Selective synthesis of propylene via homologation of ethylene with dimethyl ether at low temperatures on zeolites

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ABSTRACT

In the light of the faster growing propene *versus* ethene demand, ethene homologation with methanol or dimethyl ether shows to be a promising pathway. The route may offer a cost competitive solution for synthesis of bio-propylene from bio-ethylene and renewable MeOH. The reaction is catalyzed by conventional zeolite topologies, viz. MFI, TON, CHA.

Selection of low temperature-low conversion conditions, allowed for an extended period of time to achieve 100% propene selectivity for several medium pore H-zeolites.

Use of singly ¹³C labeled ethene in the homologation with DME allowed to establish the pathways of propene formation. Separate homologation reactions of singly labeled propene with DME over the same H-zeolites, shows selective n-butenes formation.

1. Introduction

A massive amount of gas-based investments in chemical industry and decarbonization trends in the energy sector dramatically impacted the landscape in the refining and petrochemical businesses [1,2]. Historically, most of propylene was yielded as a by-product of ethylene (steam crackers) or gasoline (refineries) production [3]. The lightening of the steam cracking feedstock triggers a need for on-purpose technologies for propylene production. However, the dominant on-purpose technologies suffer from heavy capital investment, carbon footprint, and long-term vision on the feedstock availability. In order to respond to the challenges, the routes for propylene synthesis from cleaner feedstocks should be developed [4,5]. The homologation route may offer a cost competitive solution for synthesis of bio-propylene from the bio-ethylene produced by ethanol dehydration and the renewable MeOH, which could be synthesized, e.g. by hydrogenation of CO₂. The production of ethylene from ethanol (EtOH) by dehydration is growing, supporting the view that ethylene and methanol/dimethyl ether (DME) will be future crossroad platform molecules in the continuously evolving landscape between the natural gas and bio-feedstock.

The world propene production is expected to further grow at an average annual rate of 4.4% [6,7]. Given the current startup of additional ethane-based ethylene capacities, the decreased production of propylene via steam cracking [8], the anticipated gradual shutdown in FCC capacity due to gasoline surplus and changing motor gasoline regulations/specifications, the demand for propylene is growing faster than that of ethylene, resulting in an increased interest in developing secondary propylene production technologies.

Among others, selective ethylene conversion into propylene is especially attractive. The formation of propene by methylation of ethene with methanol/DME could be useful, e.g. in adjusting propene to ethene ratio in MTO, in improving the propene/ethene ratio from steam crackers as well as in transformation of dilute ethene into propene in FCC dry gas. Both ethene and MeOH/DME could be easily produced from cellulosic biomass and natural gas, respectively. The vast variety of sources and the versatility of the production routes position methanol [9,10] and ethene as main non-petroleum sources for propene production.

Olefin homologation is a straightforward route by which “methylenes” from MeOH/DME are incorporated into alkenes, resulting in

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chain growth. At normal operating temperature, oligomerization of C_3^+ alkenes seems dominant over alkene methylation [11,12], methylation of ethene being negligible under MTH conditions [13]. Proposed mechanisms for alkene methylation are [14] co-adsorption of methanol and alkene on a single acid site and subsequent concerted reaction, and surface methoxide formation from methanol or DME dehydration, desorbing upon reaction with an alkene.

Upon co-reacting ^{13}C labeled ethene with methanol over silicalite, ethene can be converted by addition of “methanolic C_1 ” species [15]. From the even distribution of the ^{13}C label over ethene and the C_3 – C_5 products, it follows that the latter are formed by the successive addition of unlabeled C_1 species derived from methanol to labeled ethene. The results also showed that ethene formation from methanol is slow compared to the addition of C_1 species to C_3^+ alkenes.

According to Dahl and Kolboe [16–18], aromatic dealkylation reactions at 400 °C are responsible for propene and butene formation on H-SAPO-34 rather than olefin methylation. Co-feeding of ethene and $^{13}CH_3OH$ over a H-ZSM-5 catalyst shows, however, that ethene is unreactive and its methylation cannot be an important part of the reaction network, as ethene conversion is only increased in presence of methanol at rather low conversion levels [19].

In an attempt to determine primary products, Svelle et al. [20] studied the ethene - $^{13}CH_3OH$ co-reaction on HZSM-5 at standard temperatures (350 °C) and very short reaction contact times (WHSV up to 300 h⁻¹). Methylation of ethene to form propene was dominating at very low conversions, though always small amounts of aromatics were observed enriched for 85% in ^{13}C . The kinetics of C_2 – C_4 olefins methylation have been studied on H-ZSM-5 using ^{13}C -methanol [21] and on H-ZSM-5, H-BEA, H-FER, H-MOR using DME [22,23]. The following ratios were obtained for methylation rates at 350 °C: $k_{\text{ethene}}:k_{\text{propene}}:k_{\text{n-butene}} = 1 : 17: 50$ [20,21]. These studies [20–23] further show that olefin methylation is first and zero order dependent on the olefin and the methylating agent (methanol or DME), respectively. Furthermore, this kinetic behavior is consistent for all zeolite frameworks studied.

The co-reaction of propene or n-butene and $^{13}CH_3OH$ over an H-ZSM-5 catalyst [21] showed that methylation products are dominating, and their isotopic composition is in agreement with the methylation mechanism, alkene interconversion (oligomerization/cracking) reactions being strongly suppressed. Ethene fairly rich in ^{13}C , and with randomized isotopic distribution was always detected in trace amounts in all co-reaction experiments. All information was thought to point to the existence of a hydrocarbon pool mechanism.

Cui et al. [24] studied olefin homologation reactions on zeolite H-ZSM-22. As in this 1D pore structure the hydrocarbon pool mechanism and the secondary MTO reactions were inhibited, homologation of ethylene, propylene and styrene with $^{13}CH_3OH$ at high temperatures could be observed directly. Successive homologation selectivity of ethene was seen as product propylene, butenes and pentenes showed one, two or three ^{13}C atoms, respectively. It was further speculated that olefin homologation is a key reaction during the induction time of the MTO process.

Ethene homologation with methanol in standard MTO conditions over modified H-ZSM-5 with phosphorous and lanthanum oxide, was shown to yield strongly reduced feed conversions and high propylene selectivity (ca. 80%) [25]. It was concluded that the methylation of ethylene by methanol was responsible for the high propylene selectivity, the competition of different types of reactions being influenced by the acidity of the catalysts.

Zhu et al. [26] studied the methylation of ethylene with methanol to propylene over acid MFI zeolites with different heteroatoms. They found that such MFI zeolites with weak acidity prevent the formation of ethylene oligomers. It was demonstrated that in presence of ethylene MeOH could be completely converted to hydrocarbons at 500 °C with a selectivity of about 50–60% for propylene. Simoneti et al. [36] showed for DME conversion over H-BEA that under conditions when skeletal

isomerization is suppressed (<227 °C), highly branched alkenes and alkanes, particularly triptane and triptene, are the dominant products as a result of methylation reactions favoring the formation of the most substituted carbenium ion as reaction intermediate. DFT calculations on 30–46T clusters have also treated C_2 – C_4 olefins methylation via the co-adsorption mechanism and, in agreement with experimental work, show that activation energy barriers decrease while rate constants increase systematically with olefin size. An important conclusion in this respect is that the olefins methylation reactions are propagated to different extent, depending on the identity of the zeolite framework [27].

There is general agreement that ethene and propene are formed independently in MTH transformation conditions and that the majority of the propene is not formed from ethene by a reaction with DME/MeOH [28–37]. However, such transformation could be potentially promoted by addition of an excess of ethene or by a proper selection of the reaction conditions. So, the question remains whether zeolite catalysts are able to convert ethylene with higher selectivity to propylene (>80%) [25] by a reaction of homologation with MeOH/DME and what would be the conditions for such transformation.

Detailed kinetic studies of the MTO reaction allowed extrapolation of the propylene yield to initial time [38]. This proves that propylene might be at least one of the primary products in MTO reaction after the initiation step, which is formed directly from MeOH/DME. This result is consistent with earlier work [35,39]. According to Froment [40], propylene formation is very fast, though this olefin is very reactive on the ZSM-5 zeolite. With progressive deactivation by “coke” the reactor zone in which the propylene yield reaches its maximum moves further downstream [38]. This finding shows an opportunity to maximize propylene yield by slowdown of the reaction steps.

As a conclusion of what precedes, the homologation of ethylene with MeOH/DME will be a potential pathway for selective propene production. Though absent in typical MTH conditions, available data on the homologation or methylation of ethene with mainly MeOH and occasionally DME shows that with H-zeolites in standard MTO conditions propene is a primary product that can be obtained with selectivities as high as 80%. Labeling work of ethene with $^{13}CH_3OH$ done in MTO conditions seems to provide strong evidence for the presence of consecutive methylations increasing in rate with increasing alkene chain length, thus reducing the maximum achievable propene selectivity. It can also not unambiguously be concluded that such conditions isotopomer/isotopologue distributions are free of significant isotopic scrambling.

The present work aims at selecting a proper set of homologation conditions leading to enhanced propene selectivity using typical zeolites, which are known for MTO reactions. The isolation of the ethene homologation was attempted by reducing the reaction temperature as much as possible, rather than by using high feed space velocities at MTO temperatures. In contrast to prior labeling work using mainly ^{13}C -methanol, ^{12}C -DME was reacting with $^{13}C_1$ -ethylene, avoiding in absence of secondary cracking, the occurrence of multiply labeled propylene and thus facilitating the interpretation of the mass spectra. Moreover, the low temperature (<280 °C), will reduce the probability of isotopic scrambling.

2. Experimental

2.1. Catalysts preparation

Three commercial H-ZSM-5 samples from Zeolyst with low, medium and high Si/Al ratio were used. The Si/Al ratio of all samples is added in brackets to the sample notation, viz. 12, 140 and 500. H-SAPO-34(16) was bought from Zeolyst as well. H-FER(33) was a commercial sample received from Total Petrochemicals Research. ZSM-11(78) was an in house sample synthesized according to a published recipe using 1,8-diamino octane as template [41]. ZSM-22(42) was synthesized according to

a published procedure using 1,6-diaminohexane as template [42]. The MCM-22 zeolite was synthesized by hydrothermal crystallization following a published procedure [43]. The latter 3 samples were ammonium exchanged and *in-situ* heated in the catalytic reactor.

2.2. Catalyst characterization

The specific surface and porosity was measured using a TriStar 3000 instrument from Micrometrics. The nitrogen adsorption and desorption isotherms were determined at $-196\text{ }^{\circ}\text{C}$, while the specific surface area was calculated using the BET model. The external surface area, the micropore volume and the total pore volume were determined by means of the t-plot method. In this method, V is plotted against t , V being the experimental volume of nitrogen adsorbed and t the statistical thickness of the adsorbed layer of nitrogen for each experimental P/P_0 value. P and P_0 refer to the actual and saturation pressure of nitrogen, respectively.

Ammonia temperature-programmed desorption (TPD-NH₃) was carried out on a ZETON AMI-200 IP instrument from Altamira. The sample was first calcined at $600\text{ }^{\circ}\text{C}$ under a flow of 50 ml/min of helium. After cooling to $100\text{ }^{\circ}\text{C}$, the catalyst was saturated with ammonia under a 30 ml/min flow containing 10 vol % of ammonia in helium and subsequently flushed under helium (50 ml/min) during 1 h. Ammonia desorption between 100 and $600\text{ }^{\circ}\text{C}$ under a 50 ml/min helium flow was followed with a TCD detector, using a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$. The error on the TPD values was about 5%. Quantification was done using deconvolution of the signal with two Gaussian peaks.

2.3. Reaction of DME with ethene

Experiments were carried out in a quartz fixed bed reactor filled with 1 g of catalyst pellets. The compressed zeolite powder was crushed and sieved to sizes ranging from 250 to 500 μm . The zeolites were dehydrated *in situ* in the reactor at $400\text{ }^{\circ}\text{C}$ under flowing nitrogen. The feed was composed of ^{12}C -ethene from Air Liquide with purity of 99.95% or of singly ^{13}C labeled ethylene = from Isotec enriched in ^{13}C for 99% and of ^{12}C dimethyl ether (DME) from Fluka with 99.9% purity. Helium with 99.99% purity was used as carrier gas.

In a standard experiment gases were fed by digital mass flow controllers at a feed rate of 4.0 ml/min for ethylene, 4.0 ml/min for DME and 23 ml/min for helium, amounting to a total flow of 31 ml/min and a total $(\text{DME} + \text{C}_2)$ space velocity (WHSV) of 0.74 h^{-1} using a DME/C_2 molar ratio of 1. Reactions were carried out in a temperature range where low values of X_{DME} ($<10\%$) were obtained. For H-ZSM-5 this occurred in the $180\text{--}250\text{ }^{\circ}\text{C}$ temperature range. The effluent usually was analyzed after of 30, 60, 120, 300, 600 and 900 min time-on-stream (TOS). The products leaving the reactor were sampled on-line, separated and analyzed using a Hewlett Packard HP 6890 gas chromatograph with a CP-Poraplot column of 25 m, with an internal diameter and film thickness of 0.53 mm and 20 μm , respectively. The column outlet was coupled to an FID detector with built-in methanator, every component being detected as CH₄. Reagent conversion (X_i) and product distribution (S_i), both in C wt%, were calculated according to equation 2.1 and 2.2, respectively,

$$X_i = \frac{R_{i,0} - R_i}{R_{i,0}} \quad (\%) \quad (1)$$

$$S_i = \frac{P_i}{\sum_n P_n} \quad (\%) \quad (2)$$

with $R_{i,0}$, the initial amount of reactant on a % C basis, R_i , the amount of reactant after reaction, P_i , the amount of product i , and $\sum_n P_n$, the total amount of products all on % C basis. It should be stressed that the selectivities obtained are C selectivities. To obtain molar selectivities, the number of C atoms per molecule should be taken into account. Since

both reactant molecules contain 2 C atoms, the conversions stated in this work can also be regarded as molar conversions.

2.4. Alternative C₁ and C₂ feeds

Three combinations of alternative feeds were tested, viz. a DME/EtOH, MeOH/EtOH and a DME/Diethyl ether (DEE) mixture. All experiments were carried out in the reactor described sub 2.1.2. EtOH was obtained from VWR with 99.9% purity, the applied MeOH was HPLC grade with a purity of 99.99% from Acros Organics and DEE was 99.5% pure and acquired from Riedel de Haën.

For the reaction of DME with EtOH, DME vapor was fed to the catalyst at a rate of 4.6 ml/min (or 0.53 g/h) by a digital mass flow controller. EtOH vapor was fed to the reactor by bubbling nitrogen at 15 ml/min through an evaporator/saturator filled with ethanol kept at $20\text{ }^{\circ}\text{C}$ in a thermostatted bath. The saturators were of such design that constant partial pressures of the feeds used were obtained with time at the nitrogen feed rates used. This resulted in a constant ethanol partial pressure of 59 mbar and a feed rate of 0.10 g/h. The two flows were merged and further diluted with 7 ml/min nitrogen, achieving a DME/EtOH molar ratio of 5/1 and a total volumetric flow of 22 ml/min through the catalyst bed.

For the reaction of MeOH with EtOH, 20 ml/min of nitrogen was passed through an evaporator kept at $20\text{ }^{\circ}\text{C}$ filled with MeOH and EtOH in a 1/1 (v/v) composition. This resulted in a partial pressure of 130 and 59 mbar for methanol and ethanol, respectively, corresponding to a feed rate of 0.12 and 0.05 g/h, respectively. The final MeOH/EtOH molar ratio of the gaseous feed consequently was 3.2/1. Adding another 2 ml/min of nitrogen to this feed increased the total nitrogen feed to 22 ml/min.

For the reaction of DME with DEE, 4.6 ml/min of DME vapor was metered with a digital mass flow controller. DEE was added from a separate flow by passing 5 ml/min nitrogen through a saturator filled with DEE kept at $15\text{ }^{\circ}\text{C}$. The DEE vapor pressure in the evaporator was 450 mbar, resulting in a feed rate of 0.42 g/h. The final DME/DEE molar ratio was 2/1. To this flow 17 ml/min of nitrogen was added eventually in order to reach a total of 22 ml/min of nitrogen as diluent.

The gas chromatographic sensitivity coefficients were all equal as the components were detected as methane by an FID detector equipped with methanator. The reaction conversion and selectivities were calculated according to formulas 2.1 and 2.2.

2.5. Reaction of DME with singly ^{13}C labeled ethene

The column outlet of the continuous flow reactor and on-line GC could be switched to a quadrupole Quadstar 422 MS from Pfeiffer. Continuous ion monitoring was done for m/e values ranging from 37 to 46, corresponding to the m/e ranges of propylene and DME. The distribution of the respective ion masses was calculated as well.

In an experiment using DME and singly ^{13}C labeled ethene = as feed, product propene masses always were in the 38–43 m/e range, corresponding to a mixture of unlabeled ($X\%$) and singly labeled ($100-X\%$) propene. To calculate the extent to which each reaction occurs, the following data are used: i. the mass spectrum of unlabeled propene; ii. the mass spectrum of singly labeled propene; iii. the mass spectrum of propene from an experiment with singly ^{13}C labeled ethene and DME (which is expected to yield a mixture of singly labeled and unlabeled propene). Equation (3) applies with i , ranging from 38 till 43, X_i , the peak intensity percentage due to the presence of singly labeled propene, L_i , the relative peak intensity in a model spectrum of singly labeled propene, U_i , the relative peak intensity in a model spectrum of unlabeled propene, and E_i , the relative peak intensity of propene in an experiment with DME and singly ^{13}C labeled ethene. A correction of 1.1% is made for the natural abundance of ^{13}C .

$$(X_i + 1.1\%) \times L_i + (100 - X_i - 1.1\%) \times U_i = E_i \quad (3)$$

For every experiment carried out using DME and singly ^{13}C labeled ethene as feed, a similar experiment was run with DME and ^{12}C -ethene. The mass spectrum of unlabeled propene was obtained from these experiments, while for the model mass spectrum of pure singly labeled propene, the intensity values of the former spectrum were shifted to a new value of m/e , one m/e unit higher than in the spectrum of unlabeled propene. All actual values of X_i obtained for every value of i in the mentioned range, have then been averaged and will be denoted as $\bar{A}$, the average degree of labeling of propene. The mass spectrum of DME was also recorded. To determine the conversion of DME, the intensities of m/e 45 and 46 for each reaction temperature were compared to those in a DME mass spectrum recorded in conditions where no DME conversion occurred.

2.6. Reaction of DME with singly $^{13}\text{C}_2$ labeled propene

Such labeling experiments were carried out in a similar way as described in 2.4 for DME and singly labeled ethene. The feed was composed of ^{12}C -propylene from Air Liquide with purity of 99.95% or of $2\text{-}^{13}\text{C}$ propylene ($\text{CH}_3^{13}\text{CH}=\text{CH}_2$) from Isotec enriched in ^{13}C for 99% and of ^{12}C dimethyl ether (DME) from Fluka with 99.9% purity. Helium with 99.99% purity was used as a carrier gas. Gases were fed by digital mass flow controllers. In a standard experiment a molar DME/C_3 feed ratio of 1/1 or 3/1 was fed to the catalyst. For the 3/1 DME/C_3 molar ratio mixture a feed rate of 1.33 ml/min for propene, 4.0 ml/min for DME and 23 ml/min for helium, amounting to a total flow of 28.33 ml/min and total feed ($\text{DME} + \text{C}_3$) space velocity (WHSV) of 0.60 h^{-1} was applied. For the equimolar mixture, 4.0 ml/min of propene and 4.0 ml/min of DME was mixed with 22 ml of helium. This resulted in a total flow of 30.0 ml/min and total feed ($\text{DME} + \text{C}_3$) space velocity (WHSV) of 0.88 h^{-1} . Reactions were carried out in the 200–300 °C temperature range.

MS in the continuous ion monitoring mode was used for m/e values ranging from 37 to 59, corresponding to the m/e ranges of butenes, butanes and the reagents. In an experiment using DME and singly labeled $2\text{-}^{13}\text{C}$ propene, the exclusive propagation of DME would yield an unlabeled C_4 chain. If $2\text{-}^{13}\text{C}$ propene is exclusively methylated by DME, only singly labeled C_4 isotopomers will be obtained (eq. 4). If dimerization of the singly labeled C_4 isotopomers (eq. 5) followed by cracking (eqs. 6 & 7) would occur, C_4 isotopologues containing either zero (eq. 7), one (eq. 6) or two ^{13}C atoms (eq. 7) are expected. The occurrence in a standard experiment with ^{13}C -propylene/DME molar feed ratio of 1/3 of a C_4 isotopologue with three ^{13}C atoms should stem from cracking from a pool of C atoms present in a $^{13}\text{C}/^{12}\text{C}$ ratio of 1/8.

Multiply labeled C_4 isotopologues can also originate from $2\text{-}^{13}\text{C}$ propene dimers (eq. 8). These dimers either crack to propene isotopologues (eq. 9) containing zero, one or two ^{13}C labels (eq. 9) and subsequently undergo methylation to the corresponding C_4 isotopologues. Alternatively, the propylene dimers could undergo double methylation to C_8 isomers (eq. 10) containing two ^{13}C labels and subsequently crack to C_4 isomers (eq. 11).

Equations 4-11 are based on mere statistical behavior. How the presence of discrete species is affected for acid catalyzed transformations will be discussed below. Since the occurrence of multiply labeled C_4 isomers is possible and a mixture of unlabeled, singly and

doubly labeled C_4 isotopologues is expected, calculation methods for determination of the ^{13}C content different from the ones described above will be applied. The mass spectrum of a certain C_4 isomer after co-reaction of DME and $2\text{-}^{13}\text{C}$ -propene will be the sum of the different mass spectra of the respective isotopologues. To calculate the isotopologue distribution in a particular C_4 isomer in the effluent, next to the actual experimental mass spectra of a C_4 compound obtained from an experiment with $2\text{-}^{13}\text{C}$ propene and DME, the model spectra of unlabeled, singly and doubly labeled isotopologues of the particular C_4 compound are used.

For every experiment carried out using DME and $2\text{-}^{13}\text{C}$ -propene as feed, an identical experiment was done with DME and ^{12}C -propylene as feed with a fresh catalyst. The mass spectra of the unlabeled C_4 isomers, U, was obtained from these experiments, while for the model mass spectrum of pure singly (L1) and doubly labeled isotopologues (L2), the intensity values in the former spectrum were shifted to a new value of m/e , respectively one and two m/e units higher than in the spectrum of the unlabeled isotopologues. The experimentally obtained spectrum (E) after co-reaction of the singly labeled propylene and DME is thus a linear combination of spectra U, L1 and L2. To determine the contribution of the spectra of the respective isotopomers, a linear least squares method was used via the Microsoft Excel Solver add-in. For every possible combination of U, L1 and L2 a theoretical spectrum T_i is obtained (eqs. (12) and (13)). The applied method minimizes the squared difference (D_i) of the observed spectrum (E) and the theoretical spectrum (T_i) (eq. (14)),

$$T_i = a_i \times U + b_i \times L1 + c_i \times L2 \quad (12)$$

$$a_i + b_i + c_i = 1 \text{ and } a_i, b_i, c_i \geq 0 \quad (13)$$

$$D_i = (E - T_i)^2 \quad (14)$$

with a_i , b_i and c_i the respective contributions of U, L1 and L2 to the given spectrum, T_i . The lowest value of D represents then the correct composition of the experimentally observed spectrum E.

3. Results and discussion

The sample notation, origin, Si/Al ratio, nitrogen sorption data and crystal size is shown in Table 1. Fig. 1 shows a linear relationship between the high temperature ammonia desorption peak and the Al content of the samples. The line through the origin with slope 1 indicates that irrespective of the topology of the zeolite samples, the Brønsted acidity as titrated with ammonia is determined by the Al (Si for SAPO) content. Minor deviations of the individual samples could reflect topology effects on acidity.

3.1. Effect of TOS in the equimolar reaction of DME and ethylene at low temperature/conversion with H-ZSM-5(140) catalyst

When DME and ethene are reacting together in equimolar amounts at low conversions (<5%) over H-ZSM-5(140), propylene is the sole reaction product (Fig. 2). Given the presence of converted ethene and the absence of C_4 products (or higher), at least part of the propene observed should be formed via ethylene methylation with DME. As for low feed conversion conditions the conversion of DME is always higher than of ethylene, there should be a second route to propylene not involving added ethylene, implying direct formation of ethylene from DME, viz. via (methylene) propagation. Alternatively, products from initially converted DME (or ethene) might be irreversibly retained in the catalyst, yielding ethylene and/or propylene via a third mechanism, viz. re-cracking of heavy molecules via the so-called hydrocarbon pool mechanism. On-line determination of C-mass balance in such conditions is not accurate enough to exclude this possibility. Fig. 2 also shows that feed conversion is stable for at least 900 min, corresponding to 7.9 and 4.8 g

Table 1

Physical properties of the zeolite catalysts.

Sample notation	Origin	Si/Al	BET ^b m ² /g	Micropore Volume ^c cm ³ /g	Micropore Area ^c m ² /g	External Surface Area ^c m ² /g	Crystal size ^d μm
H-ZSM-5 (12)	Zeolyst	11.5 ^a	425	0.161	397	28.5	0.70
H-ZSM-5 (140)	Zeolyst	140.0 ^a	396	0.167	353	43.6	1.01
H-ZSM-5 (500)	Zeolyst	500.0 ^a	405	0.163	348	57.5	1.25
H-SAPO-34(16)	Zeolyst	16.0 ^f	554	0.187	475	79.0	<0.5
H-FER(33)	Total	33.0	382	0.144	364	17.8	1.0
H-ZSM-11(78)	COK ^e	78.0	373	0.140	351	21.4	0.5
H-ZSM-22(42)	COK ^e	38.0	212	0.069	175	37.4	1.0
H-MCM-22(42)	COK ^e	42.0	526	0.171	427	99.5	0.5

^a By manufacturer.^b From N₂ adsorption isotherm.^c t-plot analysis of N₂ adsorption isotherm.^d From SEM images.^e Own synthesis.^f Si is substituted for P in a Al/P containing framework. **Fig. 1.** Correlation between the intensity of the high temperature peak from NH₃-TPD measurements and the Al content in the H-zeolite samples, corresponding to the concentration of Brønsted acid sites. For H-SAPO-34 (silicoaluminophosphate) this value corresponds to the Si content. **Fig. 2.** C based product selectivity (S_i) and molar reagent conversion (X_i) versus TOS at 200 °C for co-reaction of equimolar amounts of DME and ethylene with fresh H-ZSM-5(140). DME + C₂⁻ feed rate (WHSV) is 0.85 h⁻¹ using a DME/C₂⁻ molar ratio of 1.

of converted DME and ethylene per g of catalyst, respectively.

At a catalyst temperature of 220 °C using the same space velocity, DME conversion is again higher than that of ethylene, while conversion of both feeds changes in a parallel way (Fig. 3). At short TOS, the conversion increases and then gradually declines. This is interpreted as heat from an exothermic effect that is dissipating over the catalyst bed. The change of the C₃⁻, C₄ and C₅⁺ selectivity curves at increasing TOS seems to indicate that the reaction is initiated by selective production of propylene, followed by consecutive formation of C₄ alkenes and C₅⁺ products. After 300 min propylene selectivity increases again at the expense

Fig. 3. Carbon-based product selectivity (S_i) and molar reagent conversion (X_i) versus TOS with fresh H-ZSM-5 (140) at 220 °C, using a DME/ethylene molar feed ratio of 1 and DME + C₂⁻ = feed rate (WHSV) of 0.85 h⁻¹.

of the C₅⁺ fraction, the increase of the C₄ fraction being only minor. This suggests that at this stage the mechanistic origin of propene at least partially changes and could then have a triple origin, viz. homology of ethylene, methylene propagation and cracking of hydrocarbon pool molecules.

3.2. Further evidence for ethylene homologation with DME at low feed conversion

In an attempt to elucidate the role of ethylene in the overall reaction network of low temperature DME conversion, a H-ZSM-5(140) catalyst was exposed to different feed compositions at low reaction temperature. The feed consisted of either ethylene or DME alone or of an equimolar mixture of both molecules and was fed to the catalyst at 200 °C. The reaction results are given in Table 2.

The results show that the addition of ethylene has a minor positive effect on DME conversion (compare feed 3 to 1). It is also obvious that ethylene when reacted alone (feed 2) undergoes mainly oligomerization. When ethylene is mixed with DME no oligomerization products are detected even though ethylene is converted. This suggests that DME

Table 2

Conversion (X_i) and selectivity (S_i) of DME (feed 1), ethylene (feed 2) and a mixture of equimolar amounts of DME and ethylene (feed 3) with H-ZSM-5(140) at 200 °C after 900 min TOS.

feed	X_{DME}	$X_{C2=}$	$S_{C2=}$	$S_{C3=}$	S_{C4}	S_{C5+}
1	3.1	–	24.9	76.2	0.0	0.0
2	–	2.4	–	23.4	46.0	30.6
3	3.6	2.2	–	100.0	0.0	0.0

inhibits alkene oligomerization and that (at least a fraction of) propylene is formed through ethylene methylation. In earlier work, it was found that MFI zeolites with weak acidity prevent the formation of ethylene oligomers at significantly higher temperatures [26]. Propylene formation from pure ethylene (feed) conversion, necessarily has another origin and could already originate from cracking of ethylene trimers. Well-selected experiments with ^{13}C labeled feeds should shed more light on this issue (*vide infra*).

3.3. Effect of zeolite properties on propene selectivity at low DME conversion

TOS experiments with molecular sieves, differing in topology and/or composition, allowed to extract ethylene conversion and product selectivity at approximately 4.0% DME conversion (Table 3). The Al-rich H-ZSM-5(12) (with MFI topology [44]) at 200 °C shows ethylene conversion and exclusive formation of propene, just as H-ZSM-5(140) in comparable conditions. Slight increase in temperature up to 220 °C, however, shows significant formation of C_4 and C_5^+ products for both zeolites. With siliceous and less active H-ZSM-5(500), selective formation of propene is still possible at 225 °C.

A zeolite with two-dimensional (2-D) MEL topology, *viz.* H-ZSM-11(78) [44], already shows (low) ethene conversion and 100% propene selectivity at 190 °C. This enhanced activity is in line with the slightly more open MEL topology compared to MFI [44]. This result is at variance with the sequence of acidity changes as determined by ammonia desorption (Fig. 1). The TON topology [44] of H-ZSM-22(38) shows low ethene conversion and 100% propene selectivity for temperatures ranging from 200 to 220 °C. This zeolite topology has mono-dimensional 10-membered ring (10R) pores running along the needle-like crystals with smallest free diameter compared to the previously mentioned zeolites MFI and MEL.

The H-FER(33) zeolite even at 180 °C and short TOS, shows reduced propene selectivity and presence of butenes and even of C_5^+ products. The topology consists of intersecting 10R and 8R pores [44], not unlike the 10R pores in MFI and MEL. The spherulitic shape of the crystals is contrasting to the twinned crystals of MFI and MEL with the same overall size (Table 1).

The H-MCM-22(42) sample even at 170 °C shows reduced propene selectivity and appearance of heavier products. The MWW pore

Table 3

Catalytic results from ethene with DME homologation at $4.0 \pm 0.4\%$ DME conversion using different zeolites. DME + C_2 = feed rate (WHSV) is 0.85 h^{-1} using a DME/ C_2 = molar ratio of 1.

Zeolite sample	Topology ^a	Temp. °C	TOS min.	$\text{X}_{\text{C}_2}^{\text{DME}}$ %	$\text{S}_{\text{C}_3}^{\text{DME}}$ %	S_{C_4} %	$\text{S}_{\text{C}_5}^+$ %
H-ZSM-5(12)	MFI	200	30	2.4	100.0	0.0	0.0
H-ZSM-5(12)	MFI	220	900	1.6	68.5	22.7	8.8
H-ZSM-5(140)	MFI	200	900	2.2	100.0	0.0	0.0
H-ZSM-5(500)	MFI	225	60	3.3	100.0	0.0	0.0
H-ZSM-11(78)	MEL	190	120	2.4	100.0	0.0	0.0
H-ZSM-22(38)	TON	200	30	2.6	100.0	0.0	0.0
H-ZSM-22(38)	TON	220	120	3.4	100.0	0.0	0.0
H-FER(33)	FER	180	60	2.3	53.2	33.4	13.4
H-MCM-22(42)	MWW	170	300	1.8	27.4	35.5	37.2
H-SAPO-34(16)	CHA	260	120	1.0	100.0	0.0	0.0
H-SAPO-34(16)	CHA	270	300	1.9	89.0	11.0	0.0
H-SAPO-34(16)	CHA	310	900	1.9	91.0	9.0	0.0

^a Ref. 44.

structure consists of two disconnected pore systems, made up either of large cages ($1710 \times 1820 \text{ pm}$) interconnected thorough 10Rs or of a 2D system of 10R channels [44]. The half-cavities terminating the crystals are probably at the origin of the low propene selectivity, together with their flake-like crystal shape.

H-SAPO-34(16) zeolite sample with CHA topology, consisting of 3D interconnected cages via 8Rs [44], is well-known for its high propene selectivity in methanol to propene reactions [45]. Table 3 shows that this is also the case in the present ethene-DME reaction. In a rather wide temperature range (260–310 °C) at least 90% propene selectivity is obtained. In the low conversion conditions only butenes fill up the product-gap. It seems that higher reaction temperatures are required to desorb propene and butenes from the CHA topology. Possibly, chabasite half-cages at the external crystal surface rationalize the selectivity together with the low activity.

3.4. Search for alternative homologation patterns

C_1 and C_2 species generating feeds different from DME and ethylene, respectively, were passed over H-ZSM-5(140). Ethylene as C_2 chain was replaced either with ethanol or diethyl ether, while methanol was substituted for DME as C_1 chain (Table 4). The main objective was to search for different homologation reaction patterns of C_2 with C_1 feeds, directly starting from oxygenates containing two carbon atoms.

When in the standard homologation reaction, substitution of DME for MeOH has occurred, the main reaction even at 250 °C is methanol dehydration till DME, with only trace formation of propene, probably from homologation. Possibly, the enhanced water vapor pressure suppresses the homologation activity of DME and ethene.

Already at 200 °C, when DME and EtOH are co-fed, ethanol is dehydrated for 100%. The main reaction with selectivity up to 89% is the cross coupling of DME and EtOH into Ethyl Methyl Ether (EME). All converted DME, *viz.* 7.3%, is coupled to ethanol. To a lesser degree ethanol is completely dehydrated to ethylene (7%) and partially dehydrated to DEE (3.6%). Upon increasing the reaction temperature to 225 °C, the feed conversion moves towards complete dehydration of ethanol into ethylene and decomposition of EME into ethene and DME.

For reaction of MeOH with EtOH already at 200 °C, high alcohol conversions of 73 and 90%, respectively are observed. Ethanol is predominantly coupled to MeOH yielding EME (26%). Some ethanol is completely dehydrated to ethylene, while the remaining fraction is converted to DEE. The major amount of MeOH, however, at this low temperature is dehydrated yielding DME, which is thermodynamically favored in these conditions. Increasing the reaction temperature enhances distinct intermolecular dehydration of methanol and mono-as well as bimolecular dehydration of ethanol.

When DME and DEE are reacted together at 200 °C, their cross coupling yielding EME is dominant. As the DME/DEE molar feed ratio is 2/1, it can be seen that all converted DME is cross coupled with DEE forming EME, while the remaining converted DEE is dehydrated to ethylene. At increasing reaction temperature, co-reaction of both feed molecules yielding EME gradually decreases, while ethylene formation is strongly enhanced. As only X_{DEE} and $\text{S}_{\text{C}_2}^{\text{DME}}$ are increasing in parallel, it seems that the majority of the ethylene stems from DEE decomposition, rather than from methylene propagation from DME.

The present results with alcohols and/or ethers as C_1 and C_2 feedstocks, at low temperature show the formation of mainly ethers, in agreement with thermodynamic expectations. Among them mixed ethers formation is significant. The formation of propylene, the dominant product at low temperature between DME and ethylene, is now suppressed. This indicates that the methylation reaction with DME (or MeOH) requires the formation/presence of ethylene and does not occur directly with EtOH or DEE. The anticipated methylene insertion (from DME) into the C–O bond of DEE or EME and the subsequent generation is of propylene is therefore not occurring. This implies that no direct homologation of ethanol or diethyl ether or even of ethoxy groups with

Table 4Conversion (X_i) and selectivity (S_i)* of Feed 1 (C_1) and Feed 2 (C_2) co-reacting over H-ZSM-5(140).

Feed 1	Feed 2	Molar F1/F2	Temp. °C	X_1 %	X_2 %	$S_{C_2}^-$ ^a %	$S_{C_3}^-$ ^b %	S_{DME} ^c %	S_{DEE} ^d %	S_{EME} ^e %
MeOH	Ethene	3.0	250	90.6	2	–	0.8	99.2	–	0.0
DME	EtOH	5.0	200	7.3	100.0	7.3	0.0	–	3.6	89.1
			225	6.5	100.0	44.5	0.0	–	1.0	54.5
MeOH	EtOH	3.2	200	73.4	90.2	1.1	0.0	71.5	1.1	26.2
			225	88.2	92.2	7.4	0.0	67.4	23.7	1.6
DME	DEE	2.0	200	34.3	74.0	9.8	0.0	–	–	90.2
			225	31.2	84.7	26.5	0.0	–	–	71.9

*Selectivity for a, ethylene, b, propylene, c, ether of feed 1 (dimethylether), d, ether of feed 2 (diethylether), and e, mixed ether from both feeds (ethylmethylether).

methylene is possible on a H-ZSM-5 catalyst as observed for ethylene. Thus for the selective production of propylene in mild temperature/low conversion conditions, the simultaneous use of DME and ethylene as feed is the preferred option. In this way the reaction is initiated with a feed already in its dehydrated form, so that the whole catalyst bed exclusively can be used for homologation and sorption competition from water is minimal.

3.5. DME transformation in presence of singly ^{13}C labeled ethene

According to the procedure described *sub* 2.4, the average degree of singly labeled propene in the propene fraction, $\bar{A}$, was determined for H-ZSM-5 and H-SAPO-34 zeolites in the homologation of singly labeled ^{13}C ethene with DME in low feed conversion conditions (Table 5). In each case, at 100% propene selectivity, the singly labeled propene is dominant, its value being higher for the ZSM-5 sample and thus topology dependent. For H-ZSM-5(140) at 220 °C the amount of singly labeled propene decreases considerably at the expense of mainly unlabeled propene. As it is evident that in the low temperature/low conversion conditions isotopic scrambling should be improbable, the singly labeled propene should stem from the homologation reaction of ethene with DME. Other propene labeled species may either contain zero, two ($m/e = 44$) or three ($m/e = 45$) ^{13}C atoms. As only trace amounts of the latter two species ($m/e = 44$ or 45) were detected in the MS spectra even for H-ZSM-5(140) at 220 °C, the second important propene species present does not contain any ^{13}C label and should dominantly stem from methylene propagation. As next to propene, only butenes and only minor amounts of C_5^+ are present, the latter should be formed by consecutive methylation of propene. Re-cracking of heavy products into propene, should result either from further and increasingly faster [20, 21] methylation of initially unlabeled and singly labeled propene and/or olefin (co-) oligomerization. Such a mechanism will inevitably result in formation of some doubly and/or triply labeled propene, making the importance of the re-cracking mechanism insignificant in the reaction conditions used.

At low temperature/conversion propene specific conditions with both zeolite topologies can be selected where only propylene is formed as product. The labeling experiments show that the methylation with DME of the added ethylene is the major source of propylene, which is at variance with claims by previous authors [20] made in typical MTO

Table 5Singly labeled ^{13}C propene from reaction of ^{12}C -DME with singly ^{13}C labeled ethene with H-zeolites in low feed conversion conditions ^a.

zeolite catalyst	reaction Temp. (°C)	X_{DME} %	$X_{C_2}^-$ %	$S_{C_3}^-$ %	S_{C_4} %	$S_{C_5}^-$ %	A ^b %
HZSM-5 (140)	200	3.6	2.2	100.0	0.0	0.0	77.5
	220	6.5	4.1	76.0	22.0	2.0	53.0
H-SAPO-34 (16)	260	3.0	1.9	100.0	0.0	0.0	58.0

^a WHSV total of 0.74 h⁻¹.^b Average value of singly labeled propylene in C_3^- fraction.

conditions, even if conversions are suppressed by the use of high space velocities, as always traces of heavy products are obtained. The formation of C_4 and some C_5 chains do not seem disturbing the mechanism operative at 100% propene selectivity. Butenes are therefore originating from consecutive methylation as well. Reactions of labeled propene with DME should be confirming this (*vide infra*). More importantly, given the objectives of this work, it can be concluded from Table 5 that formation of unlabeled and singly labeled propene occurs via two competing mechanisms.

The way propylene originates from DME can be unraveled in more detail by analyzing the mass spectrum of ethylene in the product stream of a standard homologation reaction of DME with singly labeled ethene. Values of m/e ranging from 26 till 29 were determined during a non-labeled co-reaction (in order to obtain the mass spectrum for unlabeled ethylene). When these values were compared to the mass spectrum of the ethylene effluent after a DME and $^{13}C_1$ - or ^{12}C -ethene co-reaction (Table 6), It was found for singly labeled ethene that 99% of the effluent ethene contained one ^{13}C label after a reaction at 200 and 220 °C.

It is evident that for the reaction with labeled ethene all peaks have shifted to higher values with one mass unit compared to those in the reaction with unlabeled ethene. Moreover, in all cases the relative abundance of the peaks does not differ significantly. It follows that, although there is significant DME conversion, unlabeled ethylene formed from DME alone is hardly present in the effluent, $^{13}C_1$ labeled reactant ethylene being present exclusively. Obviously, in presence of added singly labeled ethylene, the direct formation of unlabeled ethylene from DME is virtually absent, making unlabeled propylene from DME the primary product.

This observation questions the presence of a hydrocarbon pool mechanism for ethylene formation in the applied conditions. According to the dual cycle mechanism on H-ZSM-5, ethylene is derived from a hydrocarbon pool and propylene is formed mainly by ethylene methylation [46]. The formation of unlabeled propene together with the absence of unlabeled ethene formation in the homologation of singly labeled ethene implies that ethene propagation with DME should be significantly faster than its formation from DME. As a consequence sorbed “*dimeric methylene*” from DME more rapidly forms a trimer than it is desorbed from the catalyst.

With the second archetypical H-ZSM-35 MTP catalyst, essentially the same results are obtained, compared to H-ZSM-5, though at an increased

Table 6Comparison of the relative intensities of m/e peaks (%) in effluent ethylene after a co-reaction of DME and ethylene (U_i) and of DME and $^{13}C_1$ -ethylene (E_i) at two temperatures with H-ZSM-5(140) ^a.

Temp. °C	200	200	220	220
m/e	U_i	E_i	U_i	E_i
26	31	–	31	–
27	29	31	29	32
28	40	29	40	28
29	–	40	–	39

^a For feed conversions see Table 6.

temperature range (260–280 °C).

A general scheme picturing the events in the described labeling experiments at 100% propene selectivity is shown in Scheme 1. Formation of singly labeled propene and the presence of singly labeled ethene, should originate from single methylation of singly labeled ethene with DME. The presence of unlabeled propene and ethene after reaction, is attributed to fast trimerization of methylene species via a propagation reaction, in combination with a slow dimerization. Mechanistically, the present data do not allow for alkene methylation to distinguish between co-adsorption of methanol and alkene on a single acid site and subsequent concerted reaction, or surface methoxide formation from methanol or DME dehydration, desorbing upon reaction with an alkene [14].

3.6. DME transformation in presence of singly 2-¹³C labeled propene

Homologation results using equimolar amounts of singly labeled 2-¹³C-propene and DME including feed conversions and ¹³C isotopologues of propene are shown in Table 7. Compared to similar experiments with singly labeled ethene (Table 5), it is clear that feed conversion is higher with propene. Obviously, the homologation activity of propene is higher than of ethene with DME in identical conditions, in agreement with earlier work in typical MTO conditions [20,21]. Moreover, the enhanced propene/DME reactivity ratios compared to those of ethene/DME (compare Tables 7–5) indicates that dimerization of propene via carbocation chemistry becomes increasingly important.

The distribution of the ¹³C-propene isotopologues after reaction at 200 and 220 °C (Table 7) shows no significant deviations from that of the propene feed, indicating that propene formation via re-cracking is virtually absent and the homologation of propene with DME is a major reaction pathway. This is no longer the case at 250 °C, given the formation of substantial amounts of unlabeled propene, pointing to significant propene formation via re-cracking of probably “pool” molecules.

The isotopologue distribution in the individual C₄ products is given in Table 8. At 200 °C, only *cis*-but-2-ene and *trans*-but-2-ene are comprised in the C₄ product fraction, in agreement with the occurrence of a methylene homologation reaction. However, the presence of unlabeled isotopologues indicates that re-cracking of large products is already present, confirmed by the presence of small amounts of doubly labeled butene isotopologues (*vide supra*). It should be noted that this is not the case for propene. Both unlabeled n-butene isotopologues as well as the doubly labeled ones, are at thermodynamic equilibrium [47], while the singly labeled ones are present in comparable amounts. It allows speculating that propene methylation occurs via a concerted reaction between surface methoxide and singly labeled propene [14]. Alternatively, deprotonation of an n-butyl carbocation intermediate, just as in case of the acid catalyzed n-butene isomerization is not expected to yield initial *cis/trans* ratios close to one [48].

When increasing the temperature to 220 °C, all butene isomers are formed. At the same time, more advanced ¹³C scrambling among the respective butene isotopologues is found for every butene isomer. This suggests that primarily formed butenes are dimerized, isomerized and eventually are re-cracked. It seems that prior to cracking cyclization and hydrogen transfer is not dominant as isobutane is not observed as a

Table 7

Distribution of ¹³C-propene isotopologues in the homologation of equimolar amounts of singly labeled 2-¹³C-propene with DME over HZSM-5(140), using standard reaction conditions.

Temp. °C	X _{DME} %	X _{C3=} ^a %	Unlabeled %	Singly labeled %	Doubly labeled %
200	1.0	9.3	4	96	0
220	17.0	31.4	1	96	3
250	68.0	94.4	33	62	5

^a Propene conversion values may be disturbed by propene formed from re-cracking.

Table 8

Isotopologue distribution (%) in the individual C₄ products from the reaction of DME with 2-¹³C-propene (in conditions of Table 7).

Temp. °C	Product	Unlabeled %	Singly labeled %	Doubly labeled %
200	<i>cis</i> -but-2-ene	13	84	3
	<i>trans</i> -but-2-ene	23	70	6
220	<i>cis</i> -but-2-ene	28	51	19
	<i>trans</i> -but-2-ene	23	54	23
	but-1-ene + 2-methylpropene	36	40	24
250	<i>cis</i> -but-2-ene	30	46	23
	<i>trans</i> -but-2-ene	31	44	25
	but-1-ene + 2-methylpropene	36	41	23
	2-methylbutane	37	47	15

cracking product. The latter is undoubtedly the case at 250 °C. At this temperature scrambling intensity is further enhanced, probably resulting from the more important contribution of a complex mechanism involving dimerization, H-transfer, cracking and coke formation. As isobutane is now present in significant amounts with the same distribution of the labels as for the butenes, the occurrence of intense isotopic scrambling is obvious.

4. Conclusions

The homologation of ethylene with DME is a potential pathway for selective bio-propene production. Although under MTO conditions this reaction is virtually absent, literature reports selectivities as high as 80% in methylation of ethene with mainly MeOH and occasionally DME. Labeling work of ethene with ¹³CH₃OH in such conditions seems providing evidence for the presence of consecutive methylations increasing in rate with increasing alkene chain length. It can also not unambiguously be concluded that such conditions isotopomer/isotopologue distributions are free of significant isotopic scrambling.

Work performed at low temperature (<280 °C) and low conversion (<10%) shows that in the homologation of ethene with dimethyl ether for various H-zeolite topologies such as MFI, MEL, TON, and CHA, reaction conditions can be selected achieving 100% propene selectivity with productivities up to at least 8 g propene per g of catalyst. Use of alternative sources for C₁ and C₂ carbons, show that ethene and DME optimally perform and the presence of water from feed dehydration inhibits the homologation reaction in the conditions favoring selective propene formation.

Use of singly ¹³C labeled ethene in the co-reaction with DME illustrates on H-ZSM-5 and H-SAPO-34 zeolites that the absence of isotope scrambling points to the occurrence of propene formation *via* homologation as well as directly from DME.

Separate homologation reactions of singly labeled propene with DME over the same H-zeolites, shows the possibility of even selective formation of n-butenes. From the distribution of the isotopologues in the C₃[−] and C₄[−] product fraction, it can be concluded that for alkenes not formed by homologation, re-cracking of hexenes and octenes,

Scheme 1. Schematic representation of pathways for labeled propene and ethene formation in the homologation of singly ¹³C labeled ethane with DME with MFI and CHA-type zeolites in low temperature/conversion conditions.

respectively, are responsible.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Pieter Struelens: Writing - original draft, Investigation. **Pierre Jacobs:** Supervision. **Delphine Minoux:** Conceptualization. **Jean-Pierre Dath:** Conceptualization. **Nikolai Nesterenko:** Formal analysis, Writing - review & editing. **Bert Sels:** Formal analysis, Supervision.

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