Converting olefins to propene: Ethene to propene and olefin cracking

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Demand for propene as a petrochemical building block keeps growing, while its availability has been decreased by the adoption of shale gas resources, among others. Efforts to optimize its production by conventional means (including modified fluid catalytic cracking) and new on-purpose production technologies (including ethene to propene (ETP) and olefin cracking) are being pursued. This work reviews the progress made on olefin conversion processes, including the ETP reaction, which is still under development, and the cracking of butenes and higher olefins (C_5–C_8). The factors analyzed include the catalytic performance of different zeolite materials and their modifications to increase catalyst stability, yield, and selectivity to propene, as well as the effect of operating conditions, reaction thermodynamics, and mechanisms involved. The work is complemented by a survey of commercial technologies and developments on olefin conversion processes.
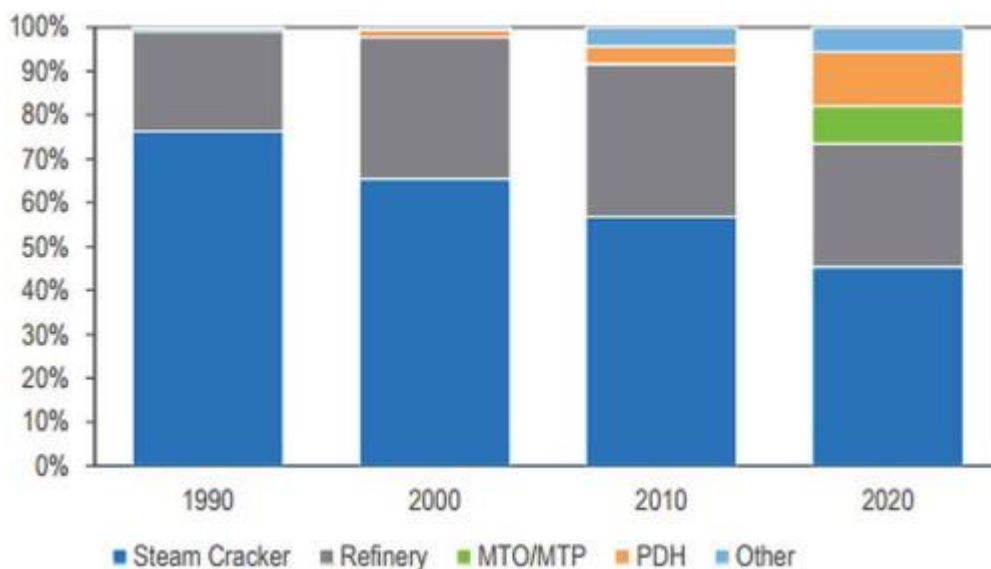
1. Context

Light olefins (ethene, propene, and butenes) and monoaromatic BTX (benzene, toluene, and xylenes) are the main building blocks of the petrochemical industry, which supplies hundreds of millions of metric tons of manufactured raw materials every year to many chemical industries (including pharmaceuticals, plastics, optics, food, dyes, *etc*.). Propene is being produced at a rate over 100×10^6 tons per year and its forecasted demand is expected to average 4.5% per year in 2016–2020 according to IHS Markit.[1]

There are different types of processes commercially available that can produce propene and other light olefins using different methods. They can be divided into two groups: (a) thermal and catalytic cracking processes (namely fluid catalytic cracking or FCC and steam cracking), and (b) on-purpose processes for propene production. So far, FCC units are probably the cheapest way to produce propene, with the sum of FCC and steam cracker accounting for around 90% of the global propene supply.

Historically, steam and catalytic crackers have accounted for the majority of the worldwide propene production, which was a coproduct in the production of ethene and fuels, respectively. However, with steam crackers moving to the use of shale gas ethane as their feedstock in the USA and the decrease in ethane cost in the Middle East, propene production from this source is declining.[2] When ethane is used as feedstock in the steam cracker, propene production is reduced by an order of magnitude. In addition to this reduction in propene production from steam crackers, a significant increase in propene demand is forecasted. IHS Markit expects a growth of 40 Mtpy from 2013 to 2023,[3] while Wood Mackenzie foresees an increase of 56 Mtpy from 2014 to 2030.[4]

As a result, the conventional processes do not fully satisfy the growing demand for propene on the petrochemical market.[5] Propene on-purpose technologies have thus been developed. These are processes that valorize different feedstocks, such as light olefins, naphtha, propane, or oxygenates, through selective conversion to propene. Propene on-purpose technologies will play a key role to fill the gap between propene supply and its growing demand, as illustrated in Figure 1. Notably, it is expected that around 75% of the expected propene capacity additions in the period 2016–2020 will be as on-purpose propene processes, thus reaching almost a 30% share of the global propene production.[1]

Figure 1. Evolution of the sources of propene by process type.

Among the technologies that are designed for on-purpose propene production, the most relevant processes at the industrial scale are olefin metathesis, propane dehydrogenation (PDH) and oxydehydrogenation, methanol to olefins/methanol to propene (MTO/MTP), and olefin cracking. This review focuses on olefin cracking and ethene to propene (ETP), the latter being currently under development. A high-level comparison of the technologies is provided in Table 1 and is briefly discussed next.

Table 1. Comparison of selected propene production technologies.

In the PDH process, propene is produced through a dehydrogenation reaction that takes place at high temperature (650°C) and with the use of a dehydrogenation catalyst (Cr/alumina or Pt/alumina). Under these operating conditions, the catalyst deactivates quickly by coke formation, so frequent regeneration of the catalyst is required. PDH is the most popular and widely used propene on-purpose process and is commercially available from a number of technology licensors, such as CATOFIN by Lummus Technology, Oleflex PDH by UOP, and STAR PDH with oxydehydrogenation by ThyssenKrupp Uhde, among others.[6]

Olefin metathesis was discovered in the 1960s by Standard Oil of Indiana and Phillips Petroleum. In this process, an ethene and a butene molecule are converted to two molecules of propene over a molybdenum- or tungsten-based catalyst. Several companies have developed this process at a demonstration or

commercial scale, namely ABB Lummus (Olefin Conversion Technology, OCT), Sinopec (Olefin Metathesis Technology, OMT), and IFP-CPC (Meta-4 process).[7,8]

Natural gas can be converted to methanol through well-known commercially available technologies.[9] Methanol can be further converted catalytically to propene (and also ethene and a small amount of naphtha) in the MTO process or in its variant MTP.[10,11] The MTO process was discovered by Mobil Oil long ago, and it is currently commercialized by ExxonMobil, JGC and Mitsubishi Chemicals, Lurgi, Lummus, Sinopec, and UOP/Hydro. Recently, there is an increasing interest in the dimethyl ether to olefins (DTO) process, as an alternative to MTO, since its conversion requires lower reaction temperature and it takes place with a lower water concentration in the reaction medium.[12]

There are also other propene producing technologies currently under development, especially those that start with biomass-derived feedstocks, such as acetone,[13] acetic acid,[14] ethanol,[15,16] isobutanol,[17] bio-oil,[18] or even algae lipids.[19] Moreover, the valorization of waste polyolefinic plastic wastes is also attracting great attention.[20]

The present review covers olefin conversion technologies. Although olefins are not present in crude oil or natural gas, they are formed upon chemical transformation in refining processes, such as catalytic or thermal cracking. In the last years, several specific processes have been developed to crack the C_4 olefinic stream produced in catalytic cracking (FCC) or thermal cracking (coking, visbreaking, and steam cracking), and even higher olefins present in olefinic naphthas, to propene, and thus obtain additional economic value from these streams.

The conventional use of this C_4 olefinic stream has been as a feedstock to produce high-octane gasoline blending components, like ETBE (ethyl *tert*-butyl ether) and MTBE (methyl *tert*-butyl ether) (from isobutene) or alkylate (from butenes and isobutene).[21] This stream can also be used to produce middle distillates by $C_4^=$ oligomerization.[22] Another low-value alternative use is liquified petroleum gas (LPG) production, which requires dilution with C_4 from crude, as commercial LPG has a maximum content of olefins permitted. On the other hand, olefinic naphtha is normally used in gasoline blending, although it is not a valuable component in the pool, due to its low octane and high olefin content, and generally requires posttreatment to improve its properties or remove contaminants. Consequently, conversion of these low-value olefinic streams to propene is considered a very interesting option.

In olefin cracking, a light olefinic feedstock is catalytically cracked at high temperature (450–600°C) and low pressure (1–2 bar). Among the advantages of olefin cracking compared with other on-purpose propene processes, we highlight that it does not compete with ethene production (unlike metathesis, which consumes ethene), it could be easily integrated within the refinery scheme, the inversion requirement is lower than in other processes, and propene selectivity is high.

On the other hand, ETP conversion is an incipient propene on-purpose technology that is also attracting much attention among researchers and olefin producers to better control the propene to ethene ratio based on its market demand. The main advantage of the ETP reaction is the only requirement of ethene. Because ethene could not only be obtained from crude oil (after steam cracking) but also from sources alternative to oil such as shale gas and natural gas (after dehydrogenation of ethane), coal (*via* syngas), and biomass (*via* dehydration of bioethanol), ETP could enable new alternatives to produce propene from renewable feedstocks.

This review focuses on the catalytic conversion of light (ethene and butenes) and higher (C_5–C_8) olefins, including already installed processes and those under development. Section 2 examines the ETP reaction, including its thermodynamics, the different catalysts (Ni-MCM-41 and acid zeolites), and the reaction mechanisms involved. The state of the art of olefin cracking is detailed in Section 3. First, we describe the reaction mechanisms proposed for olefin cracking over acid zeolites. Next, we focus on the performance of the different catalysts presented in the literature, including their modifications for enhancing propene yield and the catalyst stability in the cracking of butenes (Section 3.2) and of pentenes and higher olefins (Section 3.3).

Zeolites with different porous structure (12-, 10- and 8-MR) have been used for olefin conversion. The structural features of some of these zeolites are summarized in Table 2, whose performance will be discussed later. Among them, H-ZSM-5 is one of the most studied zeolites and several modifications have been reported to modify its texture and acid properties, including dealumination or the incorporation of different metals. Some of these initiatives will also be discussed. Finally, an overview of the commercial processes and advances for on-purpose propene production from olefins is presented in Section 4.

Table 2. Zeolites with different porous structures used in olefin conversion.[23]

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2. Ethene to propene conversion

The ETP conversion was first reported over olefin metathesis catalysts, that is, supported molybdenum[24] and tungsten[25] catalysts. However, they yielded too low activity to attract commercial interest. More recently, Le Roux *et al*. studied a tungsten hydride supported on alumina, with an initial ethene conversion of 40% and a propene selectivity up to 95% at 150°C and 1 bar.[26] The reaction would comprise ethene dimerization to 1-butene, isomerization of 1-butene to 2-butenes, and then cross-metathesis between 2-butenes and ethene leading to propene. However, the conversion was low after 10 h of time on stream (TOS).

Mazover *et al*. have been working extensively to develop alternative methods to produce propene by using alkene metathesis reactions,[27] including the cross-metathesis reaction between ethene and 2-butenes to form propene, which is an alternative process currently undergoing significant industrial development[8] and the autometathesis of 1-butene.[28] In 2013, Li *et al*. reported a dual-function $NiSO_4/Re_2O_7/\gamma\text{-}Al_2O_3$ catalyst that is active in the ETP reaction.[29] The highest conversion obtained was around 63% with a selectivity to propene of 49% at 50°C and atmospheric pressure. However, the catalyst underwent severe deactivation triggered by coke formation. It is also concluded that Ni and Re work independently for the dimerization of ethene and the metathesis of 2-butene and ethene.

Nowadays, the materials most intensively studied for the ETP reaction are Ni-exchanged MCM-41 and acid zeolites. Some results reported in the literature with these materials are presented in Table 3 and are discussed further in the following sections. A discussion of the mechanisms presently used to interpret the respective catalysis is also presented in each section.

Table 3. Selected catalytic results in the ETP reaction.

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The thermodynamics of a process is always an important consideration to keep in mind, as it can have a large effect on all the other variables, from the catalyst design to the selection of the reaction scheme. Unfortunately, it is a topic often overlooked in many studies reported in the literature, and this is also the case

for the ETP transformation. One of the most important contributions has been the work reported by Lehmann *et al.*[30] They reported that low pressures and high temperatures are advantageous to yield large amounts of propene. Substantial propene formation requires reaction temperatures above 250°C. The maximum yield of propene predicted by thermodynamics reaches a value close to 42% at 1 bar and 600–650°C. Virtually, the same conclusion was achieved starting from ethene or from ethanol.

More recently, Senchilo *et al.*[31] performed also thermodynamic calculations considering ethanol as feed for propene production. The study considered two routes for ethanol conversion. The first one included dehydration of ethanol to ethene, dimerization to butenes, and metathesis of ethene and butenes to propene. The maximum yield of propene predicted was 50%–60% at around 500°C and 1 bar. The second one included dehydration of ethanol to acetaldehyde, transformation of acetaldehyde to acetone, and dehydrogenation of acetone to propene. The maximum yield of propene was around 75% at 200°C and 1 bar. Interestingly, we have found no experimental studies devoted to the ETP transformation under equilibrium conditions so far. Thus, studies like the latter ones become particularly relevant to improve the existing catalysts and to operate the ETP transformation under optimal conditions.

2.1. ETP over Ni-MCM-41

Since its discovery in 1992 by Mobil, MCM-41 is being widely studied because of its regular pore size in the mesoporous region and high specific surface area.[32] The incorporation of Al in order to develop acidity has been extensively reported.[33,34] Hartmann *et al*. proved the activity of Al-MCM-41 in the dimerization of ethene and in the isomerization for 1-butene.[35]

The addition of Ni on MCM-41 *via* template ion exchange (TIE) has been reported by several authors. In this procedure, a Ni-containing solution is put in contact with the so-called as-synthesized (not calcined) MCM-41. Ni exchanges with molecules of the template used in the MCM-41 synthesis. The procedure was first reported by Yonemitsu *et al.*[36] and since then has been widely used by many authors,[34,37–43] as it claims to have a high catalytic activity of the Ni species introduced in the MCM-41 materials for the ETP reaction.

Iwamoto and coworkers obtained an ethene conversion of 55% with a propene selectivity of 54% at 400°C.[40] Ni-exchanged MCM-41 yielded an ethene conversion of 68% at 400°C with remarkable selectivities to propene and

butenes of 48% and 43%, respectively, as reported by the same group.[37] Alvarado Perea *et al*. reported an ethene conversion of 80% over Ni/Al-MCM-41 catalysts.[38] However, they observed a high deactivation rate at 450°C. Ni/Al-MCM-48 has also been studied by Frey *et al*., who reported a conversion of 40% and a propene selectivity up to 56%.[39] Very recently, Stoyanova *et al*. have reported ETP activity on Ni impregnated by incipient wetness on silica-alumina.[44] They found an ethene conversion and propene selectivity similar to those reported over Ni/Al-MCM-41 catalyst. They also found that NiO_x particles that are highly dispersed are also active species in the ETP reaction.

The Ni state in the catalysts synthesized by the TIE method has been subjected to discussion and analysis in the open literature. Layered nickel silicate-like structure of type 2:1 phyllosilicate-like species seemed to be the active phase in the ETP reaction and in the dimerization of ethane.[34,37,45] Thus, it is proposed that Ni^{2+} is the Ni state that is active in the ETP reaction. On the other hand, Ni/MCM-48 and Ni/MCM-41 have also been prepared using the classical incipient wet impregnation method. They have shown comparable activity in the ETP reaction to the catalysts prepared by TIE.[39,44] In these works, it is reported that NiO_x particles that are highly dispersed are active in the ETP reaction. Thus, it seems that more intensive work is needed to clarify the true active sites for the ETP reaction.

The reaction over these materials was proposed to occur *via* dimerization of ethene to 1-butene on Ni sites, which would quickly isomerize to 2-butene over acid sites and then undergo metathesis with ethene over Ni sites to yield 2-propene molecules,[37,42] as shown in Figure 2.

Figure 2. Dimerization-metathesis ETP mechanism proposed over Ni-MCM-41.[37] With permission of Springer.
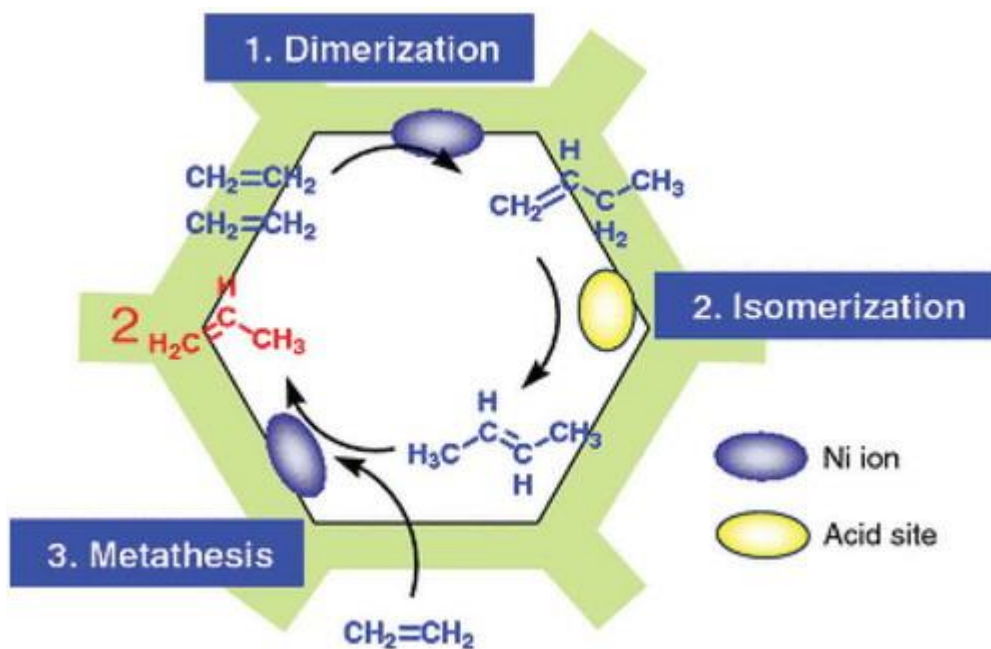
However, a different reaction mechanism based on a hydropolimerization process (conjunct polymerization) has been reported very recently over these materials.[46] The reaction mechanism proposed by Iwamoto has been questioned based on three different aspects: (1) Ni-based catalysts are active catalysts for dimerization oligomerization of ethane,[35,47] and no previous results have been reported for metathesis reactions; (2) typical metathesis catalysts are based on W, Mo, and Re metals,[8,48–50] and this reaction can proceed even at room temperature[48,51]; (3) irreversible deactivation of the catalyst due to coke formation was observed at the reaction conditions where the yield of propene reached the maximum.[52]

Therefore, the reaction mechanism proposed by Iwamoto partially explains the transformation of ethene into propene. In this sense, a hydropolimerization process explains in a better way the propene formation and the deactivation of the catalyst during the reaction ETP, as reported by Alvarado Perea *et al*.[46,52] As shown in Figure 3, a hydropolimerization mechanism explains a product that is a complex mixture of saturated (alkanes and cycloalkanes) and unsaturated (alkenes, alkapolyenes, cycloalkenes, and cycloalkapolyenes) hydrocarbons, and occasionally even aromatic compounds.[53] Thus, this complex mixture of reaction products has been observed and would explain the severe deactivation of the catalyst during the ETP reaction.

Figure 3. Schematic representation of the hydropolymerization process. Reprinted with permission from.[54] Copyright 1988 American Chemical Society.
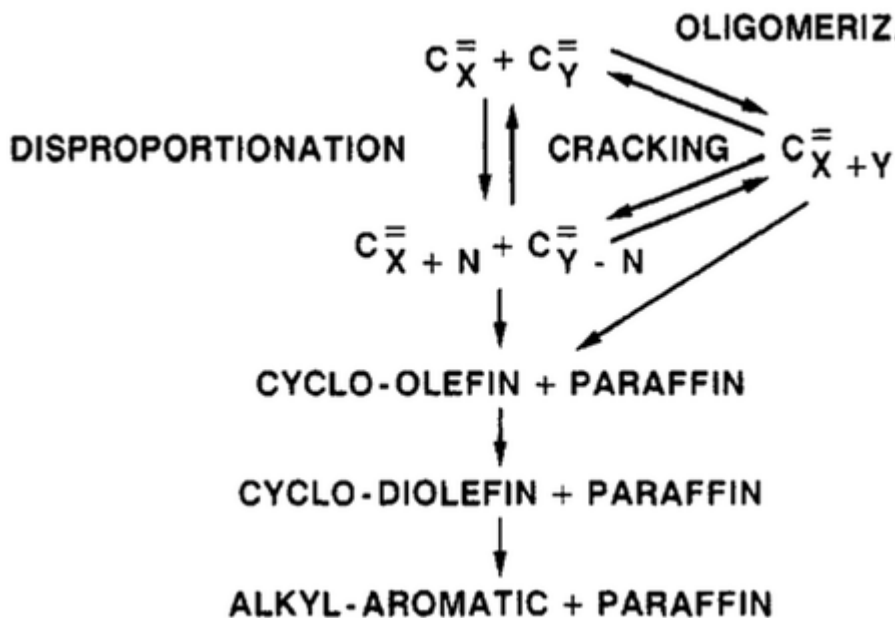
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The hydropolimerization mechanism (Figure 3) is based on that originally conceived by Quann *et al*. for the oligomerization of olefins.[54] Olefins undergo double bond and skeletal isomerization. Growing of the olefin chain takes place by condensation of two olefins $C_x^=$ and $C_y^=$ to a single higher olefin. In addition to oligomerization, any two olefins can react to disproportionate to two olefins with different carbon numbers. Olefin cracking may also occur along with oligomerization and disproportionation. Olefins may also undergo cyclization and hydrogen transfer (HT) reactions, yielding cycloolefins, alkyl aromatics, and paraffins. The occurrence of all the above reactions simultaneously is called as hydropolimerization or conjunct polymerization.

2.2. ETP over acid zeolites

The major drawback of ordered mesoporous materials (OMMs) that limits their perspectives for many petrochemical applications, and especially catalytic cracking,[32,55,56] is their low hydrothermal stability, which stems from the amorphous nature of their pore walls.[56,57] This limitation of OMMs is overcome by many zeolites. In this case, acid zeolites are most commonly applied.

In general, the transformation of ethene into propene on acid zeolites can be described as it takes place on SSZ-13[58] (Figure 4). In the initial stage, ethene

oligomerizes rapidly to aromatics. As ethene continues converting, the aromatics are gradually accumulated, and those with two or more condensed rings are formed very fast. Naphthalene-type carbenium-like species are the active reaction intermediates to which ethene is added and from which propene is split when steady state is reached. This mechanism can be compared to the hydrocarbon pool mechanism used to explain the MTO reaction over some acid zeolites.[11,59-62] These results show that the hexylcarbenium ions and/or the 4-methyl-2-pentylcarbenium ions are very fast converted to larger naphthalene carbenium species that slowly block the active Brønsted sites after a short reaction time. This blockage triggers the deactivation of the catalyst at longer reaction times. The excess of adsorbed species in the cages and pores is accompanied with their fast transformation into polycyclic aromatics. These last compounds provoke a total blocking of the pores that hinders the diffusion of the reaction products and make the active sites nonaccessible to further reactants.

Figure 4. Main reactions in the ETP mechanism over acid zeolites. Reprinted from[58] with permission from Elsevier.
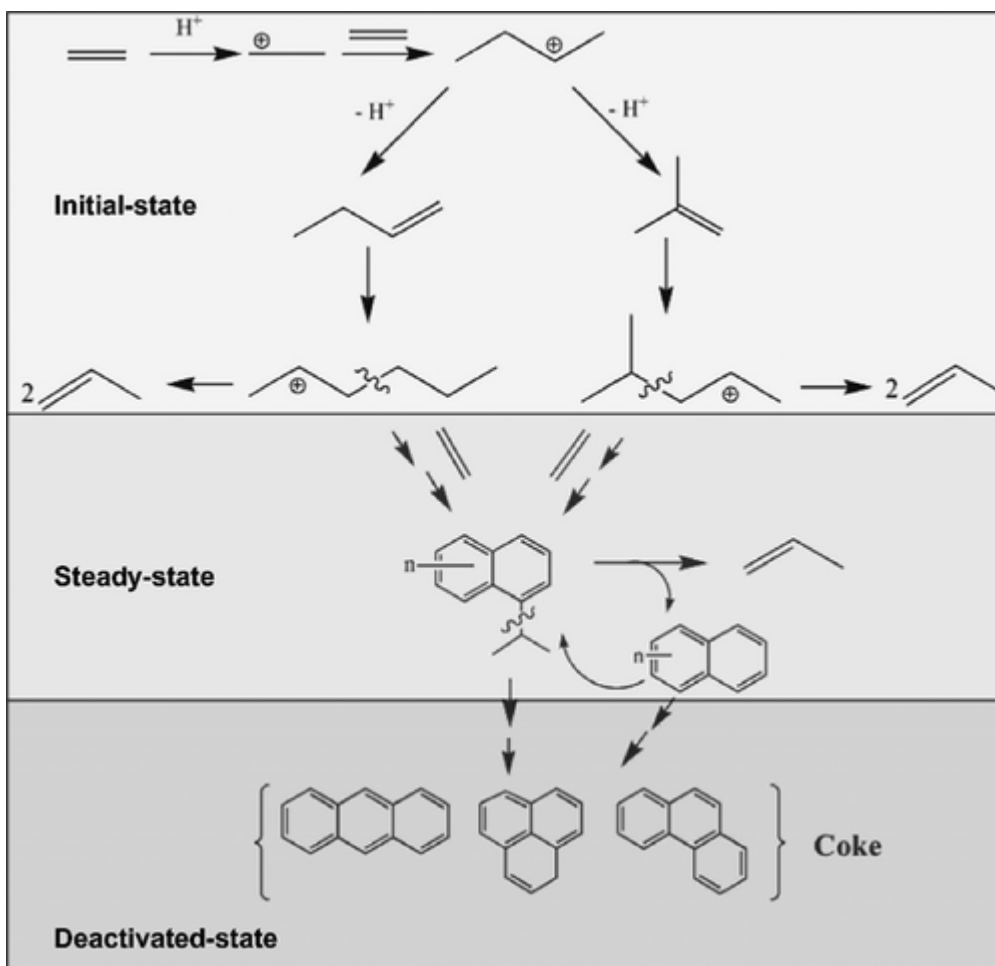
The recent results reported by Alvarado Perea *et al*. on Ni/MCM-41 materials demonstrate the formation of long-chain compounds during the course of the ETP reaction.[46,52] Additionally, the deactivation of this type of catalyst may suggest the formation of polycyclic aromatics that gradually block the access of the reactants to the active sites. In this sense, the reaction mechanism over both acid zeolites and Ni/MCM-41 seems not so different and Brønsted acidity plays a key role in the catalytic behavior of the materials. It is important to emphasize that the Brønsted acid sites have been generated by the incorporation of Al into the Ni/MCM-41 catalyst and they have a strong effect on the catalytic behavior in the ETP reaction.[38] For high Al content, Lewis acid sites are generated and the catalytic activity decreased considerably. Therefore, Brønsted acid sites are fundamental to enabling high catalytic activity.

Different zeolites have been explored for the ETP reaction, including SSZ-13, ZSM-5, SAPO-34, silicalite-1, ZSM-11, EU-1, ZSM-22, ZSM-23, Beta, and UZM-35.[63-67] Lin *et al*. examined 11 kinds of microporous and mesoporous molecular

sieves (Al-SBA-15, Al-MCM-41, ZSM-5, faujasites X and Y, Mordenite, Beta, MCM-22, SAPO-34, SAPO-44, and SAPO-18) for the conversion of ETP at 450°C.[68] No conversion of ethene was observed over mesoporous molecular sieves (Al-SBA-15 and Al-MCM-41) and some microporous molecular sieves including X, Y, and Mordenite. SAPO-34 exhibited the highest propene selectivity (84.7%) but a low conversion of ethene (4.3%). SAPO-44 and SAPO-18 also showed high selectivities but a very low ethene conversion. This low initial activity is explained by the limitation of the oligomerization steps on the micropores.[69] Beta and MCM-22 exhibited very low ethene conversion and a similar propene selectivity to ZSM-5, which was selected by these authors for further studies. They achieved a selectivity of 42% and an ethene conversion of 58% over a ZSM-5 with a Si/Al ratio of 38. P- and B-modified zeolites decreased the conversion of ethene but enhanced the selectivity to propene.

Dai *et al*. complemented the study by Lin *et al*. including some new molecular sieves such as BEA, EUO, Na-EU-1, and Na-SSZ-13 at 400°C.[58] Zeolites SAPO-34 and SSZ-13 consisting of large chabazite cages connected by 8-ring windows exhibited a higher propene selectivity than zeolite with 10-ring pores (EU-1, ZSM-5) and 12-ring pores (Mordenite and Beta). SSZ-13 showed the strongest ethene adsorption capacity, and thus this catalyst could be an alternative to SAPO-34. In addition, the dealuminated SSZ-13 showed a significantly lower coke formation due to its lower Brønsted acid site density.

By and large, the studies above emphasize the need for improved catalytic stability in the ETP reaction. Follmann and Ernst compared different zeolites of comparable Al content as a function of TOS.[70] As shown in Figure 5, the zeolite structure is a major parameter in determining the catalytic performance in the ETP reaction.

Figure 5. Time-on-stream behavior of acid zeolites with similar Si/Al ratios. Reaction conditions: T = 550°C, p_{C2H4} = 30 kPa, F_{total} = 30 Nml min^{-1}, W = 500 mg. Reprinted from.[70]
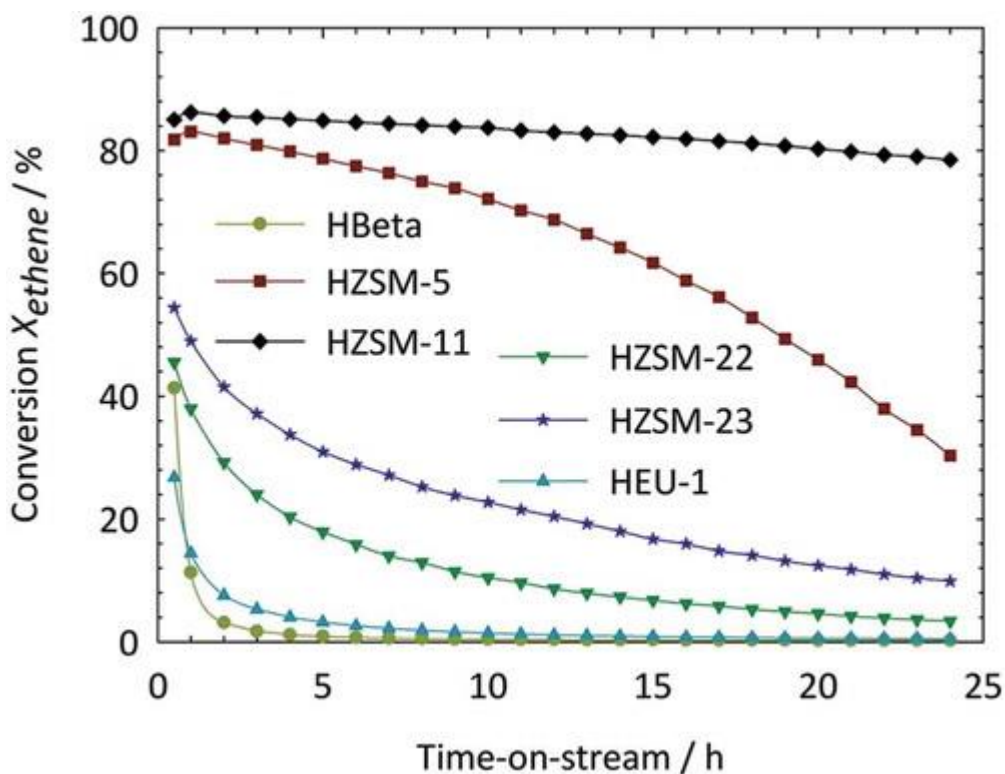
The SSZ-13 material is the current benchmark zeolite used to develop improved ETP zeolite catalysts.[58] SSZ-13 zeolites have been synthesized *via* various methods, including direct synthesis (from precursors of silica and alumina) and conversion of zeolite Y by both conventional electric and microwave heating.[67] Jun *et al*. studied the effect of Si/Al ratio on SSZ-13 in the ETP reaction. Propene selectivity increased with decreasing Si/Al ratio (up to 10), as the selectivities for butenes and C_{5+} decreased. However, SSZ-13 of moderate Si/Al[20-47,58,63,64,68–72] afforded relatively stable ethene conversion.[67]

Small and medium pore size zeolites are actively researched to maximize propene selectivity in catalytic cracking,[73-76] which has stimulated their study in the ETP reaction. Oikawa *et al*. attained a high propene selectivity of 73% over SAPO-34 at an ethene conversion of 71% and 723 K.[64] However, a rapid deactivation of this catalyst was reported by Li *et al*.[77] and Epelde *et al*.[69] Epelde *et al*. compared the performance of SAPO-18 and SAPO-34 during the conversion of ethene at 500°C. The results revealed the superior activity and stability of the SAPO-18 catalyst, thanks to its acidity and pore topology, which permitted a faster diffusion of aromatics and slowed down the coke deposition and the deactivation rate of the catalyst.[71]

However, one should always be cautious about simplifying the effect of confinement and topology to simple descriptors such as pore size. Recently, Lee *et al*. proposed UZM-35, an MSE-type large-pore zeolite related to MCM-68, as an alternative catalyst to SSZ-13.[63] Notably, they observed a better performance with the large-pore UZM-35 material. The presence of cylindrical cages would allow the easy formation of entrapped isopropylnaphthalene-based reaction centers for the ETP catalysis. Furthermore, this catalyst showed a lower deactivation rate by coke.

Although the sizes of the molecules involved in the ETP reaction *a priori* look suitable for the reaction to be carried out over microporous zeolites, usual micrometric crystals may already suffer from intracrystal diffusion limitations in this reaction, particularly if 1D zeolites are used. For instance, Follmann and Ernst carried out the ETP process over ZSM-5 and needed to substantially increase the temperature (from 450°C to 550°C), the ethene partial pressure, and the contact time to achieve similar conversion over 1D ZSM-23 of comparable Si/Al = 35.[66]

The modification of the zeolites also holds promise to improve their catalytic properties in the ETP reaction. Epelde *et al*.[72] studied several modifications in the ZSM-5 zeolites of different Si/Al ratio including doping with 1 wt.% of K or P and mild *in situ* steaming in the transformation of ethene at 500°C. Low conversions were obtained with ZSM-5 zeolites of high Si/Al ratio; however, propene selectivity was notably enhanced. Lin *et al*. also studied the effect of Si/Al ratio and observed that silicalite-1 was inert toward ethene conversion.[68] The doping with K was not appropriate for intensifying propene production, due to its excessive attenuating effect on the acid sites. P doping and steaming treatment contributed to attenuating coke deposition.[72]

Lin *et al*. reported that P- and B-modified zeolites did not enhance the catalytic performance.[68] They also studied the performance of H-Na-ZSM-5 with different H^+ exchange degree. Na-ZSM-5 was inactive for the conversion of C_2H_4. Ethene conversion notably increased with an increase in H^+ exchange degree, but the selectivity to aromatics was favored.

3. Olefin cracking

3.1. Mechanism of olefin cracking over acid zeolites

Depending on the operating conditions (temperature, partial pressure, *etc*.), olefin chain length, acid strength, and density of the zeolite catalyst, monomolecular (protolytic) or bimolecular (oligomerization cracking) olefin cracking mechanisms may occur in a greater or lesser extent[54] ([Figure 6](#)). Monomolecular cracking of olefins on zeolites is (a) usually disregarded in the case of propene and shorter olefins, (b) considered marginal, if so, in the cracking of butenes, (c) is as important or more than bimolecular cracking in the case of pentenes, and (d) is often the main route in the cracking of longer olefins.[78] Bimolecular cracking of alkanes differs from that of olefins since hydride transfer steps are involved in sustaining the active carbenium-like species on the catalyst instead of oligomerization steps ([Figure 6](#)). This, in addition to thermodynamic constraints, can lead to complex kinetic behaviors, like the one seen in [Figure 7](#), resulting from single-event kinetic modeling of real results. It can be observed that the dominating reaction pathway in 1-pentene cracking changes with temperature. At low temperatures, oligomerization to olefins $C_6^=$–$C_{12}^=$ is favored preceding cracking, but it is thermodynamically disfavored as temperature rises, leading to a decrease in the cracking rate. At even higher temperatures, monomolecular cracking, presenting higher activation energy, ends up prevailing, accompanied by a high selectivity to ethene.
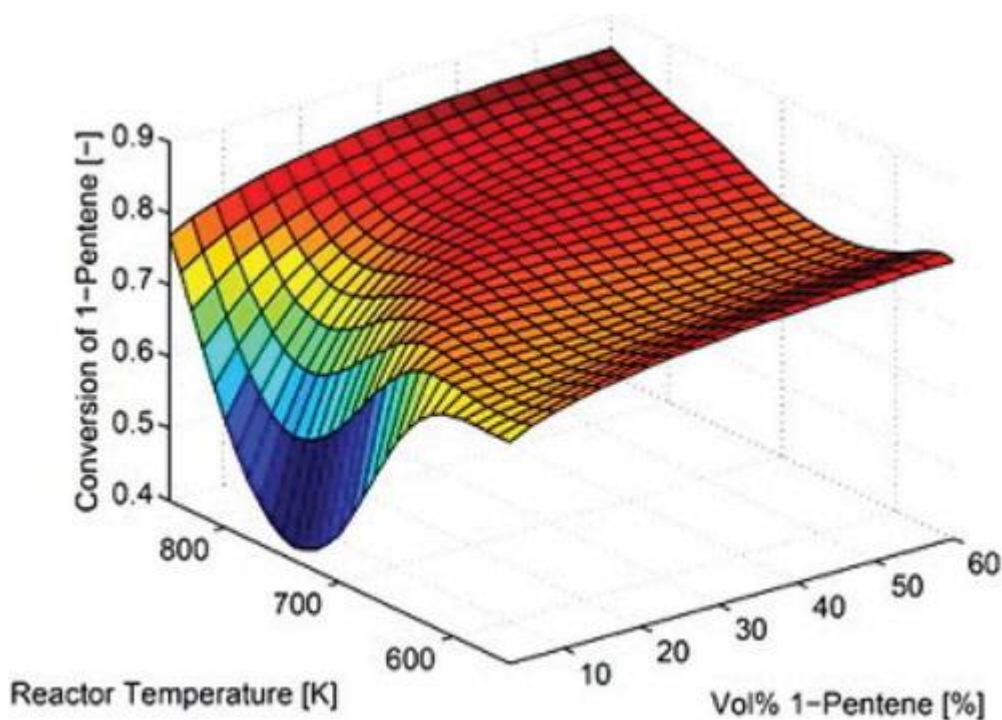
Figure 6. Monomolecular and bimolecular cracking mechanisms of alkanes and olefins on acid zeolites.

ALKANE CRACKING

MONOMOLECULAR

BIMOLECULAR

OLEFIN CRACKING

MONOMOLECULAR

BIMOLECULAR
(OLIGOMERIZATON-CRACKING)
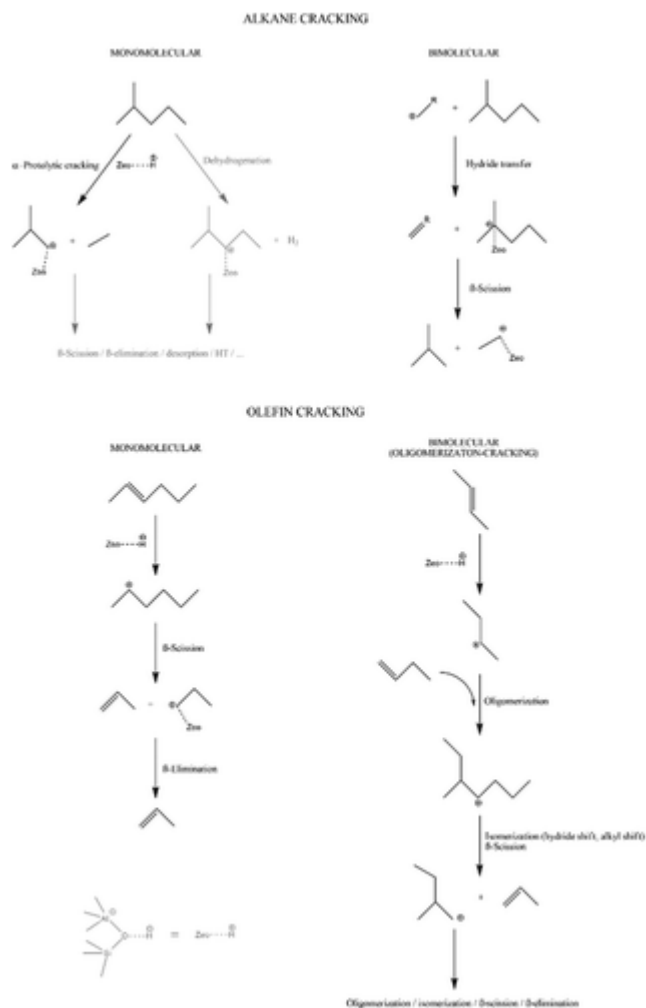
Figure 7. Conversion for an isothermal reactor at a constant residence time (28.6 kg cat s mol pentene^{-1}, TOS = 6 h, ZSM-5 Si/Al = 90). Reprinted from[79] with permission from Elsevier.

3.1.1. Monomolecular cracking of C_{5+} olefins

If we consider the cracking of C_{5+} olefins over acid zeolites, the monomolecular cracking route can be predominant. In the cracking of pentene, both monomolecular and oligomerization cracking can be relevant, depending on the conditions. Focusing on the monomolecular mechanism, Haag *et al*. observed that olefins crack much faster than paraffins with the same number of carbon atoms.[80] In addition, the variation of the apparent rate of monomolecular cracking with the chain length of paraffins is much smaller than in the case of olefins (Figure 8a). This is because activation of paraffins requires the formation of a high-energy carbonium-like species,[81] which is not the case in olefin cracking. Initially, it was considered that the differences in rate were solely due to differences in adsorption energies. However, recently, it has been demonstrated that there are actually differences in the intrinsic monomolecular cracking rate coefficients and the activation entropies.[82] In the case of olefins, activation of the double bond by direct protonation is fast and the limiting step is the β-scission itself. The ease of β-scission depends strongly on the substitution of the carbenium ions in the reactant and transition states. Hence, apparent cracking rates vary more strongly with chain length and are also accompanied by fast isomerizations. Nevertheless, Chen *et al*. calculated that adsorption constants for tertiary alkoxides were the lowest among surface

alkoxides, actually restricting their contribution to alkene cracking pathways (Figure 8c).[83]

Figure 8. (a) Apparent cracking rate constants for monomolecular cracking of linear hydrocarbons over ZSM-5 (Si/Al = 650, T = 510°C, p < 0.14 bar). Reprinted from[80] with permission from Elsevier. (b) Adsorption constants of primary, secondary, internal secondary, and tertiary hexoxides, (c) apparent rate constant of the eight C_6 olefin isomers according to their mode of cracking. Adapted with permission from.[83] Copyright 2014 American Chemical Society.
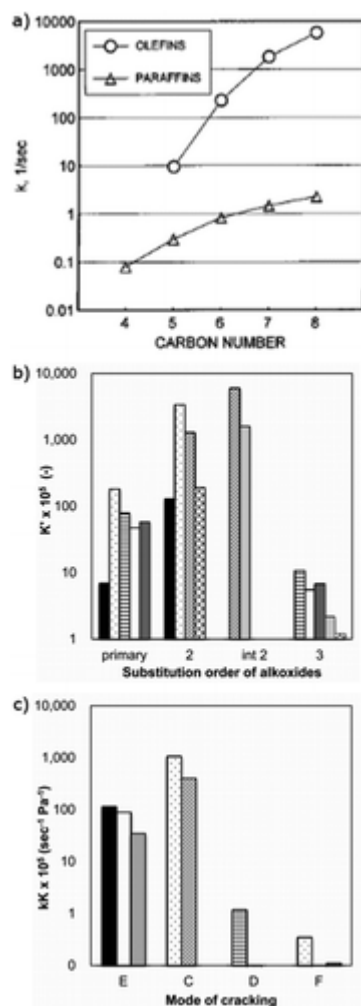
Display full size

Thermodynamics is an important factor in the conversion of olefins. Zhang *et al*.[84] considered the equilibrium distributions of various groups of olefins ranging from C_2 to C_7 (Figure 9). At high enough temperature, ethene ends up being the most favored olefin, whereas at low temperature thermodynamics favors the longest olefin considered in the equilibrium. In its turn, low pressure

favors ethene, whereas high pressure favors the longest olefins. Maximum propene yields are predicted for pressures between 0.1 and 0.25 bar when operating at 527°C (800 K). As could be expected, real catalytic cracking yields are lower than those allowed by the equilibrium of C_2–C_7 olefins, due to the formation of species not considered in the modeling, such as alkanes, hydrogen, aromatics, or coke. Interestingly, catalysts limiting olefin branching are predicted to yield substantially higher $C_2^=$ and $C_3^=$ yields. This is because an olefin isomer group will have a lower free energy than any of its components, which will favor equilibrium yields to C_{4+} olefins. These results evidence that appropriate catalyst design allowing only the formation of a restricted set of olefin products holds promise for substantial improvement of propene yields beyond current results.

Figure 9. Equilibrium distributions of C_2–C_7 olefins. (a) Effect of temperature at $P = 1$ bar; (b) effect of pressure at $T = 800$ K; (c) equilibria considering all isomers, only linear olefins or only linear α-olefins at 800 K and 1 bar. Reprinted from[84] with permission from Elsevier.

a), b), c) charts
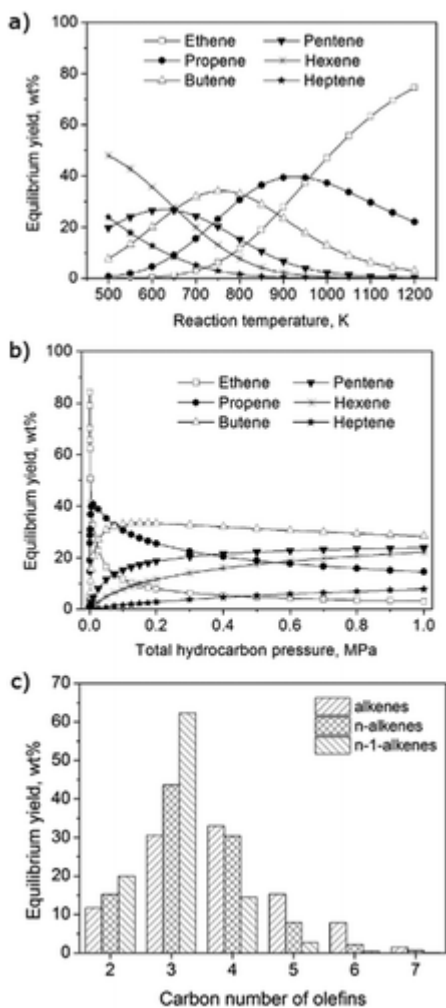
3.1.2 Oligomerization cracking of butenes

Guisnet *et al.* proposed a kinetic scheme for 1-butene transformation over ferrierite (Si/Al = 13.8) catalyst,[84] which is schematically shown in Figure 10a. According to this mechanism, the controlling step is the formation of C_8 intermediate carbenium ions, which crack into i-$C_4^=$, $C_5^=$ + $C_3^=$, and $C_6^=$ + $C_2^=$. The authors concluded that step 2 was four times faster than step 4, and that step 3 was 20–50 times faster than step 4 over their material. HT to *n*-butene (step 5) was 15 times slower than butene isomerization (step 1 and step 2), whereas HT to propene (step 7) and ethene (step 8) occurred at similar rates to step 5. HT reactions were considered irreversible steps, whereas dimerization, alkylation, and cracking reactions were reversible. A more general oligomerization-cracking scheme neglecting HT reactions is shown in Figure 10b.

Figure 10. (a) *n*-Butene dimerization-cracking mechanism on ferrierite zeolite catalyst. Reprinted from[85]with permission from Elsevier. (b) More general oligomerization-cracking scheme neglecting HT reactions.[93] With permission of Springer.

a)

b)
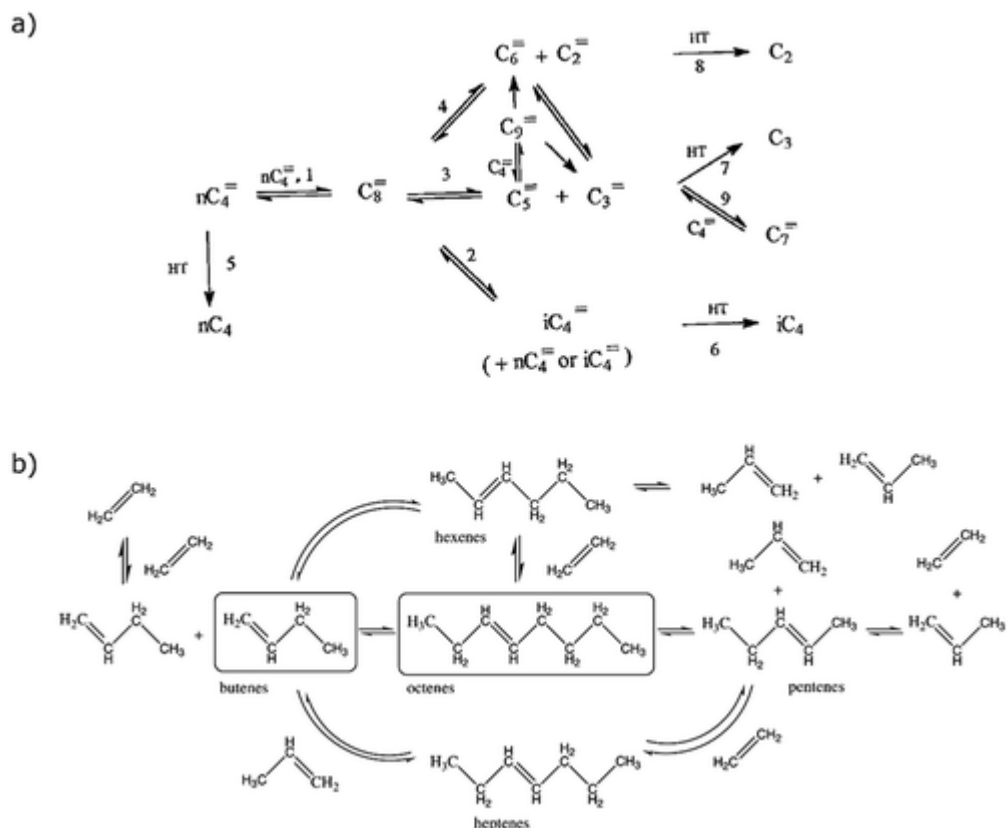
Several reaction pathways for butene catalytic cracking on MCM-22 zeolites have been proposed in the literature.[86-88] According to Xu *et al.*, the following reactions are involved in the process[88]: (1) isomerization of 1-butene, (2) oligomerization, (3) cracking, (4) dehydro-aromatization, (5) HT reaction, (6) alkylation, and (7) coking, where polycyclic aromatics are considered as coke precursors.

Arudra *et al.* proposed a simplified reaction pathway of 1-butene cracking on silicalite-1.[89] 1-butene is protonated by Brønsted acid site to form a 2-butyl cation. The 2-butyl cation converts to *trans-* and *cis-*2-butene by deprotonation, octane, and dodecene isomers by oligomerization and isobutene by skeletal isomerization. Octene and dodecene isomers undergo cracking to form alkenes. Alkenes undergo HT to form alkanes and aromatics.

Zhu *et al*. proposed a comparable reaction network for the transformation of butenes on a ZSM-5 zeolite of Si/Al = 25.[90] An intermediate $[C_8]^+$ carbenium-like species is cracked by *β*-scission into propene and a $[C_5]^+$ carbenium ion (step 1), which may crack further into propene and ethene or be desorbed as $C_5^=$. Furthermore, $[C_8]^+$ may produce higher oligomers $[C_{12}]^+$, which can crack into lighter hydrocarbons. Aromatic and paraffin formation takes place by dehydrocyclization and HT reactions, respectively. Zhao *et al*. also proposed a bimolecular mechanism for C_4 olefin cracking on both parent and P-modified ZSM-5 zeolites.[91] Meng *et al*. also suggested a bimolecular mechanism based on the experiments they carried out for the catalytic pyrolysis of *n*-butene at temperatures between 480 and 560°C.[92]

For commercial operations, however, relatively high conversion levels are necessary. Under these conditions, a range of olefins with different chain lengths are available to oligomerize with butenes, leading to intermediate carbenium-like species of different chain lengths adsorbed on the zeolite acid centers. This contributes to the observation of pentenes, hexenes, heptenes, and so on, in addition to the most abundant octenes, as illustrated in Figure 10b.[93] Each of these species can also participate in HT reactions, leading to different alkanes, cyclic, and aromatic molecules.

Lin *et al*. studied the conversion of 1-butene and pentene over ZSM-5 zeolites with similar aluminum content but different acid strength distributions.[94] This is achieved by different treatments. For instance, a phosphoric acid treatment allows to remove very preferentially weak acid sites, a nitric acid treatment (6 M) removes both strong and weak acid sites, while a treatment with nitric acid (2 M) allows increasing the proportion of strong/weak acid centers. The authors observe that the *P/E* ratio is the highest over the zeolite with the least acid strength. The authors defend that a lower acid strength would favor a less demanding type B cracking mode of the C_8 adsorbed intermediate to propene and pentene vs. the more demanding type E β-scission to ethene and hexene. Overall, the authors conclude that, to maximize the *P/E* ratio, butene is a suitable feedstock (since monomolecular cracking is minimal in this case) and that low temperatures (450°C) and low acid strength are favorable to this end. By contrast, to maximize ethene, cracking of pentene at high temperature (550°C) over a strong acid zeolite would be favorable.

In spite of the mechanisms proposed to explain the catalytic results observed, very few kinetic models have been reported in the literature. Zhou *et al*. developed a kinetic model of 12 reactions for light olefin interconversion on the

SAPO-34 catalyst.[95] The authors grouped the different carbenium-like species in a single lump (C_x^+), which can crack to light alkenes (C_2–C_4), methane, and C_{5+} olefins. Light paraffins (C_2–C_4) were formed by HT reactions. Notably, the marked shape selectivity of SAPO-34 inhibited C_5 and C_{5+} paraffin formation. In addition, they observed a higher propene yield at low partial pressures of the reactant. Oliveira *et al*. studied the catalytic transformation of ethene and 1-butene on sodium-exchanged ZSM-5 zeolites at different temperatures and partial pressures.[96] They proposed a kinetic model which took into account the acid strength heterogeneity of the catalyst by resorting to Polanyi-type equations that linked the activity of an acid site with its acid strength.

Epelde *et al*. deeply studied the effect of operating conditions on a K-modified ZSM-5 zeolite (Si/Al = 140) catalyst with a high selectivity to propene in the transformation of 1-butene.[97] They established a region of optimum propene yield >30% and propene selectivity >50% for temperatures above 500°C and space times varying depending on the reaction temperature. Furthermore, they recommended co-feeding 50% of inert gas to minimize deactivation by coke. Based on their results, a kinetic model of eight lumps (methane, ethene, propene, C_2–C_3 paraffins, butanes, butenes, C_{5+} hydrocarbons, and aromatics BTX) was established, with elementary reaction steps for the transformation of 1-butene.[98] The model is suitable for quantifying the evolution of lump concentrations (especially propene) in a wide range of operating conditions: 400–600°C, space time up to 1.6 (g catalyst h)(mol CH_2)$^{-1}$, and 1-butene partial pressure in the feed between 0.375 and 1.35 bar.

Notably, in addition to the scarcity of kinetic models developed in the literature for olefin cracking, no model has been developed to account for catalyst deactivation in this application. Yet, as will be shown in the following sections, catalytic stability has been recognized as an important variable in the academic works, notably spurred by the interest of developing lower-cost processing schemes, some of which will be described at the end of this review (Section 4).

3.2. Cracking butenes

In this section, a survey of recent results obtained in the cracking of $C_4^=$ olefins is presented. We have grouped these efforts on the application of zeolites with different porous structure (Table 4) and on the modification of the properties of ZSM-5 in order to enhance propene selectivity (Table 5). It should be noted that most of the studies in the literature are focused on the transformation of the

isomer 1-butene. However, 1-butene will rapidly reach the thermodynamic equilibrium (among the *n*-isomers) at the entrance of the reactor.

Table 4. Summary of the main zeolite systems studied for $C_4^=$ olefin cracking.

[CSVDisplay Table]

Table 5. Selected butene cracking results over modified ZSM-5 zeolites.

[CSVDisplay Table]

3.2.1. Zeolites with different porous structures

Zhu *et al*. studied the cracking of 1-butene at 620°C on different zeolite structures.[90] Their work shows that zeolites with relatively large pore size and high acid strength (Y, Beta, MCM-22, ZSM-5) lead to high olefin conversion. By contrast, small pore zeolites ZSM-35 and SAPO-34 are less active in spite of a high acidity, which is attributed to mass transfer limitations. In its turn, zeolite ZSM-22 leads to low conversion due to its weak acid strength. Results on ZSM-23 are intermediate. Wang *et al*. studied the cracking of 2-butene on ZSM-23 (MTT topology) with different Si/Al ratios.[99] With a Si/Al ratio of 30, the highest propene yield (32.94%) and 2-butene conversion (79.8%) were achieved at 600°C and WHSV = 2.5 h^{-1}.

Nevertheless, zeolites with smaller pores afford a tighter restriction on the development of secondary reactions which proceed through bulky intermediates, particularly bimolecular HT reactions leading to undesired paraffins and aromatics. This restriction can be compared by means of a HT index (HTI), usually defined in the case of cracking butenes as HTI = (selectivity to propene + butenes)/(selectivity to propane). Some results are plotted in Figure 11. One should consider, however, that this index may differ depending on the operating conversion level and the aluminum content of the material, among other factors.

Figure 11. Hydrogen transfer index in the cracking of butenes over different zeolite structures. Reprinted from[90] with permission from Elsevier.
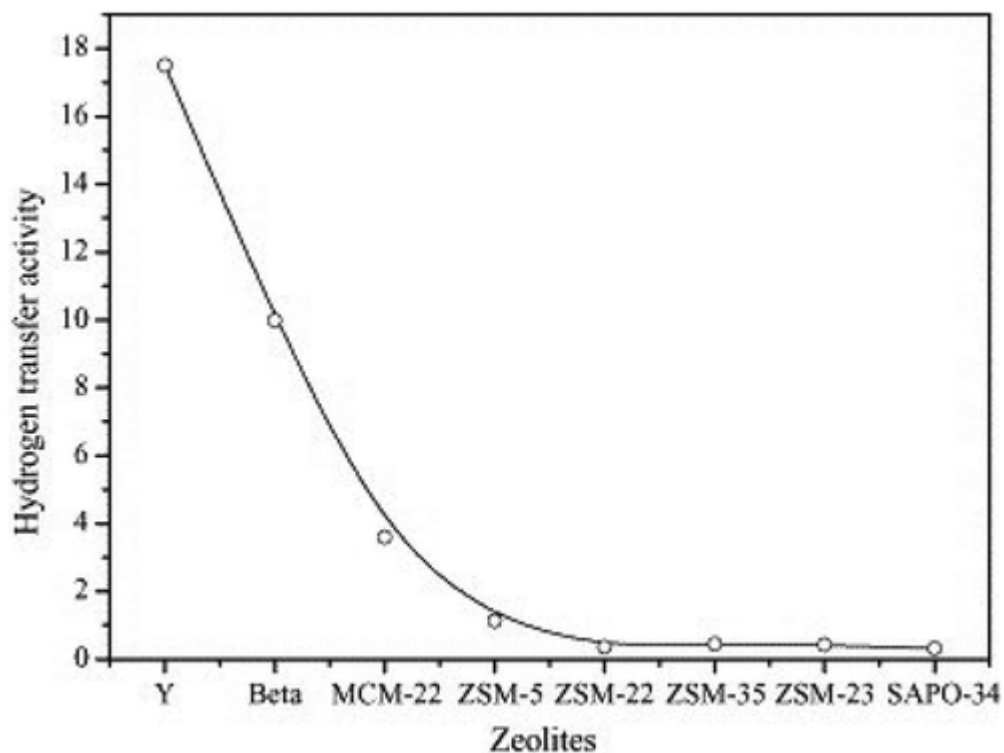
Since its development by researchers at Mobil in 1986,[100] MCM-22 zeolite has been widely used in many hydrocarbon processing reactions, including the isomerization of 1-butene to isobutene.[86] Due to its unique porous structure which consists of two independent pore systems, it is receiving much attention for the catalytic cracking of C_4 alkenes. Zhu *et al*. compared the performance of MCM-22 and ZSM-5 on the cracking of 1-butene at 620°C.[87] The former exhibited high selectivities of propene and ethene. However, MCM-22 exhibited lower activity and stability in comparison to ZSM-5 zeolite, which could be attributed to the fast coking of the large supercages of MCM-22 at the initial reaction stage. Xu *et al*. established an optimum temperature of 580°C and a suitable feed conversion of 50–60% for enhancing propene production from 1-butene on a high silica MCM-22.[88]

Zhao *et al*. studied a series of ZSM-48 samples for the cracking of C_4 olefins.[101] ZSM-48 of relative low Si/Al ratio was suitable to produce high propene yield. Moreover, ZSM-48 zeolite provided higher propene selectivity and lower coke deposition in comparison to ZSM-5 due to its lower acidity.

Yang *et al*. studied the performance of MCM-49 zeolite on the cracking of 1-butene.[102] A propene and ethene selectivity of 51.4% was obtained for a 1-

butene conversion of 90.8% at 580°C, WHSV of 9.4 h^{-1}, and 1-butene partial pressure of 1 bar.

Mordenite, which possesses stronger acid strength than ZSM-5, has also been studied in the cracking of 1-butene.[91] Its initial selectivity to ethene and propene was comparable to ZSM-5, but its deactivation was much faster.

ITQ-13 is a recent zeolite first synthesized by Boix *et al*.[103] It is the only zeolite reported to date that possesses 9- and 10-membered ring channels. Over this material, Zeng *et al*. obtained a propene yield of 36.5 wt.% at 500°C and WHSV = 3.5 h^{-1}.[104]

The group of Baba proposed a model in several articles defending that shape selectivity in olefin cracking occurs mainly over the transition state. In particular, they studied a number of zeolites with 8-, 10-, and 12-membered rings and found a correlation between selectivity to propene and diameter of the zeolite cavity rather than acid strength or pore diameter.[105] This is attributed to the confinement effect that the cavity exerts on the carbocation reaction intermediate. Hence, 1-butene cracking would occur through octyl carbenium-like species, which would be better accommodated in cavities of around 180 Å^3, like those in Beta, MCM-68, ferrierite, or SAPO-34, which show indeed high propene selectivity.[106] The authors have also used this model to interpret cracking results feeding ethene, pentene, or hexane.[107]

SAPO-34 is being widely studied as a catalyst for processes selective to propene, including ETP, MTP, and olefin cracking. In the case of olefin cracking, its porous structure, composed of big cages (0.67 x 0.11 nm) interconnected through small windows (0.38 x 0.38 nm) formed by 8-membered rings, is suitable to suppress secondary reactions, leading to heavy and branched hydrocarbons. Thus, compared to ZSM-5, SAPO-34 could limit isobutene formation, which would rise the propene and ethene concentrations in the equilibrium between light olefins.[108] Zhou *et al*. studied the interconversion of light olefins on SAPO-34 at 450°C.[95] They observed that a partial equilibrium between *n*-butenes, propene, and ethene can be reached in the direction of the strongest descend in Gibbs free energy, while HT reactions occur at slower rates. Liu *et al*. further demonstrated that interconversion between propene and ethene occurs extensively under usual naphtha cracking conditions.[109]

Epelde *et al*. studied the differences among the deactivation pathway on ZSM-5 zeolite and SAPO-34 in the transformation of 1-butene to propene at 500°C.[69] The structure of SAPO-34 mentioned above prevented the diffusion of

alkylated aromatics out of the structure, leading to the eventual blocking of the active sites. By contrast, ZSM-5 structure, with a higher connectivity and no cavities, favored the diffusion of the aromatics that evolved for a longer time outside of the micropores. However, the deactivation observed by Epelde *et al.* was slower than the one reported by Tang *et al.*[108] and Zhu *et al.*,[90] which could be related to the binding of SAPO-34 with bentonite and alumina that contributed to delaying micropore blockage.

Another silicoaluminophosphate related to SAPO-34 (CHA) is its isomorphic structure SAPO-18 (AEI). In fact, SAPO-18 can be intergrown along with SAPO-34, which was patented as an MTO catalyst by ExxonMobil.[110] These intergrown catalysts, as well as the pure phases, were recently explored for 1-butene cracking by Hu *et al.*[111] A high selectivity ethene + propene of 90% at 70% conversion was reported for the intergrown catalyst at 500°C with a feed of pure 1-butene. Moreover, their results suggest that selectivity of SAPO-18 to propene could exceed that of SAPO-34 in this reaction. More recently, the same group compared zeolites Beta, ZSM-5, and pure SAPO-18 with varying aluminum contents for the cracking of 1-butene.[112] SAPO-18 yielded the highest selectivity to propene at a given conversion level. However, coke deposition and deactivation were the highest on SAPO-18 due to its small pores. The authors defend that SAPO-18 is particularly selective to propene, thanks to the transition state shape selectivity of its pear-like cages of 1.27 × 1.16 nm, which would favor the dimerization of 1-butene and the subsequent β-scission of the octyl cations.[112] This is also corroborated by Epelde *et al.*, who compared the transformation of 1-butene on both isomorphic structures SAPO-34 and SAPO-18 at 500 °C.[71] The latter showed a higher stability, where the propene selectivity and yield increased over time, as secondary reactions were selectively neglected and coke condensation was slowed down.

Among all the catalysts summarized in Table 4, ZSM-5 is being widely studied in the literature. Several initiatives are being suggested in order to modify its porous structure and alter its acidity by different methods. Postsynthesis methods, in particular, will be addressed in the next section. The effect of the Si/Al of ZSM-5 zeolites in the cracking of butenes has been analyzed in detail.[72, 90, 97, 113, 114, 115, 116] In general, the number of acid sites goes in hand with the framework aluminum content of the zeolite.[117] Therefore, a high Si/Al ratio is recommended for olefin cracking in order to decrease the number of acid sites as well as to enhance hydrothermal stability. High propene selectivity is achieved as secondary reactions are suppressed to some extent, although this increase also entails a decrease in conversion. With a Si/Al = 183, the authors

achieve a molar yield to ethene + propene close to 55% and stability for hours at 620°C.[90] Accordingly, Epelde *et al*. selected a Si/Al ratio of 145 as the most suitable for 1-butene cracking at 500°C, W/F = 1.6 g cat h mol^{-1}, and 1.35 bar.[114]

Arudra *et al*. studied 1-butene cracking over ZSM-5 zeolites and silicalite-1 at a given GHSV.[89] They observed that silicalite-1 yielded a product slate much richer in olefins and propene, whereas with Al-containing ZSM-5 paraffins and aromatics form extensively. The authors defend that silanols present on silicalite-1 are able to catalyze isomerization, and oligomerization cracking of butene, but not HT reactions. Silanol concentration was increased with NH$_3$ treatment, slightly increasing selectivity to propene. It may be argued, however, that contact times are too long in these experiments (2 ml cat, 5 ml min^{-1} feed, 25 ml min^{-1} N$_2$). Consequently, aromatization and HT occur extensively. On the other hand, silicalite-1 may contain Al traces (Si/Al around 2000) which might become relevant at long contact times. Ammonia treatment, in its turn, desilicates slightly the catalyst, hence affecting the small amount of aluminum loaded in the reactor.

3.2.2 ZSM-5 postsynthesis modification for propene production

Postsynthetic modification of zeolites to improve their properties for the desired application is a common practice. A classic example is the steaming of faujasite-type zeolite to produce ultrastable Y zeolite (USY), which is the basic component of the catalysts used for catalytic cracking in the oil refining industry.[75] This procedure partially dealuminates the zeolite. Is it also frequently accompanied by a treatment in which rare earth metals and/or other cations are incorporated into the zeolite to increase the framework resistance to dealumination.[118, 119] Naturally, similar treatments aiming to modify the zeolite crystals (e.g., by introducing mesopores or by passivating the external surface) or to introduce different species in the zeolite have also been explored in olefin cracking. In this section, we review some of these initiatives that have been applied for C$_4^=$ olefin cracking on ZSM-5 zeolites, a summary of which is presented in Table 5.

The incorporation of P to increase ZSM-5 stability in cracking has been studied in depth.[117, 120, 121, 122, 123, 124] Diverse P sources have been employed, including organic (($CH_3O)_3P$, $(CH_3)_3P$, $(C_6H_5)_2POH$, *etc*.) and inorganic (H_3PO_4, PCl_3, PCl_5, $(NH_4)_3PO_4$, $(NH_4)_2HPO_4$, $(NH_4)H_2PO_4$, *etc*.) compounds.[123, 125] The effect of P incorporation depends on the P source used and usually involves a decrease in the concentration and acid strength of the acid sites remaining.[126] This

increases the hydrothermal stability of the ZSM-5 zeolite and its selectivity to propene.[123, 125, 127, 128] According to Xue *et al.*, some bridging OH groups in the zeolite are substituted by P-OH groups that are stabilized by the framework and become hydrothermally stable.[123] Blasco *et al.*[125] highlight the reversibility of the P interaction with the zeolite structure, in agreement with the results by Liu *et al.*[129] The latter authors also attributed to the P incorporation a decrease in the micropore volume and a partial blocking of the same. These authors also studied the evolution of P-containing zeolites subjected to stream treatment. The catalytic performance of several P-modified zeolites is summarized in Table 5.

Wang *et al.* analyzed the effect of 0.1–6 wt.% P addition to ZSM-5 zeolite in the conversion of different feedstocks: methanol, 1-butene, and methanol + 1-butene mixture.[130] The highest yield to propene (44%) was obtained upon reaction of the mixed feedstock, exceeding by 7.4% and 4.5% the yield to propene in the conversion of pure 1-butene and methanol, respectively.

Zhao and coworkers observed that P addition caused dealumination, reducing the strength and acidity of their materials, and the appearance of certain mesopores, resulting in reduced propane formation and higher propene selectivity.[120] According to the authors, reducing the number of acid centers hinders biomolecular reactions leading to coke, which improves the catalytic stability. As consistently reported by other NMR studies,[126, 131] phosphorus affected the coordination of tetrahedral framework aluminum atoms to distorted tetrahedral or pentacoordinated, although these species remained active in C_4 olefin cracking.

Li *et al.* also studied P and Fe addition to ZSM-5 (Si/Al = 25).[132] P addition drastically reduces Brønsted and Lewis acid sites, whereas the exchange of Fe cations may increase Lewis acidity. P incorporation causes some dealumination in the form of aluminum phosphate (−14 ppm). This octahedral EFAl linked to the phosphorus would play an active role preventing further dealumination. Addition of Fe releases phosphate coordinated to EFAl. In absence of P, iron agglomerates as clusters and Fe_2O_3 particles, but it is dispersed as isolated Fe^{3+} cations in the presence of P. Upon addition of P, cracking of 1-butene is more selective to pentenes and less selective to ethene, which would be related to a lower acid strength favoring an oligomerization-cracking mechanism of butene. Pérez-Ramírez *et al.* demonstrated that by postsynthesis incorporation of Fe, the nature of the resulting Fe species can depend on the structure of the zeolite employed.[133] Thus, extraction of Fe isomorphically substituted in

framework positions is proposed as a method to obtain more comparable Fe distribution.

Li *et al*. studied the effect of Ni addition on P-modified ZSM-5 zeolites in the cracking of butene and pentene.[134] The interaction of Ni with P promoted the migration of some phosphorous species from channels to external surface of the zeolite and broke part of the Al-O-P bonds, which gave way to an increase in EFAl content. Some Brønsted acid sites were also restored, which were previously neutralized by P modification. Thus, an increase in Ni content enhanced butene conversion and ethene selectivity, while a maximum propene selectivity of 54.15 wt.% was achieved for a 1 wt.% Ni content.

Epelde *et al*. studied P- (1–5 wt.%) and K (1–5 wt.%)-modified ZSM-5 zeolites (Si/Al = 140) to increase propene selectivity in the cracking of 1-butene.[114] Al environment was greatly modified by H_3PO_4, where a significant conversion of FAl^{IV} sites into P-$EFAl^{VI}$ sites was achieved. The catalyst lifetime was enhanced by this P treatment. KOH treatment led to a notable change in the acid distribution (measured by *t*-butylamine) caused by desilication.[135] The authors defend that modification with 1 wt.% K improves substantially the selectivity to propene while slightly reducing the conversion. Moreover, it seems that K reduces slightly the stability of these materials due to a micropore volume reduction, since a lower coke deposition results in a stronger deactivation. Zhu *et al*. also proposed K contents in the 0.7–1.0 wt.% range as appropriate to maximize propene throughput in butene cracking.[113]

Xu *et al*. studied the incorporation of different alkaline metals (Li, Na, K) on ZSM-5 (Si/Al = 13) for cracking LPG (48% butenes and 52% butanes).[136] The presence of Li^+ and Na^+ decreased the concentration of strong Brønsted acid sites, whereas K^+ affected acid centers of different strength. Consequently, the three metals can be incorporated in different amounts to fine-tune the selectivity to propene, which the authors proposed to be 0.5 wt.% Li, 1.5 wt.% Na, and 1.5 wt.% K for their material.

On the other hand, Zhang *et al*. studied the modification of ZSM-5 by incorporation of Ag. Although Brønsted acidity, activity, and selectivity of the materials in 1-butene cracking remained intact, their resistance to dealumination was substantially improved with Ag loading.[137] The authors defend that Ag cations can replace protons while steaming or regenerating in humid air, preventing dealumination, whereas in a reducing atmosphere, these Ag^+ cations are reduced to Ag atoms.[138]

Rare earth metals have also been explored in order to modify the basicity of ZSM-5 zeolite, which gives way to a decrease in the readsorption of the basic compounds of the cracking products, such as ethene and propene, being one of the major causes of higher light olefin formation.[139] Xue *et al*. observed a notable increase in the propene yield upon W incorporation on ZSM-5 zeolite.[122] A higher coke deposition took place, which could be related to the higher activity of the catalyst. However, the authors did not observe a significant effect upon W addition to a P-modified ZSM-5 zeolite. On the other hand, the same group reported that La incorporation to P-modified ZSM-5 zeolites afforded zeolites hydrothermally stable and selective to propene in the cracking of 1-butene.[123] According to the authors, La retards the dealumination process and provides Brønsted acid sties associated to the hydrolysis of La in the zeolite cavities.

Zhu *et al*. modified ZSM-5 zeolites by steaming treatment for their use in 1-butene cracking.[140] They concluded that with increasing treatment temperature and time, the acid density and the acid strength of ZSM-5 decreased, which is the desirable effect to enhance propene selectivity. In addition, by leaching out the nonskeletal Al produced by the steam treatment with citric acid, the pore volume of ZSM-5 was enlarged and had a better capacity of accommodating the carbon deposit; thus, catalyst life was prolonged.

Zhang *et al*. applied several posttreatments to ZSM-5 zeolites and were tested in 1-butene cracking: alkaline treatment, steam treatment, and a combined alkaline-steaming treatment.[141] These treatments contributed to enhancing propene selectivity and catalyst stability.

Gao *et al*. treated ZSM-5 zeolite (Si/Al = 14) with NaOH.[142] By this alkali treatment, new mesopores were created due to the removal of siliceous species. The density of Brønsted acid sites in the material was decreased, whereas new Lewis sites were generated by the treatment. Low NaOH concentration (0.1–0.2 M) was recommended to achieve high ethene and propene yields in the cracking of butene, of 81.6% and 79.4%, respectively. Jung *et al*. cracked *n*-octane over NaOH-treated ZSM-5 zeolites. They concluded that the treatment did not result in a higher overall selectivity to alkenes but that selectivity for propene could increase, thanks to the rapid elution of primary cracking products.[143] Careful assessments are therefore necessary about the value of the whole product slate obtained,[144] particularly as these alkali treatments often lead to a loss of valuable zeolite material.[145] As an alternative to introduction of mesopores[146, 147] as the authors observed in the cracking of gasoil,[148] one could

also anticipate benefits in the use of smaller zeolite crystals[147] to boost propene selectivity in the cracking of olefins, particularly of longer more reactive olefins[149] and/or over zeolites structures of low dimensionality.

Lv *et al*. synthesized hierarchically structured ZSM-5 zeolites by a mesoporogen-free procedure and subsequently modified with varying amounts of phosphorus (1–3 wt.%) through impregnation of phosphoric acid solution.[150] The hydrothermal stability of ZSM-5 was enhanced by this treatment due to the additional mesopores formed.

Fluorination with NH_4F has also been studied as a possible modification of ZSM-5. Although it is proposed that fluorine can replace some surface oxide or hydroxide groups, polarize the framework, and affect acid strength and cracking activity.[151, 152] However, this treatment also leads to significant dealumination of the material, which itself will affect acid strength and catalytic stability.

Recently, Abdalla *et al*. studied the surface modification of ZSM-5 catalyst by silica deposition using chemical liquid deposition method as well as core-shell silicalite composite.[116] Core-shell composite showed higher propene yield and higher *P/E* ratio for catalytic cracking of 1-butene, which was attributed to an effective surface passivation. Moreover, this composite also showed a better stability, with a 50% lower deposition of coke.

3.2.3 Tuning the Al distribution for propene production

In addition to the incorporation of heteroatoms and hierarchization treatments, a very promising strategy is that of affecting the distribution of Al atoms, and hence acid centers, among the different crystallographic positions in a given zeolite framework.[153, 154] This can be achieved by different strategies, as we reviewed recently.[155] Among these, it is possible to modify the synthesis conditions and, in particular, the structure directing agent.

Sazama *et al*. studied the effect of the Al distribution in the framework of ZSM-5 by controlling the conditions of zeolite synthesis.[156] They performed the cracking of 1-butene on ZSM-5 zeolites with similar Si/Al framework ratio and crystal size, but with different relative concentrations of "close" and "single" framework Al atoms. They concluded that distant single Al atoms supported cracking of butenes and octenes, while close Al atoms enhanced HT reactions leading to aromatics. They also compared the effect of the Al content on the yields of products ([Figure 12](#)) at 500°C and GHSV = 15 h^{-1}.

Figure 12. Yield results in the cracking of 1-butene over zeolites with similar Al concentration but different Al distribution. $T = 500°C$ and GHSV = 15 h^{-1}. Reprinted from[156] with permission from Elsevier.
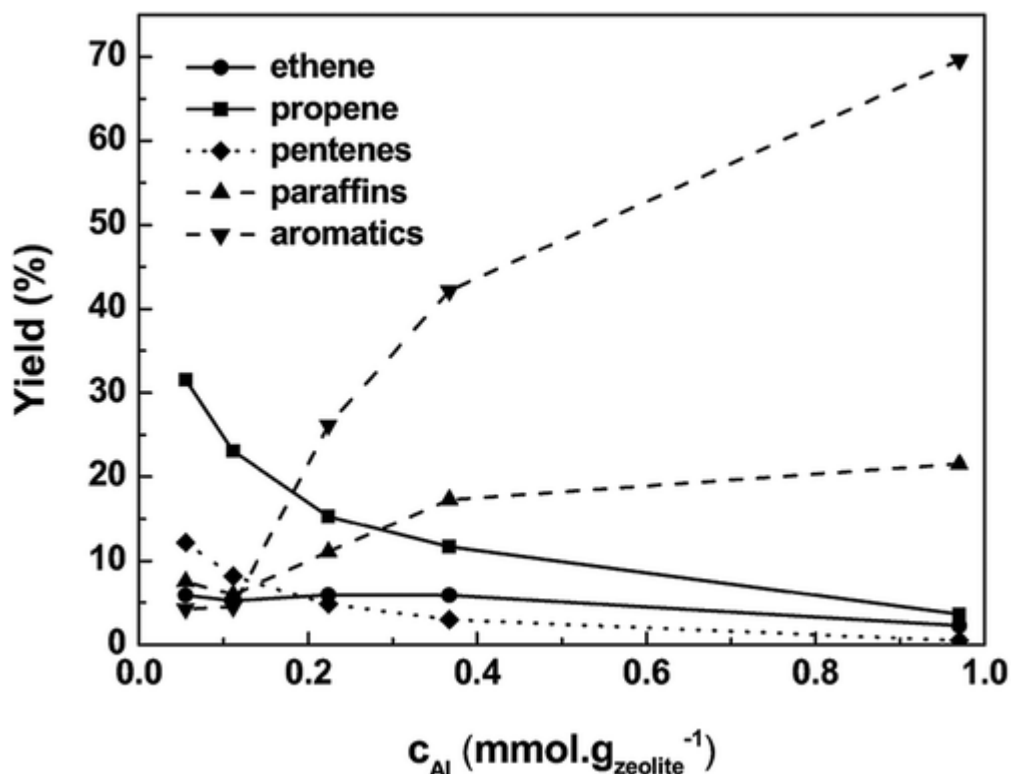
Wu *et al*. compared a ZSM-5 zeolite synthesized with the aid of TPA$^+$ to a template-free ZSM-5.[157] The template-free ZSM-5 was also further modified by TMOS (tetramethyl orthosilicate) impregnation, aiming to passivate the acid sites on the crystal surface. Upon exchange with Co(II), the TPA$^+$-assisted ZSM-5 shows a preferential location of acid sites at the channel intersections, in agreement with the location of TPA$^+$ during the synthesis. By contrast, the template-free ZSM-5 shows a notably higher proportion of Al located in pore channels (Figure 13). These results are in agreement with those reported previously by the groups of Kubota, Tatsumi, and Dĕdeček about the effect of synthesis conditions on ZSM-5.[158,159,160] As a result, the template-free zeolite leads to a 5 wt.% increase (from ca. 46 to 51 wt.%) in the yield to propene + ethene at a butene conversion level around 93%.[157] TMOS modification reduced butene conversion and increased ethene + propene yield. Unfortunately, conversion levels in this work are very high, which makes it difficult to gauge real benefits. At these conversion levels, sequential reactions of the light olefins formed may occur to a notable extent so that small changes in butene

conversion may lead to large changes in yields to light olefins. Moreover, a total yield of ethene + propene around 55 wt.% could be close to the maximum allowed by the thermodynamic equilibrium among olefins.[84]

Figure 13. (a) Possible locations of Co^{2+} in the channels of ZSM-5 zeolite (a: sinusoidal channels; b: straight channels; c: channels intersections). (b) Vis absorption spectra of ZSM-5 zeolites with different Al distributions. Reprinted from[157] with permission from Elsevier.
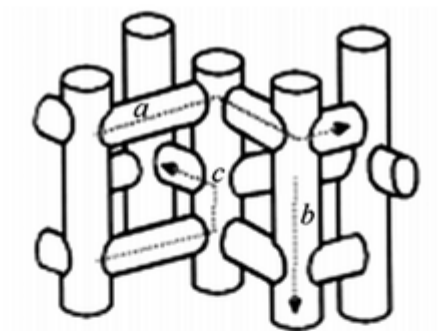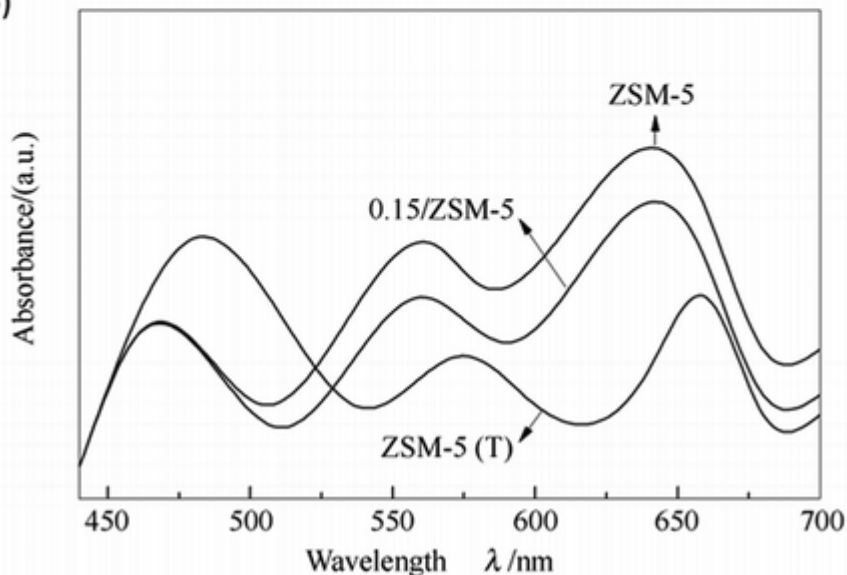
Jin *et al.* proposed a mild dealumination method for adjusting ZSM-5 acidity which is also applicable to Y and Beta zeolites.[161] They named this method "dry steaming dealumination," as this treatment does not need additional chemicals or steam. The dealumination was carried out by making use of the self-adsorbed water on the zeolite, at temperatures above 400°C. Thus, the control of operating variables as well as treatment methodology is simpler than in the

conventional steaming method. Ibáñez *et al*. studied the effect of this modification on 1-butene cracking.[162] Dealumination took place transforming specific strongly acid, framework tetrahedral Al species (located within the micropores) into distorted and extra-framework species. In addition, the acid site density was shifted toward the intersections of the zeolite micropores (of weaker acidity), which leads to the selective suppression of HT reactions, with the corresponding increase in propene selectivity. A 500°C-steamed catalyst boosted propene selectivity up to 69% with a drop of coke deposition by 34% compared with the parent ZSM-5 zeolite (Si/Al = 15).

3.3. Cracking pentenes and higher olefins

Although the availability of butenes in a refinery or petrochemical plant is usually higher than that of pentenes and higher olefins, these are also produced in important amounts in processes such as FCC, metathesis, or MTO. Furthermore, cracking olefin-rich C_4 streams may present difficulties, such as the accumulation of C_4 paraffins in the recycle loops. In fact, separation of isobutene from C_4 olefins is not easy and often requires extractive distillation. Alternatively, this C_4 olefin-rich stream could be subjected to an oligomerization step to olefins in the C_5–C_8 range, as proposed in.[163] Remarkably, the authors already reported the activity of silicalite-1 in olefin cracking back in the 1980s, although only recently this material has started to attract interest for some catalysis. Other catalysts they proposed include boralite or Cr-silicalite. Interestingly, it has also been reported that the incorporation of substantial amounts of olefins to the cracking of paraffins could increase their conversion and selectivity to propene.[164] From a mechanistic point of view, we interpret that this could be due to an easier start of the catalytic cycle through formation of reactive carbenium-like species on the catalyst surface. The reaction would further proceed through bimolecular hydride transfers and β-scissions without the need of high-energy pentacoordinated carbocations to activate the alkanes.

Long *et al*. report on the high amounts of C_5–C_8 alkenes in Chinese FCC gasoline.[165] They propose their conversion to isoparaffins and aromatics on ZSM-5. At low temperatures of 200°C, isomerization and HT reactions take place, but cyclic olefins are formed instead of aromatics. Selectivity to aromatics increases with temperature, whereas selectivity to isoparaffins peaks at 300–350°C. At 450°C and short contact times, propene, butenes, and pentenes are formed, but their selectivity decreases markedly with contact time.

Wang *et al*. studied 1-pentene cracking on USY at temperatures between 250 and 350°C.[166] They observed that the initial high activity of cracking and HT reactions decreased rapidly in the first minute of reaction along with a strong coke deposition (13%–16% wt. coke/wt. catalyst), after which double-bond isomerization remains the main reaction. For a given TOS, a higher temperature favors desorption of coke precursors; therefore, the total amount of coke deposited is lower, but it becomes more aromatic.

Recently, Lin *et al*. studied the cracking of 1-pentene over ZSM-5 zeolites with different Si/Al ratios, some of which were treated postsynthesis to affect their acid strength distribution.[94] They observed an increased propene/ethene ratio, with catalysts possessing a lower acid strength, which would point to a higher extent of oligomerization-cracking reactions. However, it should be acknowledged that this ratio is strongly dependent on the feed conversion. They also studied the co-cracking of pentene and butene and discussed the mechanisms: monomolecular cracking of 1-pentene but not butene would be possible over strong acid centers. Conversions obtained are lower than expected, which the authors attribute to a feed composition closer to equilibrium, although the effect of contact time or deactivation is not taken into account.

As mentioned above, Koyama *et al*. propose that the pore volume of the zeolite is a chief factor to enhance propene selectivity in olefin cracking. In particular, the pore volume of the zeolite could be selected to accommodate the volume of the carbenium-like transition state that yields propene by β-scission.[105] This way of thinking could orient the design of novel zeolites in other reactions, too.[167] The authors examined the effect of the pore volume of zeolite on the propene selectivity in the conversion of pentenes (2-pentene and 2-methyl-2-butene) and 1-hexene on different zeolite catalysts including MCM-35, ZSM-22, SAPO-34, Y, and ZSM-5 at 500°C.[100] ZSM-22 and MCM-35 showed similar ethene and propene selectivity for the conversion of 2-pentene, while the catalytic activity of ZSM-22 was about 10 times higher than that of MCM-35. On the other hand, SAPO-34 and ZSM-5 zeolites with larger pore volumes than ZSM-22 and MCM-35 showed lower selectivities. The cracking of 2-methyl-2-butene was performed on 10-MR zeolites (ZSM-5 and ZSM-22). ZSM-22 (TON) was more selective to propene than ZSM-5, which is related to the differences in dimensionality. 1D porous structures are favorable to the monomolecular cracking of pentenes. This proved even more beneficial in the cracking of 1-hexene over TON-type Theta-1 zeolite.[168] Conversion seems to proceed mainly through monomolecular cracking and it is highly selective to propene (up to

90 wt.% at 90% conversion), which may be related to a particularly appropriate acid strength and/or solvating environment within the channels of this zeolite.

The role of topology was also studied by Bortnovsky *et al*. on the cracking of 2-methyl-2-butene at 500 °C.[169] Monodimensional 10-MR zeotypes and zeolites (*i.e*., SAPO-11 and ferrierite) catalyzed the cracking of pentene predominantly *via* β-scission, as there is not enough space for the formation of the oligomeric intermediates, and, thus, a low activity was observed. 12-MR 1D zeolites (*i.e*., mordenite and ZSM-12) exhibited high activity and selectivity to light olefins, where the reaction would proceed by the formation of oligomeric adsorbed intermediates. Beta zeolite (12-MR, 3D) showed a very rapid deactivation and low conversion. 10-MR and 3D zeolites (ZSM-5 and ZSM-11) showed the best performance for C_5 olefin cracking by the formation of oligomeric adsorbed intermediates. They suggested the following ZSM-5 modifications in order to modify acid strength and, thus, increase propene selectivity: (i) ZSM-5 of Si/Al > 160, (ii) moderate steaming (Si/Al = 12.5–200), and (iii) partial ammonium ion exchange of Na-ZSM-5 (Si/Al = 12.5–37.5).

Le Van Mao and coworkers studied catalysts which combine the acid function of a ZSM-5 zeolite (modified with Mo and P) and a co-catalyst dispersed on a mesoporous catalyst.[170] According to the researchers, the acid centers associated to Mo and P allow cracking bulky hydrocarbons, whereas the resulting molecules are cracked on the centers of ZSM-5. The co-catalyst consists of Ni or noble metals dispersed on yttria-stabilized alumina. This co-catalyst is thought to limit coke formation by means of hydrogen spillover coming from steam reforming of minor amounts of the hydrocarbon fed according to the authors.[171, 172] A suitable bentonite binder would allow transfer of such active hydrogen species. The propene/ethene ratio obtained in the presence of the co-catalyst is higher than in its absence (3.5 *vs*. 2.0 in 1-hexene cracking). The process is carried out at high temperatures (610–640°C) and in the presence of steam (steam/olefin wt. ratio = 0.5).[173] These catalysts have also been studied in the cracking of naphtha and gasoil at higher severity (715–725°C).[170, 174] Interestingly, other feeds have also been proposed, such as biomass-derived methanol or glycerol, which would be an interesting addition to FCC given their present surplus and tendency to generate aromatics.[175]

Lee *et al*. proposed the use of a phosphorous-modified ZSM-5 zeolite with different Si/Al ratios, incorporating lanthanum, to produce ethene and propene from a C_5 raffinate stream.[176] These catalysts have both acid and basic functionality. The acidity of LaX-P/ZSM5 catalysts decreased with increasing

lanthanum content, while basicity of LaX-P/ZSM5 catalysts increased with increasing lanthanum content. It was shown that the acid and base balance of the catalyst has a strong effect on the conversion and selectivity to olefins. Conversion increases with increasing acidity, but selectivity to olefins decreases with decreasing basicity.[176]

Li *et al*. studied the effect of Ni on P-modified ZSM-5 (Si/Al = 25) zeolites in the cracking of pentene (90% of 2-methyl-2-butene and 10% of 2-methyl-1-butene).[134] Pentene conversion increased with Ni loading owing to the increased Brønsted acidity. Propene and ethene selectivities are favored with an increase in Ni content, whereas *P/E* ratio as well as butene selectivity decreased, which indicates that the cracking route of pentene is altered where the monomolecular cracking is favored.

Nawaz *et al*. studied the catalytic cracking of 1-hexene to propene on SAPO-34 catalysts.[177] The catalyst texture was modified by mixing with or by using kaolin as the source of Si and Al in the synthesis. By using kaolin in the synthesis, a mesostructured slit-shaped material was obtained.[178] Its catalytic activity and stability were notably enhanced compared to the conventional SAPO-34 in 1-hexene cracking, thanks to improved diffusional access to the active sites, while propene selectivity at a given conversion level was preserved (Figure 14). Over this mesostructured SAPO-34, the authors achieved a propene selectivity of 73.9 wt.% at a feed conversion of 98.2% at 575°C (WHSV = 14 h^{-1}, TOS = 1 min).[179]

Figure 14. Bulk structures of SAPO-34 zeolite (a), mixed with 70% kaolin (b), and synthesized using a kaolin precursor (c). 1-Hexene catalytic cracking activity and propene yields at 500°C. Reprinted from[177] with permission from Elsevier.
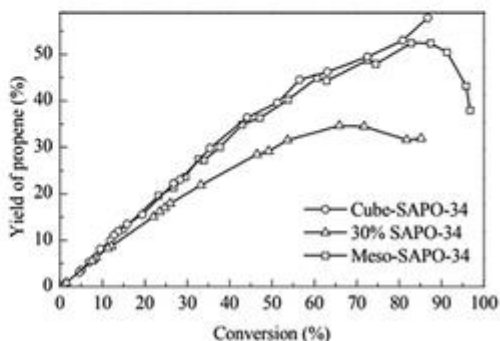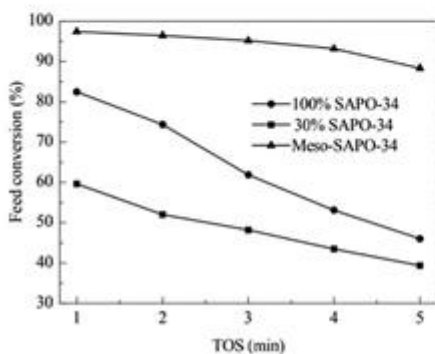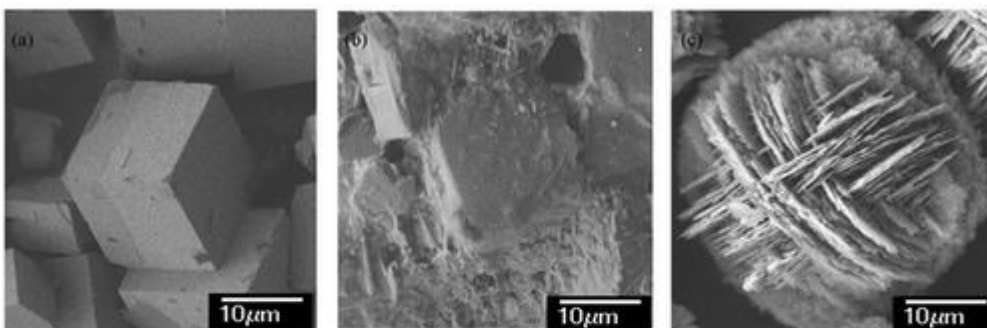
Another important consideration that is often neglected in academic studies is considering catalytic results not only for a given reaction time—be it initial or not—but during the entire catalyst lifetime. Mitchell *et al*. synthesized micron- and nanosized ZSM-5 zeolites with comparable acidity and tested them in 2-methyl-2-butene cracking.[149] They found that micron-sized zeolites were initially more selective to light olefins and produced less BTX, but they deactivated faster. However, selectivity to light olefins increased as the catalyst deactivated and thus desilicated nano-ZSM-5 zeolites, having up to six times longer lifetimes, were able to achieve the same average light olefin productivity over extended cycle lengths.

4. Industrial conversion processes for olefinic feedstocks

4.1. Ethene conversion

Processes to produce butenes and ethene by metathesis of propene were developed decades ago. With the need for on-purpose propene, these processes were reoriented to produce propene from other light olefins. However, the success of these metathesis processes for propene production has been limited due to the also growing demand of the other light olefins. For instance, a metathesis process was developed by Axens and the Chinese

Petroleum Corporation, called ICP-CPC Meta-4 process. A demonstration plant using this technology was run between 1998 and 1990, although, to the best of our knowledge, the process has not been commercially implemented so far.

Other licensors seem to have been more successful, though. Sinopec has also developed an ETP process, known as OMT. It uses a bifunctional catalyst based on WO_3/SiO_2 and MgO to achieve the metathesis and butene isomerization reactions, respectively. With this catalyst, the process can reach a propene selectivity higher that 95%, with a conversion up to 70%.[180] The process can be on stream for more than 900 h before requiring regeneration in diluted air.

However, the metathesis process that has reached the greatest commercial implementation is the OCT, which was developed by Phillips (Triolefin) and is currently licensed by ABB Lummus.[8, 181] To achieve high production, nonreacted ethene and butenes are recycled back to the reactor. OCT uses a heterogeneous W-based catalyst in a fixed-bed reactor. In this process, butene conversions between 60% and 70% could be achieved, with over 92% selectivity to propene. A small amount of coke is produced, which deactivates the heterogeneous catalyst used in the reaction, so periodic regeneration is necessary. To this end, the process uses swing reactors (*i.e.*, one fixed-bed reactor is on stream while the other is being regenerated with nitrogen). The licensor has stated that at least 18 units are currently in operation worldwide, while a similar number are in the engineering or construction stage. These processes can be integrated within various refinery processes, like a steam cracker, FCC, or etherification unit in order to increase the propene production by reacting the low-value C_4 olefins or raffinate with ethene.

Remarkably, in cases when butene is not available, it is possible to produce propene only from ethene, by ethene dimerization to 1-butene in a separate unit and subsequent isomerization to 2-butene and metathesis of 2-butene with excess ethene in the OCT process. In Table 6, we summarize the main processes to convert olefinic feedstocks to propylene through metathesis or cracking that have reached demonstration or industrial stage. The next-generation one-pot ETP catalysts that we have reviewed in Section 2 have not found translation to the commercial scale yet. Importantly, they will have to demonstrate substantial economic advantages over this classic proposal of coupled reactions to reach commercial implementation.[182]

Table 6. Main commercial processes available for converting olefins to propene.

4.2. Olefin cracking

The research and development efforts with respect to the cracking of low-value light olefinic feedstocks into petrochemical feedstocks (ethene and propene) continue by many technology licensors, catalyst vendors, petroleum refiners, and petrochemical companies. There are several proprietary olefin conversion processes under development and at various stages of commercialization, such as Propylur (Linde/Lurgi), propene catalytic cracking (PCC, by ExxonMobil), olefin catalytic cracking (OCC, by Sinopec), Superflex, or advanced catalytic olefin (ACO, by KBR).[5, 183] Modification of the conventional FCC unit to process light feedstocks and maximize olefin production is extensively applied.[76] However, the largest drawbacks of the modified FCC processes continue to be satisfying the heat balance of the unit, while preventing the degradation of the catalyst under high severity conditions, and the capital costs associated with some designs that require multiple processing trains.

The Propylur process was originally developed by Lurgi[184] and is currently licensed by Linde. Propylur converts a C_4–C_5 feedstock into propene, and some ethene and butenes. The process employs an adiabatic fixed-bed reactor, similar to that employed in a Claus unit, which operates at 500 °C and 1–2 bar to convert the olefinic hydrocarbon streams to light olefins by using a ZSM-5-type catalyst and steam injection. The first Propylur demonstration facility was installed in 2003 at a BP refinery in Germany. This unit processes an olefinic subproduct with a 60% yield of propene and an additional 15% yield of ethene.[185]

The olefin cracking process is licensed by UOP/Total and was developed to produce propene and ethene, with a high ratio of propene to ethene (P/E = 3–4) by catalytic cracking of light olefins (C_4 or naphtha olefins up to C_8) from steam cracker, FCC, delayed coker, or even methanol-to-olefins. This is a catalytic cracking process in a fixed-bed reactor, which operates at high temperature (500–600 °C) and moderate pressure (1–5 bar) and uses a proprietary UOP zeolite that must be periodically regenerated, using several reactors in parallel to allow regeneration. The first unit of this process was installed at AtoFina's (now Arkema) Antwerp refinery in 1998.
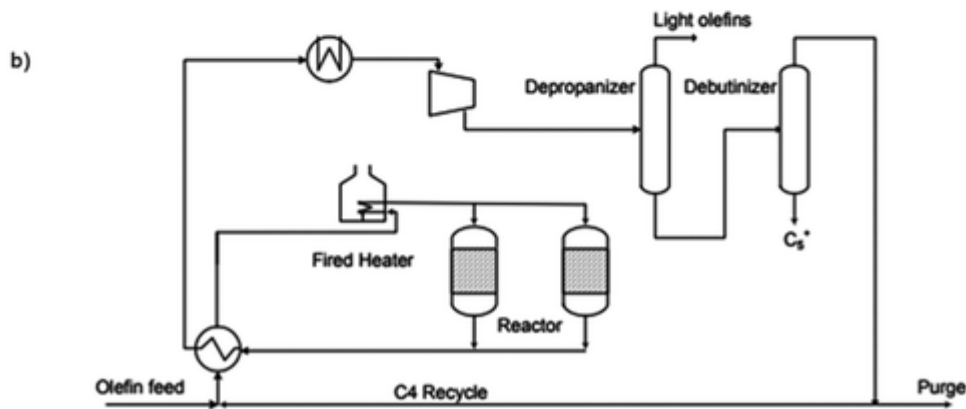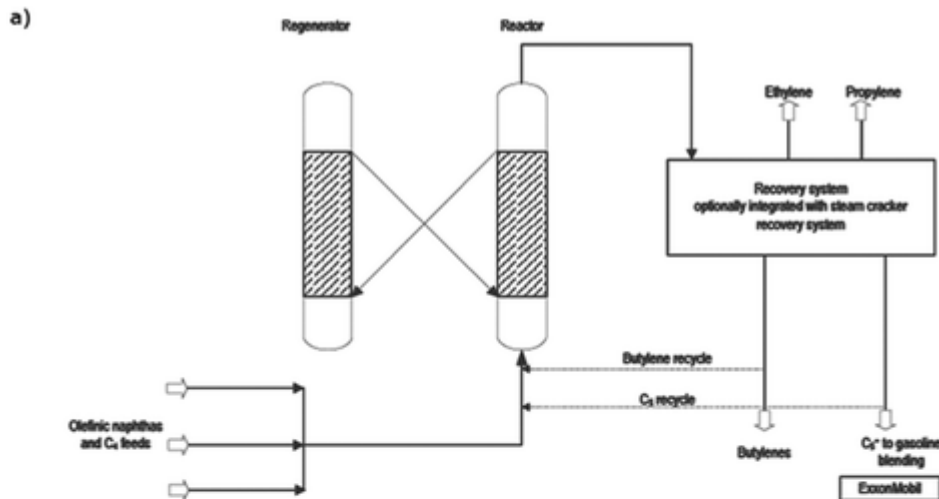
Superflex is a technology originally developed by Arco Chemical Technology (now LyondellBasell) that is now licensed by KBR. It comprises an FCC-based process that produces light olefins (yields to ethene and propene up to 50%–

70%) as well as some aromatic naphtha. The process is fed with olefinic C_4–C_8 streams, which generally come from a conversion process (light coker, visbreaking, FCC naphtha, steam cracker subproducts or olefins from other units like etherification, butadiene conversion, *etc*.). The olefinic feedstock is completely cracked in the riser, which operates at higher temperatures than a conventional FCC unit (500–700 °C) and at the same pressure (1–2 bar). Recycle of nonconverted products to total extinction can also be used in order to increase conversion of the feedstock.[183, 186] The process uses a proprietary catalyst, based on a ZSM-5 zeolite. Coke generation is low, so in order to satisfy the heat balance it is necessary to burn fuel oil in the regenerator. The first commercial Superflex unit was started up at Sasol in South Africa in 2006. This unit converts a highly olefinic C_6–C_7 stream to propene and ethene and has a propene capacity of approximately 250 ktpy. Jihua is the second licensee, located in Jilin City, China. The capacity of that unit will be 200 ktpy of propene from C_4 and C_5 olefinic feedstocks.

KBR and SK have also jointly developed another process for olefin cracking: the ACO. This process consists of an FCC-type unit with dual-riser system, closed cyclones, a third separator, and a proprietary zeolite catalyst especially designed to improve its hydrothermal and mechanical resistance. The ACO process operates at very high temperatures, up to 650 °C, to maximize yields of ethene and propene from naphtha streams.[183, 187]

PCC is another process for light olefin production (ethene, propene, and butenes) from olefinic naphthas coming from other cracking process (mainly FCC, steam cracking, coker, *etc*.), developed by ExxonMobil.[188] The PCC process uses a fluidized-bed reactor configuration (Figure 15a) that incorporates some proprietary modifications compared with the conventional configuration. The company has patented a combination of a catalyst, reactor design, and optimum operating conditions. So far, ExxonMobil has demonstrated the technology at pilot plant scale and is planning to demonstrate it at commercial scale in one of its petrochemical sites.

Figure 15. (a) Fluidized (ExxonMobil PCC) and (b) fixed-bed (Sinopec OCC) reactor schemes proposed for olefin cracking.[180]

a)

Regenerator

Reactor

Ethylene   Propylene

Recovery system
optionally integrated with steam cracker
recovery system

Butylene recycle

C₄ recycle

Olefinic naphthas
and C₄ feeds

Butylenes

C₅⁺ to gasoline
blending

ExxonMobil

b)

Light olefins

Depropanizer   Debutinizer

Fired Heater

C_5^+

Reactor

Olefin feed

C4 Recycle

Purge

Display full size

ExxonMobil also licenses another process for propene production from light olefinic streams, called the Mobil olefin interconversion (MOI) process. MOI is an olefin conversion technology that provides high yields of ethene and propene from refinery streams rich in light olefins (C_4–C_8) like FCC and steam cracker C4s and light naphtha, as well as other streams like raffinate or coker naphtha. The process is based on the conventional FCC design, as it incorporates a reactor where the cracking reaction takes place and a regenerator for continuous regeneration of the catalyst. However, the operating conditions are quite more severe compared with the typical VGO (vacuum gasoil) FCC unit. The reaction temperature is higher than 530°C to shift the reaction equilibrium toward ethene and propene production. The reaction pressure is moderate, normally maintained between 1 and 2 bar. The process also produces an amount of C_4 and C_5 olefins that can be recycled back to the reactor for further conversion. One key aspect of the process is the use of a proprietary ZSM-5 zeolite specifically tuned to maximized olefin production by reducing secondary

reactions of HT, aromatization, and coke formation. The ZSM-5 catalyst is continuously regenerated and no feed pretreatment is required if the olefinic feedstock has low levels of nitrogen, sulfur, and metals. However, if the diene content is high, selective hydrotreatment is recommended in order to avoid excessive catalyst deactivation.

The OCC is another propene production process that has been developed by the Sinopec Shanghai Research Institute of Petrochemical Technology.[189] The process catalytically cracks C_4–C_5 olefins from an FCC or steam cracker unit into ethene and propene as main products, in two or more fixed-bed reactors that run in a swing mode ([Figure 15b](#)), at high temperatures (500–600 °C) and low pressures (1–2 bar), using a ZSM-5-based catalyst with a very low crystal size (<0.5 μm) to prevent quick deactivation by coke deposition. Steam is also injected into the reactor in order to improve the selectivity and reduce coke and gum formation.[190]

Besides these processes that have reached demonstration or commercial scale, there are considerable efforts in the development of cracking $C_4^=$ and higher olefins to propene. Lotte Chemical Corp. patented the production of ethene and propene by the extractive distillation of the C_5 fraction in the naphtha steam cracker and its subsequent catalytic cracking.[191] Sinopec is one of the most active companies that develop processes for light olefin cracking. One of their patents[192] describes a process to catalytically convert C_4–C_8 olefins to propene at high temperatures (550–650 °C) in a fluidized-bed reactor in which the olefins contact countercurrent with a mesoporous molecular sieve, composed by modified rectorite and/or gamma-type zeolite that incorporates phosphorous and transition metal. Sinopec also disclosed in a patent[193] a process for production of propene that comprises reacting C_4–C_{12} hydrocarbons and olefins, at 500–650 °C, 0–1.5 bar, LHSV of 10–50 h^{-1} over a catalyst. The catalyst comprises a ZSM-5 zeolite of Si/Al = 200–800, with a 0.1–2 wt.% of group VIII element, and a 10–50 wt.% of a binder comprising silicon oxide or aluminum oxide.

SK Innovation disclosed a method for producing light olefins by catalytic cracking that involves supplying a naphtha/kerosene feedstock and dilution steam/lift gas into a riser under the fast fluidization flow regime, at high temperature (550–800 °C) and contacting with a zeolite component (preferably ZSM-5).[194] It is claimed that the one advantage of this process is that the fast fluidization flow regime in the riser improves the efficiency of light olefin production compared to a conventional dilute pneumatic conveying regime. By and large, we observe

that the developments filed in patents evolve in parallel to the findings at the academia. Catalysts with low acid site density and short contact times operated at high temperatures favor a high selectivity to propene. Lower-cost processing schemes and cheaper catalytic materials are also rising trends to look at.

5. Concluding remarks

The present review has evidenced the enormous interest by the market, the academia, and the industry to develop more selective propene-producing technologies. Olefin conversion technologies are particularly promising because their functional group could enable more efficient and selective chemical reactions compared to the less reactive alkanes present in crude oil and natural gas.

The ethene conversion to propene was proposed long ago by coupling ethene dimerization with isomerization and metathesis of the formed butenes. Carrying out this transformation in one pot would be highly preferred, and this is possible, among other materials, over acid zeolites and Ni-MCM-41, as surveyed in this review. However, clear performance objectives remain to be identified, and these are actually dependent on the relative pricing of ETP in the market. The mechanism proposed initially over Ni-MCM-41 comprised a metathesis reaction, although the latest findings support a mechanism of oligomerization cracking closer to that occurring over acid zeolites. In either case, it is necessary to increase the yield of propene under reaction conditions where the catalyst can be stable. This poses several challenges for which multiple strategies should be adopted: optimization of the catalyst formulation to avoid the high production of by-products, process intensification trough reactor design and reactor configuration, and modeling of the chemical system to understand the nature of the observed products.

As for olefin cracking, the research efforts observed are a natural extension of those observed in cracking alkanes. The importance of thermodynamics and the facile activation of the double bond over acid zeolites, however, must be duly recognized to identify optimal reaction conditions. Additional parameters in the catalyst formulation may also provide further benefits that remain unexplored so far. As in the ETP process, stability improvement would be highly desirable because it could enable fixed-bed reactor schemes with lower operation costs than FCC-type processes. This should be accompanied by a higher catalytic selectivity to light olefins, as the buildup of minor amounts of secondary

products can cause the rapid deactivation of the catalyst, as demonstrated by the latest works reviewed. By and large, it appears that, although very complex, a holistic understanding of the conversion of short and intermediate olefins over the different materials surveyed could report profits far beyond their current use, justifying the great research interest observed in this review and that, certainly, will continue in the coming years.

Acknowledgments

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