Available online at www.sciencedirect.com
SCIENCE DIRECT
Catalysis Today 106 (2005) 103–107
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Recent advancements in ethylene and propylene production using the UOP/Hydro MTO process

John Q. Chen [a,*], Andrea Bozzano [a], Bryan Glover [a], Terje Fuglerud [b], Steinar Kvisle [b]

[a] UOP LLC, P.O. Box 5017, Des Plaines, IL 60017-5017, USA
[b] Hydro ASA, P.O. Box 2560, N-3901 Porsgrunn, Norway

Available online 22 August 2005

Abstract

The UOP/Hydro MTO process utilizes a SAPO-34-containing catalyst that provides up to 80% yield of ethylene and propylene at near-complete methanol conversion. This paper discusses new advancements related to the technology which can increase the carbon selectivity from methanol to ethylene-plus-propylene to about 85–90% and can extend the range of propylene-to-ethylene production ratios to more than 2.0.

The MTO technology has the potential to play an important role in the European olefin industry as part of a segregated gas-to-olefins (GTO) chain, utilizing dedicated imported methanol or DME as a low-cost feedstock. Furthermore, the ethylene/propylene product flexibility can contribute to meet the increasing propylene demand. The technology is also attractive due to low specific CO_2 emissions.

Keywords: UOP/Hydro MTO process; Gas-to-olefins; Ethylene/propylene product

1. Introduction

Worldwide demand for ethylene and propylene has been growing steadily. Projected growth rates for light olefins are expected to remain above worldwide GDP growth rates and there is a growing need to utilize technologies that favor higher ratios of propylene-to-ethylene production. Growing global demand for oil and more generally for energy will have significant impact on the availability and pricing of traditional feedstocks for light olefin production. This has led to a great increase in the exploration of using natural gas and coal as raw materials for the production of petrochemicals. While such a direct conversion is not yet feasible, technology for the production of methanol from syn gas is readily available and practiced today. Syn gas can be easily produced from just about any hydrocarbon feedstock, from natural gas to heavy residues or coal. The combination of methanol production using state-of-the-art mega-scale methanol technology and methanol-to-olefin (MTO) technology developed by UOP and Hydro provides an economically attractive route from natural gas or coal to ethylene and propylene. The MTO technology has been extensively demonstrated at a demo plant owned by Hydro in Norway. The process converts methanol to ethylene and propylene at about 75–80% carbon selectivity [1]. The first world-scale MTO commercial project is currently underway [2–4]. This paper will discuss some of the significant advancements made during the past few years to further enhance performance of the UOP/Hydro MTO process.

2. Methanol-to-olefins (MTO) process and catalyst

Methanol-to-hydrocarbon conversion reactions were first discovered in the early 1970s using ZSM-5 (MFI) catalysts [5,6]. In the 1980s, scientists at Union Carbide discovered SAPO-34, a silicon, aluminum and phosphorous based molecular sieve, which is an excellent catalyst for conversion of methanol to ethylene and propylene [7–9]. The structure of SAPO-34 along with the small sizes of certain organic molecules are keys to the MTO process. The small (about 4 Å)

* Corresponding author.
E-mail address: qianjun.chen@uop.com (J.Q. Chen).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.07.178

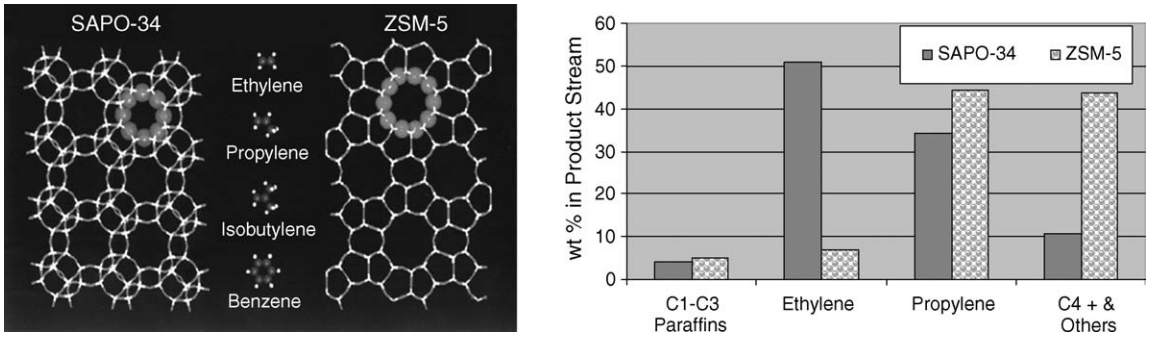

Fig. 1. Framework of SAPO-34 (CHA) and ZSM-5 (MFI) molecular sieves and their comparative performance at maximum ethylene mode.

pore size of SAPO-34 restricts the diffusion of heavy and or branched hydrocarbons, and this leads to high selectivity to the desired small linear olefins. ZSM-5 molecular sieve used in other processes [10] produces much lower light olefin yield primarily due to larger pore openings (about 5.5 Å) of the MFI structure (Fig. 1).

Another key feature of the SAPO-34 molecular sieve is its optimized acidity relative to aluminosilicate based zeolitic materials. The optimized acid function on SAPO-34 leads to much lower paraffinic by-products formation due to hydride transfer reaction. The UOP/Hydro MTO process can produce light olefins with purities of about 97% purity without requiring splitter columns. This makes it easy for the UOP/Hydro MTO process to produce polymer-grade olefins by including splitter columns when the highest purity olefins are desired.

3. UOP/Hydro MTO process description

The MTO process utilizes a fluidized bed reactor that offers a number of advantages. Constant catalyst activity and product composition can be maintained via continuous regeneration of a portion of used catalyst by coke burning with air. Catalysts manufactured at commercial scale have demonstrated the required selectivity, long term stability, and attrition resistance. The fluidized bed reactor also provides flexibility to adjust operating conditions and better heat recovery from the exothermic methanol-to-olefins reaction. This type of reactor has been widely used in the FCC area, particularly for catalyst regenerators.

Reactor operating conditions can be adjusted to the desired product requirements. Pressure is normally dictated by mechanical considerations. Lower methanol partial pressure leads to higher selectivity to light olefins especially ethylene. Therefore, some yield advantage can be obtained by using a crude methanol feed that typically may contain around 20 wt.% water. Temperature is an important control variable with higher temperature leading to higher ethylene yield. Too high of temperature will lead to lower total light olefin yield due to excessive coke formation. First generation MTO process converts methanol or dimethyl ether (DME) to ethylene and propylene at about 75–80% carbon selectivity and ethylene to propylene ratio can be varied between 0.50 and 1.5. The overall yield of light olefins (ethylene-plus-propylene) changes slightly over this range with the highest yields achieved with about equal amounts of ethylene and propylene, roughly in the 0.75–1.25 range. This envelope provides the lowest methanol requirements, but the ratio can be adjusted to reflect the relative market demand and pricing for ethylene and propylene.

Conventional treating methods have been shown to be effective for removing by-products to the specification levels required for olefin polymerization processes. In fact, it has been demonstrated that the ethylene and propylene produced from the UOP/Hydro MTO process pilot plant are suitable for polyolefin production.

4. Recent advancements in MTO technology

Significant advancements have been made over the past few years which further enhance the performance of the UOP/Hydro MTO process.

On the process side, the MTO process can be integrated with the olefin cracking (OC) process based on technology developed and demonstrated by Total Petrochemicals and

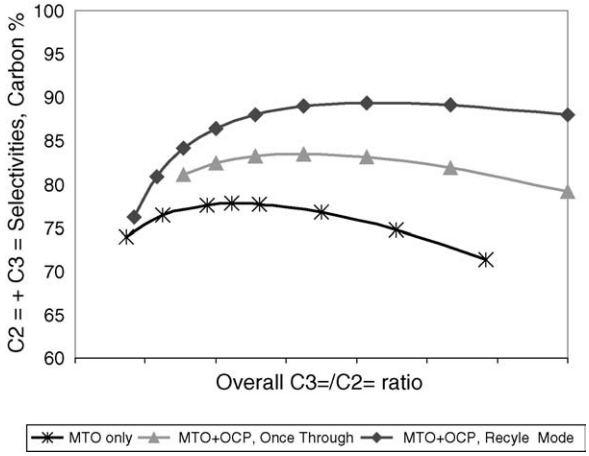

Fig. 2. Olefins selectivity vs. operating severity with and without OCP.

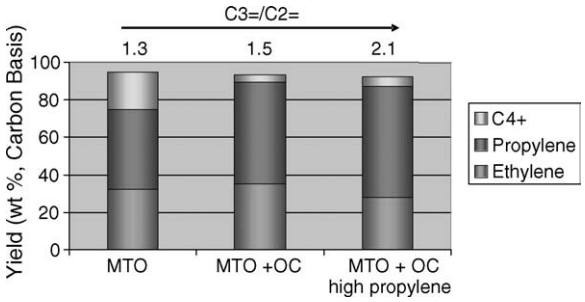

Fig. 3. Combination of optimized MTO catalyst and MTO and olefin cracking process improvements provide propylene-to-ethylene ratios over 2.0 with reduced by-product formation.

UOP [11]. This can be used to increase the carbon selectivity from methanol to ethylene-plus-propylene to about 85–90% (Fig. 2). With the integrated process, C_4 to C_6+ olefins generated as by-products from the MTO unit can now be fed to the olefin cracking unit in which the heavier olefins are cracked to ethylene-plus-propylene, but with a preponderance of propylene. The combined process has great flexibility to produce a product with a range of propylene/ethylene ratios up to 1.75, or even higher as will be discussed later. Furthermore, nearly an 80% reduction in C_4+ by-product formation and a 20% increase in light olefin yield can be achieved.

The recovery section of the MTO unit remains unchanged, except that it has to be sized to accommodate the added circulation to and from the olefin cracking unit.

On the catalyst side, continued development has led to MTO catalyst with superior performance compared to earlier formulations. The optimized catalyst offers greater flexibility to achieve higher propylene production as propylene-to-ethylene ratios can be almost 20% higher than were available using earlier catalysts. With the optimized catalyst and in combination with well-integrated MTO and olefin cracking units, the enhanced MTO and OC processes can produce propylene to ethylene product ratios over 2.0 to meet the growing demand for propylene (Fig. 3).

5. European olefin market situation and role of MTO technology

The MTO technology can play a role in the European olefin industry in relation to important issues such as:

- Feedstock situation.
- Increasing propylene demand.
- CO_2 emissions.

These issues are briefly discussed in this section.

Naphtha cracking is the major source of light olefins in Europe and will remain the primary route in the future. However, high crude oil prices represent a cost challenge to the European petrochemical industry and alternative, lower cost feedstocks are increasingly important. One such alternative is a *segregated* GTO concept. This concept is based on methanol production in a location with low natural gas prices compared to western Europe and transport of methanol in dedicated, large vessels to an MTO plant located in Europe.

The competitiveness of such a plant in Europe is dependent on the delivered cost of methanol amongst other factors. In order to illustrate this we have developed a generic economical comparison of a naphtha cracker and an MTO plant, both located in northwestern Europe. Fig. 4 highlights this comparison.

The figure shows ROI for a naphtha cracker as a function of crude oil price. This curve is based on cracker investment, operating costs, and historical relationships between the prices of crude oil, naphtha, olefins and by-products. The figure also shows ROI for an MTO unit with different delivered costs for methanol. These curves are based on the same prices for olefins and by-products as used for the naphtha cracker curve.

The results in Fig. 4 illustrate how different methanol feedstock costs give different break-even economics with the cracker. With crude oil prices above US$ 20–22/bbl we see that the MTO process is competitive based on methanol feedstock price in the order of US$ 90–100/t. If future crude oil prices average in the US$ 30–40/bbl range, the MTO process would be much more attractive. These economics are of course generic, but nevertheless illustrate how methanol through a segregated GTO concept can play a future role as an alternative, cost advantaged feedstock for olefin production in Europe.

An obvious question is of course if methanol can be supplied to Europe at the costs mentioned above, for instance, below US$ 100/t. The answer is yes, mega-scale methanol plants located in areas with low cost natural gas can supply methanol at this cost to Europe with good margin. This is illustrated in Fig. 5.

A typical 2700 t/d plant in an industrialized location based on rather expensive gas has high production costs. Several such plants have consequently been shut down in recent years. A plant with the same capacity but located in a remote area with low cost natural gas, has significantly lower production costs. Specific production costs are reduced further due to economy of scale if the capacity of the plant is

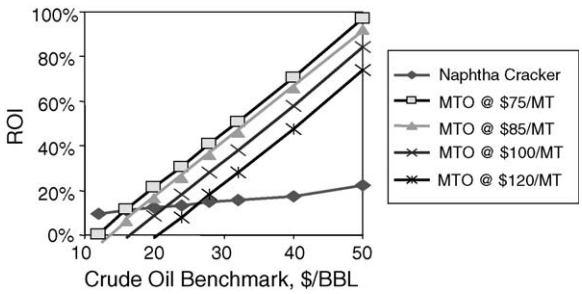

Fig. 4. Light olefin production. MTO vs. naphtha cracking economics.

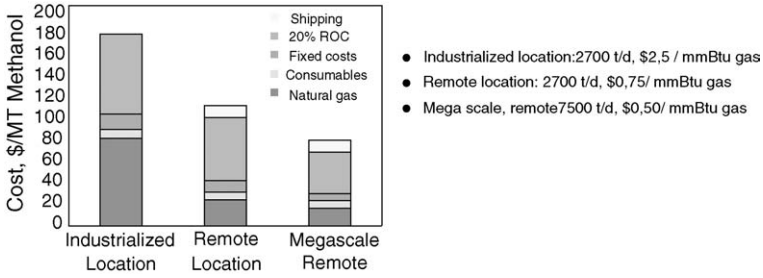

Fig. 5. Effect of gas price (location) and scale on methanol production costs.

doubled or tripled, still assuming a single train plant. Capacities in the range of 5000–10 000 t/d, and even bigger, are studied or under construction. Actually, the first 5000 t/d plant started up at Trinidad in 2004 (Atlas). Mega-scale methanol plants delivering low cost methanol are therefore becoming a reality. It should be noted that with large and dedicated vessels, methanol transport costs have also been reduced very significantly in recent years. Methanol delivered to Europe at a cost below US$ 85/t is therefore a realistic option.

An MTO unit in Europe, based on imported low-cost methanol, would need a long-term contract for the methanol supply which also requires a long-term contract for the gas supply. Different business and contract models can be developed for such a gas-to-olefins chain (GTO), but this will not be discussed any further in this paper. It should be mentioned that a number of mega-scale plants seem to be realized in coming years, and that the existing chemical methanol market cannot absorb this very significant capacity increase.

Another issue where the MTO process can play a role in Europe is the strong growth in propylene demand compared to ethylene.

A development trend in Europe as in several other regions is that a gap between propylene consumption and production capacity will develop. For Europe this is illustrated in Fig. 6.

Steam crackers cannot fill this gap due to the low propylene/ethylene ratio from these units. Even if alternative propylene sources are included, as they are in Fig. 6, a propylene gap will develop.

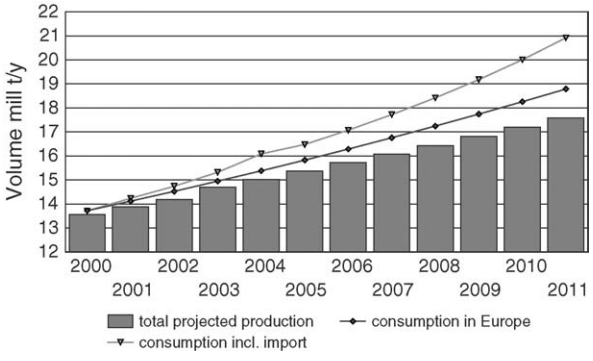

Fig. 6. Propylene gap developing in Europe.

The ability of the MTO technology to vary the ethylene/propylene ratio over a broad range, as discussed above, is therefore another advantage of an MTO plant located in Europe. Propylene/ethylene ratios up to 2.1 can be obtained in an MTO unit integrated with an olefin cracking unit.

Finally, as CO_2 emissions increasingly become an issue in Europe, the low CO_2 emissions from an MTO plant add to the attractiveness of this technology, although olefin production is not yet included in the European quota regulation. Today's quota value is approximately € 15/t CO_2. Compared to a naphtha cracker an MTO unit emits approximately 1 t of CO_2 less per tonne of light olefins produced (most of the CO_2 in the GTO chain is linked to the methanol production). The potential CO_2 benefit could therefore become very significant. Furthermore, this could also develop an interest in replacing furnaces in existing naphtha crackers with MTO units, while keeping or only slightly modifying the downstream product recovery section.

6. Conclusions

The UOP/Hydro MTO process provides an economically attractive route to convert cost advantaged raw materials such as natural gas or coal to high value-added ethylene and propylene products. Recent advancements both in process technology via integration of the MTO process with the olefin cracking process and optimized catalyst synthesis chemistry have led to significant improvement in process performance. Total light olefin yield can be increased from about 75–80% up to 85–90% on a carbon basis. Propylene-to-ethylene product ratios can be adjusted easily from 0.7 up to 2.1. The new combined MTO and OC processes also essentially eliminate the need to market less desirable C_4+ by-products.

The MTO technology can play a future role in the European olefin industry for several reasons. A segregated GTO chain represents a realistic, alternative feedstock option and could make MTO very attractive with the new crude oil price regime that exists. Furthermore, the ethylene/propylene product flexibility can contribute to meet the increasing propylene demand and the low CO_2 emissions

from an MTO plant also add to the attractiveness of the technology.

References

[1] B.V. Vora, T.L. Marker, P.T. Barger, H.R. Nilsen, S. Kvisle, T. Fuglerud, Stud. Surf. Sci. Catal. 107 (1997) 87.
[2] Chemical Week, October 2, 2002.
[3] European Chemical News, October 14–20, 2002.
[4] London, CNI, March 31, 2003.
[5] C.D. Chang, W.H. Lang, A.J. Silvestri, U.S. Patent 4,062,905 (1977).
[6] C.D. Chang, Catal. Rev.-Sci. Eng. 26 (1984) 323.
[7] S.W. Kaiser, U.S. Patent 4,499,327 (1985).
[8] S.W. Kaiser, Arabian J. Sci. Eng. 10 (1985) 361.
[9] J.M.O. Lewis, in: J.W. Ward (Ed.), Catalysis, Elsevier, Amsterdam, 1998, p. 199.
[10] C. Higman, P. Konig, F.W. Moller, H.D. Holtmann, U. Koss, EP 0882692 A1, 2001.
[11] J. Gregor, W. Vermeiren, in: Proceedings of the Fifth EMEA Petrochemicals Technology Conference, Paris, June 25–26, 2003.