world's first large-scale GTL plant and expanded it during the 1980s, with Sasol-II and Sasol-III for a total capacity of around 125,000 barrels per day (BPD) of syncrude production [26]. In 1993, Shell [27] began operating its 12,000 BPD GTL plant in Malaysia to primarily produce wax. More recently, Exxon, Rentech and Syntroleum have announced their versions of an improved F–T process [28–30]. With more than 40 years of commercial experience, Sasol also has made advances in the F-T process and their new 35,000 BPSD plant in Qatar came on stream in early 2007 [31]. The overall chemistry is:

$$\underset{\text{Methane}}{n\mathrm{CH_4}} + \underset{\text{Oxygen}}{(n/2)\mathrm{O_2}} \rightarrow \underset{\text{Syngas}}{n(\mathrm{CO}+2\mathrm{H_2})} \rightarrow \underset{\text{Hydrocarbons}}{(-\mathrm{CH_2}-)n} + \underset{\text{Water}}{n\mathrm{H_2O}}$$

3.5. Methanol to gasoline and methanol to olefins

This indirect, two-step process involves first the production of methanol and then its selective conversion in a second step to ethylene and propylene. The overall chemistry can be written as

$$\underset{\text{Methane}}{nCH_4} + \underset{\text{Oxygen}}{(n/2)O_2} \rightarrow \underset{\text{Methanol}}{n(CH_3OH)} \rightarrow \underset{C_2-C_4\ \text{Olefins}}{n(-CH_2-)_x} + \underset{\text{Water}}{nH_2O}$$

The use of molecular sieves to catalyze the conversion of methanol to hydrocarbons dates back to at least 1977 when Chang and Silvestri at Mobil Oil used zeolites such as ZSM-5 [32]. During the early 1980s, Anthony and Singh were also particularly active in the use of zeolites to convert methanol to olefins [33]. Later, in his 1984 review of the catalytic conversion of methanol to light olefins (MTO), Chang primarily addressed the performance of small and medium pore zeolites [34]. The conversion of methanol over medium and large pore zeolites (such as ZSM-5) normally produces large amounts of aromatics and paraffins Because small pore zeolites adsorb linear hydrocarbons but exclude the larger branched or aromatic hydrocarbons, these bulkier species, if formed internally, cannot diffuse out. Data for the small pore structures erionite (ERI), zeolite T (ERI/offretite [OFF] intergrowth), chabazite (CHA), and ZK-5 (KFI), showed that products consisted predominantly of light olefins (C_2–C_4) at low conversion but significant paraffins at higher conversions.

By far the most extensively studied medium-pore zeolite for methanol conversion reaction is ZSM-5. Because ZSM-5 normally exhibits higher selectivities to aromatics and paraffins, both zeolite and the process conditions have been modified to improve selectivity to light olefins. The effective shape selectivity was increased by the deposition of silica [35] in the channel system. Phosphorus modification [36] with trimethylphosphite followed by air calcination improved olefin selectivity by lowering acid site strength and probably also by reducing the effective pore size. Ion exchange with Mn^{2+} [37], Mg-modification [38], and higher SiO_2/Al_2O_3 ratios (lower site density) [39] were all reported to improve olefin selectivities.

In 1984, scientists in the Molecular Sieve Division of the Union Carbide Corporation reported the synthesis of a new family of SAPO molecular sieve materials with a broad range of structure-types and compositions [40,41]. Some of these materials exhibited mild acid strengths and selectivities in hydrocarbon transformations that were not typical of zeolite compositions [42]. In 1985, Kaiser first described the conversion of methanol to light olefins over small-pore SAPO molecular sieves [43]. Samples of SAPO-34 (CHA), SAPO-17 (ERI), SAPO-35 (LEV), SAPO-44 (CHA), and SAPO-16 (AST) were prepared and tested (Table 1) under comparable conditions. All of the structures with 8-ring pore openings showed methanol conversion predominantly to small olefins. The SAPO-16 has a pore size too small to admit methanol and produces essentially no olefinic products. Although SAPO-34 and SAPO-44 both have the CHA framework topology, the two materials differ in their catalytic behavior.

Table 1
Comparison of several SAPO structure-types for the MTO reaction

SAPO	−17	−34	−44	−16	−35
$C_2^=$	36.5	35.0	17.7	0.5	42.8
C_2	0.5	0.6	6.3	Trace	0.4
$C_3^=$	29.3	43.0	13.3	0.6	31.2
C_3	Trace	0.4	9.5	Trace	1.3
$C_4^=$	12.2	15.8	7.4	Trace	8.0
C_5's	4.9	3.6	1.1	ND[1]	2.9
C_6's	2.0	Trace	ND	ND	1.4
C_1	2.9	1.5	5.5	ND	11.5
CO_2	0.2	0.2	2.8	ND	0.6
DME	0.0	0.0	36.4	98.9	0.0
Hours on stream	4.7	6.3	1.0	2.0	1.0
WHSV (h^{-1})					
Methanol	0.86	1.17	0.85	0.87	2.60
H_2O	2.00	2.73	1.99	2.03	2.43
Conversion (%)	100	100	45	53	100

Conditions: 375 °C, 1.34 atm [Ref. [43], Examples 25, 26, 27, 29, 30].

Table 2
Methanol conversion to light olefins over SAPO-34

	Molar selectivity (%)			
	375 °C	400 °C	425 °C	450 °C
$C_2^=$	43.0	46.7	51.4	61.1
C_2	0.8	0.6	0.6	0.7
$C_3^=$	41.8	36.7	32.5	27.4
C_3	0.5	0.5	0.5	Trace
$C_4^=$	10.8	11.9	9.3	5.4
C_5's	1.7	1.6	1.4	0.6
C_6's	Trace	Trace	Trace	Trace
C_1	1.3	2.0	4.3	4.8
DME	Trace	–	–	–
C_2–C_4 olefins (%)	95.6	95.3	93.2	93.9
$C_2^=/C_3^=$ molar ratio	1.03	1.27	1.58	2.23
Hours on stream	5.2	6.3	6.2	11.0
Methanol conversion (%)	100	100	100	100
CO_2 eff. (%)	0.9	1.5	5.5	1.0

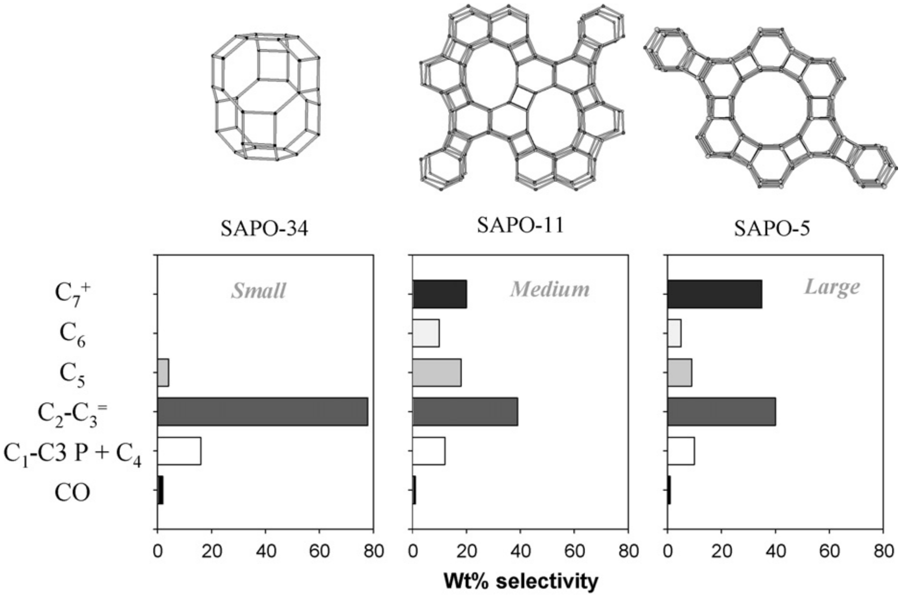
Ref. [43], Example 32. Conditions: 1.34 atm; WHSV (h^{-1}): 0.83–0.87 MeOH, 1.95–2.04 H_2O.

The effect of temperature on the distribution of olefin products over SAPO-34 is noted in Table 2 [43]. As the temperature increases, the molar selectivity to ethylene increases, and selectivities to propylene and butene decrease. The catalyst can be regenerated to full activity by calcination in air at 500 °C or greater.

Fig. 5 shows product distribution in methanol to olefins reaction with small, medium and large pore SAPO materials [44]. Small pore SAPO-34 gives highest selectivity to light olefins. Both, ZSM-5 and SAPO catalyst systems use the shape selectivity of the material to guide the formation of a specific product composition. Fig. 6 shows a comparison of the SAPO-34 and ZSM-5 structures and the relative molecular sizes of ethylene, propylene, isobutene and benzene to the pore opening sizes of ZSM-5 and SAPO-34. ZSM-5, having a medium pore opening size of about 5.5 Å, allows the larger molecules in the gasoline range to pass, such as C_5–C_8 paraffins and aromatics. On the other hand, SAPO-34 having a smaller pore opening of 3.8 Å, only allows movement of linear hydrocarbons. Fig. 7 shows a comparison of the product distributions obtained using ZSM-5 and SAPO-34 catalysts in the MTO reaction [45].

In their study of SAPO-34, Marchi and Froment found that aromatics formation, chain growth, and light paraffin production were all suppressed by adding water to the feed [46]. They attributed this effect to competitive chemisorption between the water and olefin molecules on the strongest acid sites. When the partial pressure of methanol in the feed was reduced by nitrogen instead of water, the resulting effect was closer to that observed with pure methanol feed at a reduced partial pressure.

In addition to the conversion of methanol to olefins, Kaiser observed that SAPO-34 also catalyzed the inter-conversion of small olefins [47]. For example, ethylene, propylene, or butene in the presence of SAPO-34 at 648 K was converted into mixtures of the three olefins.



350C, WHSV = 0.3 h^{-1}, MeOH = 0.02 bar, N_2 = 0.98 bar

Fig. 5. Small, medium and large pore SAPOs have MTO activity.

Yuen et al. [48] evaluated the effects of acid site density and strength on methanol conversion to light olefins over chabazite structure-types with different compositions: SAPO-34 and SSZ-13. Both SSZ-13 and SAPO-34 show high olefin selectivities, but the SAPO-34 is the most selective. The SSZ-13 produces significantly more alkane products, as noted in the earlier zeolite work cited by Chang.

In addition to shape selectivity and acid-site strength, other catalyst characteristics that influence the catalytic performance of SAPO-34 have also been identified. The effects of particle size and silica content were studied by Barger and Wilson [49]. They varied particle size from 1.4 to 0.6 μm, and Si mole fraction in the product was varied from 0.14 down to 0.016. They reported increase in catalyst life with a reduction in particle size. The data show that improved performance, in terms of reduced propane by-product formation and increased catalyst life, is obtained by using a catalyst having an average particle size of less than 1.0 μm or less than 0.05 mole fraction Si. Superior performance is obtained with catalysts that combine these two properties.

Methanol conversion exposes SAPO-34 to both thermal and hydrothermal cycling at elevated temperatures. The SAPO-34 catalyst requires frequent carbon-burn regenerations to remove nonvolatile coke deposits from within the micropores of the molecular sieve. Accelerated hydrothermal aging of the SAPO-34 powder was studied by Barger and Lesch to understand the structural changes that might occur during the multiple reaction–regeneration cycles [50]. They observed no degradation of the structure after either lower temperature hydrothermal aging (450 °C) or 205 cycles of reaction and regeneration in the MTO process. Partial SAPO-34 structural collapse did occur, but only under severe hydrothermal conditions (650 °C). These findings indicated that SAPO-34 structure collapse does not appear to be a major concern for the long-term stability of the MTO catalyst. Other reported studies of thermal [51] and hydrothermal stability [52,53] have supported these findings.

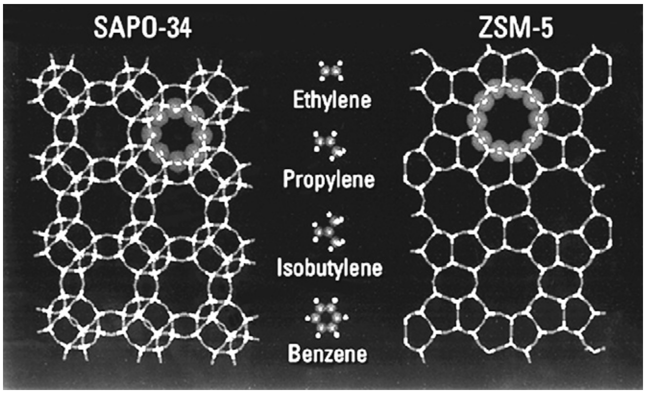
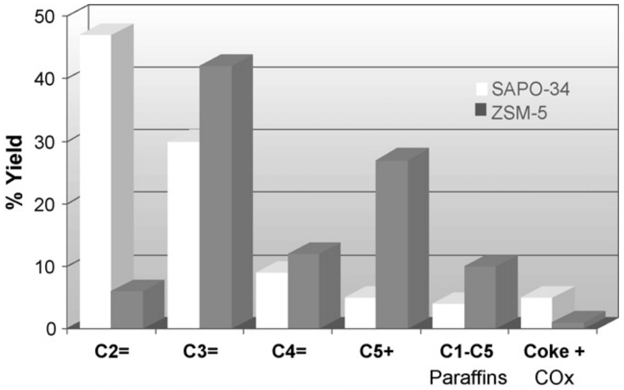


Fig. 6. Structures of SAPO-34 and ZSM-5.

3.6. Mechanism for olefins production in MTO

The mechanism of higher hydrocarbon formation from methanol over acidic molecular sieves has been a subject of interest ever since the first discovery of MTG chemistry in the 1970s. In the past few years the Haw and Kolboe/Olsbye groups have demonstrated the importance of a hydrocarbon pool of adsorbed molecules, in particular methylated aromatics, in the



SAPO-34 Catalyst: Once through C2= + C3= yield of 80%
ZSM-5 Catalyst: Once through C2= + C3= yield of 50%

Fig. 7. Product yields from methanol: SAPO-34 and ZSM-5 catalysts.

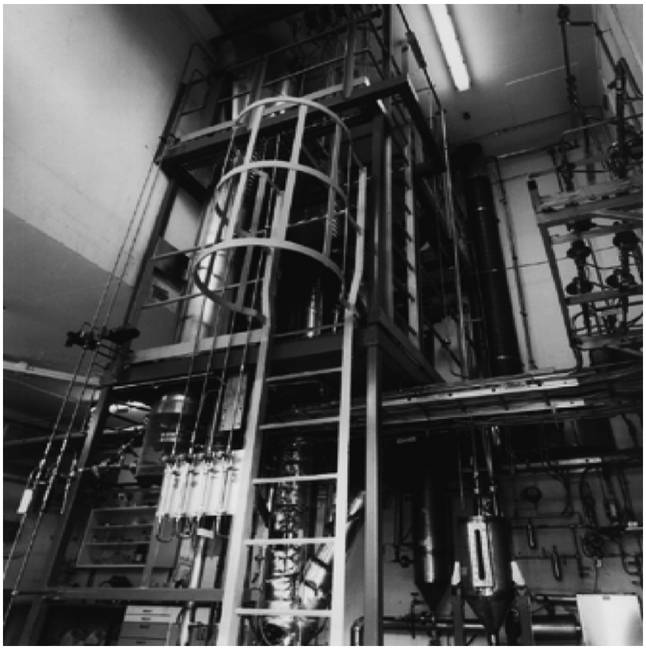


Fig. 8. MTO demonstration unit at HYDRO R&D center in Norway.

conversion methanol to higher olefins [54,55]. Isotopic labeling studies have shown exchange between side-chain and ring carbons of adsorbed aromatics at typical MTO conditions [56]. This is consistent with the involvement of aromatics in methanol conversion, probably via methylation, ring contraction and expansion and dealkylation. Direct methylation of ^{12}C–ethylene with ^{13}C–methanol has also been observed at low conversion [57]. Thus, it appears that the formation of higher hydrocarbons from methanol involves a complex series of steps including aromatic methylation, rearrangement and dealkylation as well as olefin methylation and cracking [55]. These pathways appear to occur on a wide variety of molecular sieves ranging from large-pore beta zeolite to medium-pore ZSM-5 and small-pore SAPO-34. The key differences in the performance of these materials are relative steric constraints on product diffusion out of the molecular sieve structure. In the case of SAPO-34, this constraint favors the formation of the small olefins, ethylene and propylene.

Chen et al. have studied the role of coke deposition in the conversion of methanol to olefins over SAPO-34 [58]. They found that the coke formed from oxygenates, referred to as active coke, promoted olefin formation while the coke formed from olefins, referred to as inactive coke, had only a deactivating effect. The yield of olefins during the MTO reaction was found to go through a maximum as a function of both time and amount of coke. Coke was found to reduce the DME diffusivity, which enhances the formation of olefins, particularly ethylene. The ethylene to propylene ratio increased with intracrystalline coke content, regardless of the nature of the coke.

4. UOP/HYDRO MTO process

As pointed out earlier, a number of different technologies are available for the first step of the GTO process: methanol synthesis from natural gas. Recently, new plants of 5000 metric tons per day (MTD) methanol production capacity are being built and a single-train methanol plant with a capacity of up to 10,000 MTD is possible [25]. The UOP/HYDRO MTO process converts crude methanol to ethylene and propylene. Thus, significant savings are realized in methanol synthesis by not requiring the methanol purification–distillation section.

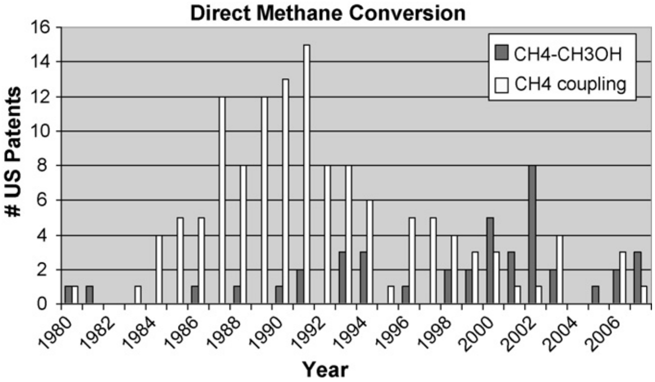


Fig. 9. Patent activity in U.S. for direct conversion of methane.

UOP and Norsk Hydro (Norway) have jointly developed the UOP/HYDRO MTO process, an economic process for the conversion of natural gas to ethylene and propylene. Over the last few years, details on this technology have been disclosed in numerous publications [59–62]. An integral part of this process is the catalytic conversion of methanol to light olefins over the UOP proprietary SAPO-34 catalyst. Though ZSM-5 is most widely studied zeolite, as it has several interesting applications, such as, catalytic cracking, isomerization, MTG and others, the SAPO-34 is the most widely studied catalytic system for MTO reaction and gives the highest light olefin yield. A 1-ton per day demonstration unit integrating the process and catalyst regeneration has been in operation at the Hydro Research Center in Porsgrunn, Norway since 1995 (Fig. 8).

The UOP/HYDRO MTO process has a wide range of operating flexibility depending on the demand for ethylene or propylene. The catalyst is continuously regenerated in a fluidized-bed regenerator, where coke on the catalyst is burned.

The key benefits of the UOP/HYDRO MTO process are

- High ethylene and propylene yields improve profitability. Recent advances have increased ethylene plus propylene yield to near 90%.
- Product slate flexibility allows high-ethylene or high-propylene production.
- Simple fluid-bed reactor and regenerator design enables steady-state operation at high efficiency.
- Low production of diolefins and acetylenes makes product purification easier.
- Low production of H_2 and methane results in less expensive simplified cold-box design.

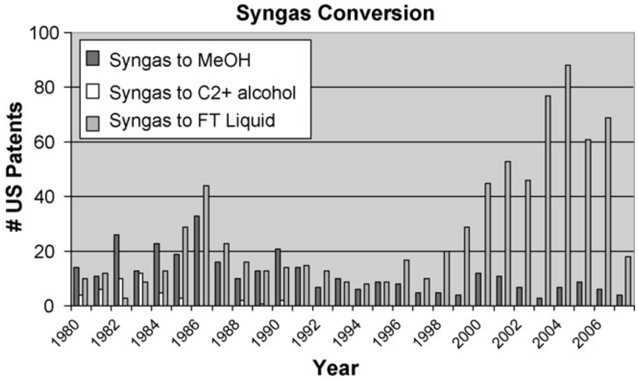


Fig. 10. Patent activity in U.S. for indirect methane conversion via syngas.

- Low production of ethane and propane allows the production of chemical-grade ethylene and propylene without ethane–ethylene or propane–propylene splitter columns.
- Low emissions make the process environmentally friendly.

Although interest in direct conversion of natural gas continues (Fig. 9), a significant increase in patent activity is seen for indirect conversion of methane via synthesis gas (Fig. 10). This is coincides with where the methane conversion industry going.

Among all the current technologies available, the UOP/HYDRO MTO process provides the most-attractive option for upgrading natural gas to higher-value ethylene and propylene. The process is flexible over a wide range of ethylene-to-propylene ratios and with recent advances in process and catalyst, combined ethylene and propylene yield of 90% can be achieved.

5. Conclusions

While we wait for a major breakthrough in direct conversion of methane, at present, conversion of natural gas, methane, to petrochemicals via synthesis gas offers best economic advantage. In this respect methanol can play a major role as it can be readily transported. Methanol can be directly used as a fuel or can be easily converted to dimethylether as a LPG substitute. Alternatively, it can be converted to polyethylene and polypropylene, the largest volume petrochemical polymers. Once a first methanol to olefins commercial plant based on SAPO-34 catalyst is successfully operating, future growth of ethylene and propylene is more likely to come via methanol.

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