Influence of process parameters on single bed Ni/(Al)MCM-41 for the production of propene from ethene feedstock

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HIGHLIGHTS

- Direct production of propene from ethene feedstock using Ni/(Al)MCM-41.
- Reaction network analysis indicates the occurrence of cracking reaction.
- Cyclic reactor operation is suggested, including deactivation and regeneration.
- A single catalyst bed was applied for more than 2000 h on stream.

GRAPHICAL ABSTRACT
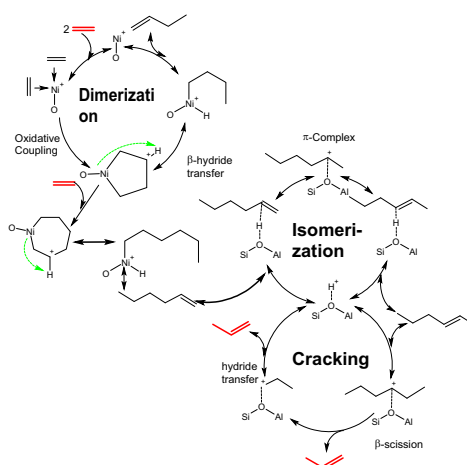
ARTICLE INFO

ABSTRACT

A Ni aluminized mesoporous MCM-41 catalyst was prepared and applied for the direct conversion of ethene to propene. Suitable ethene conversion and good selectivity for the desired molecule propene were achieved. The catalyst placed in a packed tubular reactor was stable for more than 2000 h with time on stream. A reaction network analysis was performed evaluating the product spectrum observed covering a large range of operating conditions. Thereby, temperature and feed concentration can be considered as significant influence parameters on the product distribution. Based on the product spectra, a modified reaction network including a catalytic cycle is suggested, which adds cracking of long-chain olefins to the conventionally considered dimerization/oligomerization and isomerization steps. Following previous publications, the catalyst presented strong deactivation behavior. It was observed that the regeneration

conditions (oxygen concentration and regeneration time) are crucial parameters concerning long-time stability. Finally, a cycling reactor operation of deactivation-regeneration steps is suggested.

1. Introduction

Over the last decades, propene became one of the central building blocks for the petrochemical industry (Lavrenov et al., 2015). This is mainly due to its use for the production of polypropylene and propene oxide. The growing demand cannot be satisfied with the current production technologies (Lavrenov et al., 2015). Therefore, new, flexible and innovative technologies are required. The dehydrogenation of propane (Kogan and Herskowitz, 2001), the catalytic cracking of butenes (Mol, 2004; Zhu et al., 2005, 2009) and the metathesis of ethene and butene (Mol, 2004; Huang et al., 2005), as well as the direct conversion of ethene to propene (ETP) (Alvarado Perea et al., 2013; Iwamoto, 2008), are intensively investigated.

Dehydrogenation processes present very selective chemistry involving a catalytic abstraction of hydrogen from propane to give propene. One of its drawbacks is the high reaction temperature required (>600 °C) based on the chemical limitations and, thus, the occurrence of enhanced side reactions (Cavani et al., 2007). Above 700 °C, cracking to ethene and methane is strongly pronounced (Wittcoff et al., 2013). Various process technologies are available, which vary in terms of reactor design, reaction conditions and catalyst (Zhu et al., 2009).

The catalytic cracking of longer chain olefins is an alternative route to provide propene. These olefins have to be provided by other processes. The cracking reactions proceed in complex reaction networks (Buchanan et al., 1996). These include multiple undesired side reactions, such as aromatization, oligomerization and hydrogen transfer. As a result, this leads to a wide spectrum of products (Corma et al., 2005) and a subsequent separation problem as well. Zeolites like ZSM-5, ZSM-23, and MCM-22 have shown high conversion of butenes in the classical catalytic cracking temperatures range between 600 and 650 °C (Zhu et al., 2009; Wang et al., 2004; Zhu et al., 2005, 2005; Lu et al., 2006). Modification of the zeolite ZSM-5 with potassium showed a decrease in the conversion of 1-butene (Zhu et al., 2005).

With the metathesis, a fundamental organic reaction is available for the production of propene. Typical metathesis catalyzing metals are tungsten, molybdenum and rhenium. Rhenium supported on alumina oxide is applied in the Meta-4 process, (Mol, 2004), in which ethene and 2-butene react at 35 °C and 60 bar in the liquid phase. It selectively produces propene at a conversion of around 60%. However, due to the sensitivity of the rhenium to catalyst poison, highly purified feedstock is required. Another major application is the Olefin Conversion Technology (OCT) developed by Lummus. Tungsten supported on silica dioxide is used in a fixed bed at temperatures above 260 °C and pressures between 30 and 35 bar. The process converts 60% of the butene and offers a propene selectivity of up to 90% (Mol, 2004).

All the above-mentioned technologies are characterized by major drawbacks, regarding the reaction conditions or the need for valuable feedstock. Ethene is easily obtained by conventional steam cracking. It is produced independently and constantly. Therefore, the direct conversion of available and cheap ethene to propene (ETP) is considered as very attractive. Significant research was dedicated to developing suitable catalytic systems. Taoufik et al., have reported the direct transformation of ethene into propene over a tungsten hydride supported on alumina (Taoufik
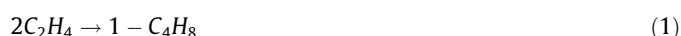
et al., 2007). The conversion was only 10% after 10 h on stream. Oikawa et al. (2006) and Lin et al. (2009) presented silicaaluminophosphate microporous molecular sieves, like SAPO-34 and H-ZSM-5 zeolite, as highly active catalysts for the ETP-reaction, but also faced severe deactivation with time on stream. Iwamoto (2008, 2011) investigated nickel doped MCM-41 and found it to be active for the ETP reaction. Lehmann et al. (2011, 2012) and Alvarado Perea et al. (2013) studied the characteristics of Ni/MCM-41 and Ni/(Al)MCM-41.

Experimental results with ethene as the feedstock present a wide range of possible results for the conversion of the reactant and the selectivity to the desired product propene. Depending on the aluminum doping, Alvarado Perea et al. (2013) achieved conversion in the range of 0–85%, with propene selectivity falling from just under 60% to around 40% with increasing conversion. Amin and Anggoro (2003) investigated ZSM-5 and dealuminized variations of this catalyst. A conversion of about 20% could be achieved with varying selectivity between 5 and 30%, depending on the aluminum content. However, the main products of the reaction were C5-C10 components. Using a Ni/AlSBA-15 + MoO$_3$-SiO$_2$ Andrei et al. (2016) achieved 40% conversion and an initial selectivity of 70%, which drops to 46% in 5 h.

Dai et al. (2014) used a variety of different catalysts, including H-beta, SAPO-34 and H-SSZ-13. In this order, conversion increased from 9.1% to 61.4% and 82.9%, with selectivity achieving 43.4%, 68.3% and 59.5% respectively. In comparison, Oikawa et al. (2006) realized only 7.9% conversion to SAPO-34 and a significant selectivity of 79.5%. Ding et al. (2009), Lin et al. (2009) and Liu et al. (2004) used H-ZSM-5 with strongly varying results. Ding received 40% conversion and 30% selectivity, whereby the main products were methane and ethane. In contrast, Lin achieved 58% and 42% for conversion and selectivity. Liu added hydrogen at a reaction temperature of 675 °C and achieved a conversion of 12% and 65% propene selectivity.

Frey and Hinrichsen (2012) used Ni/MCM-48 with constant values of 68% conversion and 50% propene selectivity. Another form of MCM was used by Henkel (2013), Iwamoto (2008, 2011) and, Lehmann et al. (2011). All studies showed that conversion decreases significantly over time and that selectivity increases analogously. For all investigations a conversion of approx. 40% and a propene selectivity of 45% were achieved. Li et al. (2013) combined NiSO$_4$ with rhenium oxide to gamma-Al$_2$O$_3$ by 59% in ethene and 49% in propene selectivity. Lavrenov et al. (2015, 2016) followed a similar approach, but with PdO and Re$_2$O$_7$ on ZrO$_2$. At a temperature of 80 °C, 86% conversion and 65.4% propene could be obtained.

The widely accepted mechanism as proposed by Iwamoto (2008) and extended for this present work, consists of three reaction steps. First, a dimerization reaction of ethene to 1-butene (Eq. (1)) on the nickel ion of the catalyst, followed by an isomerization of 1-butene to cis-/trans-butene (Eq. (2)) catalyzed by the acidic sites. Finally, a metathesis step of the generated 2-butene and unconverted ethene to provide two moles of propene (Eq. (3)).

$$2C_2H_4 \rightarrow 1 - C_4H_8 \tag{1}$$

$$1 - C_4H_8 \leftrightarrow 2 - C_4H_8 \tag{2}$$

$$C_2H_4 + 2 - C_4H_8 \rightarrow 2C_3H_6 \qquad (3)$$

It is supposedly assumed that Nickel initiates the metathesis step (Alvarado Perea et al., 2013; Lehmann et al., 2012). The postulated network does not take into account the formation of relevant byproducts and their influence on the course of the reactions and a more detailed reaction network is desirable. To design and optimize the reaction system quantitative description of the underlying reaction mechanisms and kinetics is of large interest. For the investigation an aluminized MCM-41 with a Si/Al ratio of 60 and incorporated nickel was chosen. This catalytic system has been tested with varying structural ratios and amounts of nickel (Alvarado Perea et al., 2013). The composition used here proved to be optimal in terms of catalytic activity and selectivity to the desired product, propene. The conducted experiments are chosen to obtain information about the ongoing processes. Based on the findings the reaction mechanism is verified based on the conversion of the ethene feed and the selectivity of the main reaction products. Additionally, the stability of the catalytic system is validated.

2. Preparation of the support and catalyst

The (Al)MCM-41 support was prepared by the method recently described by Alvarado-Perea et al. (Noreña-Franco et al., 2002). The precursor mixture had a molar composition of 1 SiO_2: 0.35 CTABr: 0.31 TBAOH: 0.000–0.2 $NaAlO_2$: 55 H_2O and was manually stirred for 15 min. Sodium aluminate (NaAlO2:Al2O3 50–56% and Na2O 40–45%) was used as the aluminum source, with its amount being adjusted for generating a Si/Al ratio of 60. Subsequently, the mixture was filled into a Teflon bottle and aged 48 h at 100 °C in an oven. The resulting white solid was recovered by vacuum filtration and washed with deionized water. The produced powder was dried and calcinated, as reported by Alvarado Perea et al. (2013), to carry out the corresponding characterization. The Ni/(Al)MCM-41 catalyst was prepared using the template ion exchange method (Alvarado Perea et al., 2013). Nickel nitrate (Merck, Ni2 (NO3) 2·6H2O ≥ 99.0%) was used as Ni precursor. The resulting mixture was thermally treated in a Teflon bottle in a muffle furnace. The light green solid was subsequently recovered through vacuum filtration, washing and drying. The final product was calcinated at 600 °C for 6 h in air. The characterization of Ni/(Al)MCM-41 using XRD, N2-Physiosorption, TEM, AAS, TPR, TPO, Si CP-MAS NMR and Al MAS NMR was reported in Alvarado Perea et al. (2013), Alvarado Perea (2014).

3. Experimental procedures

3.1. Testing of the catalyst

The evaluation of the catalytic activity was carried out in a fixed-bed laboratory reactor equipped with an oven (high-temperature kinetic reactor HTKR), controlled using a thermos element in the middle of the catalyst bed. The applied quartz tube had an inner diameter of 0.6 cm. All experiments were performed at atmospheric pressure, with a sample mass of 0.5 g of catalyst, corresponding to bed length of 11.8 cm.

The feed consisted of ethene (Linde 99.9%) and nitrogen (Linde 99.9993%). Different sets of experiments were performed. The following conditions were varied during the experimental study: the space velocity (weight of catalyst/flowrate, W/F) in the range of 250–2000 kg_{Kat}·s/m³ and the molar fraction of ethene in the feed between 2.5 and 25%. The entity of the numerous performed steady state experiments, corresponding to different operating conditions, adds up to 120 runs with the use of a single catalytic bed. To quantify the corresponding dependence, the temperature was varied between 50 and 350 °C in increments of 25 °C.

To investigate the catalyst bed over a longer period it was operated for 24 h varying the temperature stepwise at constant W/F and feed ratio. To set the initial temperature, the catalyst was heated under nitrogen to the desired reaction temperature. When this temperature was reached, the inlet flow was adjusted according to the desired reaction conditions. The analysis of the composition of the reactant inlet stream and the reaction products was carried out using gas chromatography (Agilent 6890 GC/TCD with a 5973 MSD) equipped with a 30 m HP-Plot Q column (Agilent Technologies).

After each experimental run, the catalyst bed was regenerated to retrieve the catalysts initial activity. For this, the fixed bed was heated to 500 °C under nitrogen flow. When the desired temperature was reached, compressed air was added to the feed stream and the conditions were kept constant for three hours. After the catalyst oxidation, the reactor was cooled under nitrogen down to 50 °C. The catalyst showed a consistent activity and properties in subsequently carried reference runs with good reproducibility. The full set of experiments performed consisted of 120 runs. However, not all experimental runs are presented, rather a representative series of reaction conditions.

3.2. Data analysis

To evaluate the performance of the catalyst the conversion of ethene, selectivity and yield for the 7 products involved (i = 1,..., L) were calculated, namely propene, ethane, 1-butene, cis-butene, trans-butene, pentene and hexene. Iso-butene was not taken into account, because it was not detected with sufficient confidence during the experiments carried out. Additionally, the isomers of pentene and hexene were lumped into C_5H_{10} and C_6H_{12} components, because the identification of the single isomers was not possible, by the analysis used.

Thus, the outputs, defined by Eqs. (4)–(6), were evaluated.

Conversion of ethene $\quad X_{C_2H_4} = \dfrac{\dot{n}_{C_2H_4}^0 - \dot{n}_{C_2H_4}^{ex}}{\dot{n}_{C_2H_4}^0}$ $\qquad (4)$

Selectivity of component i $\quad S_i = \dfrac{\dot{n}_i^{ex}}{\sum_{k=1}^{L=7} \dot{n}_k} \qquad i = 1,...,L = 7 \quad (5)$

Yield of component i $\quad Y_i = \dfrac{\dot{n}_i^{ex}}{\dot{n}_{C_2H_4}^0} \cdot \dfrac{(-\nu_{C_2H_4})}{\nu_i} \qquad i = 1,...,L = 7$

$$(6)$$

Within the equations, $\dot{n}$ denotes the molar flow of a component and ν the stochiometric coefficient of a specific component i. The index 0 is related to the initial quantity. Furthermore, ex stands for the experimentally obtained value of molar current.

4. Results

4.1. Influence of feed concentration and W/F

Fig. 2 shows the results of experiments for ethene feed concentration of 2.5, 5 and 10%, and weight-to-flow ratios (W/F), of 250, 500 and 750 kg_{Kat}·s/m³. Several trends can be identified in the graphs. With increasing reactant concentration and decreasing flow rate the conversion of ethene increases (Fig. 2a). For the largest feed concentration (10 mol-% ethene) and residence time (W/F = 750 kg_{Kat}·s/m³) the highest conversion was obtained at
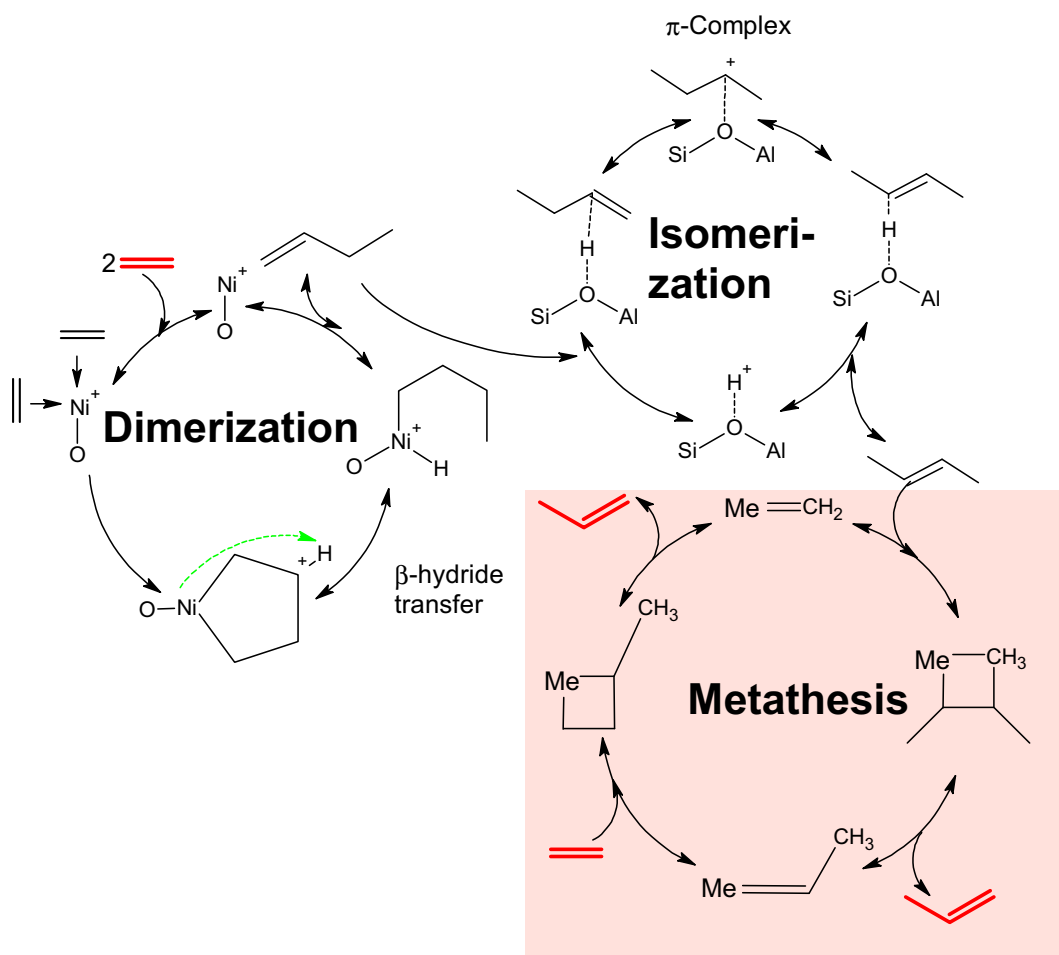
Fig. 1. Mechanism of the ethene to propene (ETP) reaction based on the assumed reaction steps by Iwamoto (2008).

350 °C (roughly 20%). In the temperature range of 150–250 °C the change in ethene slightly increases at a rather constant rate. For further increased temperatures, the ethene conversion steeply increased (except for the case of the 2.5% ethene feed).

Both, the 1- and 2-butene are produced already at temperatures around 100 °C. Therefore, the initiation of the dimerization and the faster proceeding isomerization (Kiedorf et al., 2014) are pronounced over the entire temperature range. The catalyst is highly selective towards 2-butenes, consisting of the cis- and trans-isomer, as the main reaction product. The decreasing 2-butene selectivity at 250 °C corresponds to the steep increase in ethene conversion and the generation of propene. Based on similar observations Iwamoto (2008) proposed metathesis to be the key reaction at higher reaction temperatures (see Fig. 1). However, no typical metathesis catalyst is applied in neither his nor the present work.

A different trend can be seen for the selectivity for the desired product propene (Fig. 2d). The highest selectivity (44.9%) was observed for the lowest feed concentration. The propene selectivity decreases with an increasing mole fraction of ethene indicating the occurrence of side reactions, e.g. enhanced oligomerization. No dependence on the selectivity on the W/F ratio was observed for the conditions considered. It was essentially influenced only by the reactant fraction in the feed stream.

The results further reveal that the route toward the C3-olefin is kinetically hindered up to 250 °C. At higher temperatures, certain pathways seem to be more pronounced leading to the desired product. The maxima of selectivity and yield observed in the entire

range of the reaction conditions covered in this study are visualized in Fig. 2 and summarized in Table 1. Additional information regarding the observed yields of the main reaction products is available in the supporting information (S) Fig. S1.

A clear maximum of propene selectivity has not been reached for the operating temperature considered. Preliminary investigations revealed deficits of the Ni/(Al)MCM-41 catalyst concerning the occurrence of severe deactivation, observed at temperatures required to achieve higher propene yields, namely T = 450 °C (Alvarado Perea et al., 2017). After performing experiments at these temperatures, due to the irreversible blocking of active sites by coke and possibly sintering, the catalyst could not be regenerated. The blocking is probable due to possible oligo- and aromatization of the compounds involved. Thus, to maintain sufficient catalysts activity, the reaction temperature has to be limited to approximately 300–350 °C. Therefore, the experiments were carried out up to 350 °C. This causes the limited ethene conversions and propene yields found.

4.2. Revision of assumed reaction cycle

From the product analysis and the obtained experimental perceptions, the mentioned reaction steps by Iwamoto and shown as a catalytic cycle in Fig. 1 were found to be not sufficient to account for all phenomena observed. Formation of larger olefins, as pentenes and hexenes, can be explained by metathesis of the intermediates and oligomerization of ethene, following a pseudo-Wittig mechanism (Amakawa et al., 2012). However, the appearance of
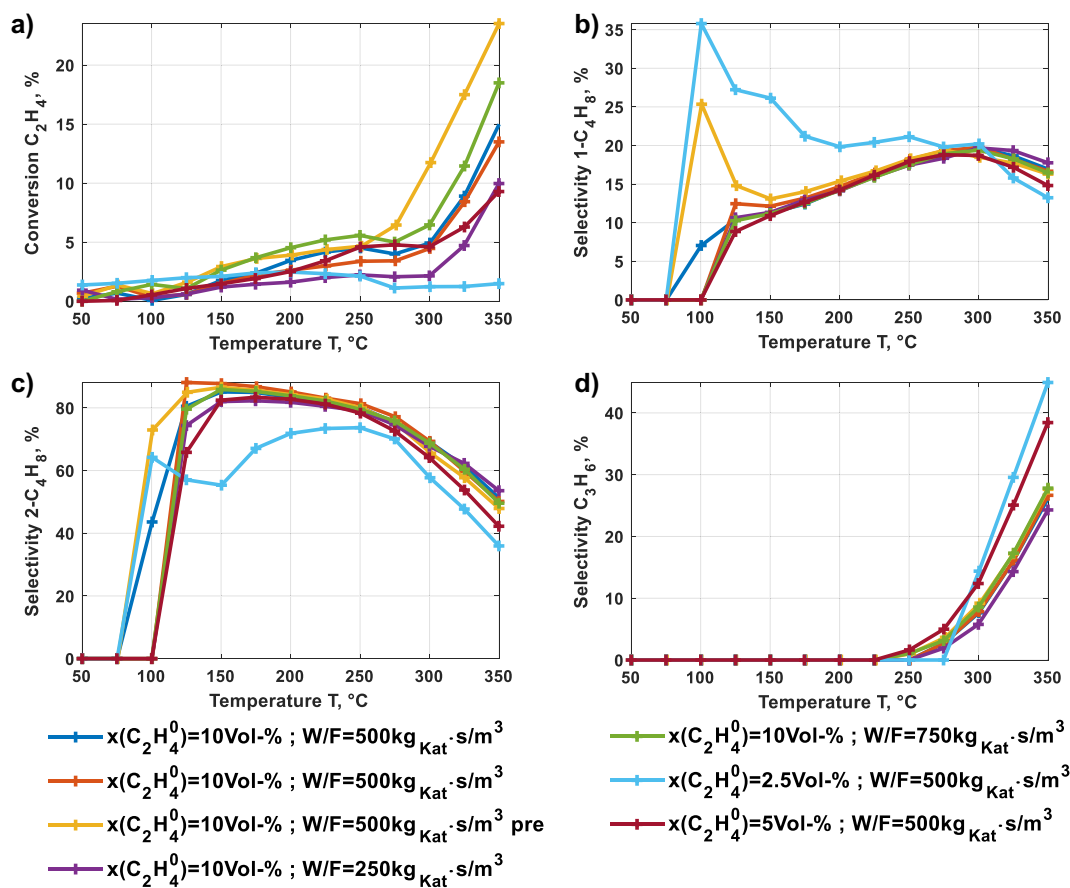
Fig. 2. Conversion of ethene (a), selectivity of 1-butene (b), 2-butene (c) and propene (d) over temperature for Ni/(Al)MCM-41 (Si/Al = 60).

Table 1
Highest selectivity and yield data detected of the investigated temperature, feed concentration and W/F ranges covered.

	Desired product	Intermediates		Undesired side products		
	Propene	1-Butene	2-Butene	Pentene	Hexene	Ethane
Selectivity, % Eq. (5)	**44.9**	35.8	**88.1**	4.1	3.4	3.7
Temp, C_{Feed}	350 °C, 2.5%	100 °C, 2.5%	125 °C, 10%	350 °C, 10%	350 °C, 10%	300 °C, 10%
Yield, % Eq. (6)	4.6	3.6	10.7	1.0	1.0	0.2
Temp, C_{Feed}	350 °C, 10%	350 °C, 10%	350 °C, 10%	350 °C, 10%	350 °C, 10%	350 °C, 10%

saturated hydrocarbons, like ethane, and the generation of coke species cannot be explained sufficiently (Argyle and Bartholomew, 2015). Based on an alternative extended reaction mechanism illustrated in Fig. 3 an extended set of reaction equations is given below. According to the literature (Sohn and Park, 2000; Sohn et al., 2006; Broene et al., 2005; Hartmann et al., 1996; Bonneviot et al., 1983), nickel active sites catalyze the oligomerization of ethene. The main product of this step are butenes. This mechanism proceeds via oxidative coupling of ethene (Rabeah et al., 2016; Andrei et al., 2015). However, ethene could be further oligomerized to hexene. In addition, the butenes may dimerize as well and the coupling of ethene with butenes can occur, respectively resulting in longer chain olefins, e.g. hexene or octane. These molecules can isomerize to the thermodynamically favored internal olefins, via π-allylic carbanion using acidic sites of the catalyst (Baird and Lunsford, 1972). The mechanism proposed here involves a conjunct polymerization up to hexene (Alvarado Perea et al., 2017; Dejavifve, 1980) and the subsequent cracking (Buchanan et al., 1996; Bortnovsky et al., 2005; Chen et al., 2014; Corma and Orchillés, 2000). The wide range of possible molecules can interact with the acidic sites, creating a complex network of cracking reactions. The described pathway explains the product spectrum observed in our investigations and the reaction towards propene.

The postulated cracking reaction proceeds via monomolecular protolytic cracking by β-scission of the longer chain olefins, as shown in Fig. 3. Further oligomerization, aromatization and deprotonation may occur as side reactions. This is an explanation for the generation of alkanes and the severe deactivation, due to the production of coke and the following blocking of active sites. Thus, a reaction network including catalytic cracking of formed 3-hexene is suggested, which pre-dominantly results in our desired product propene. To reduce the complexity all isomers of pentene and hexene were lumped together as C_5H_{10} and C_6H_{12}.

Based on the proposed mechanistic cycles a more accurate derivation of reaction rates is possible. Therefore, the basis for mechanistic, kinetic models is achieved. Possibly accounting for more of the occurring effects.
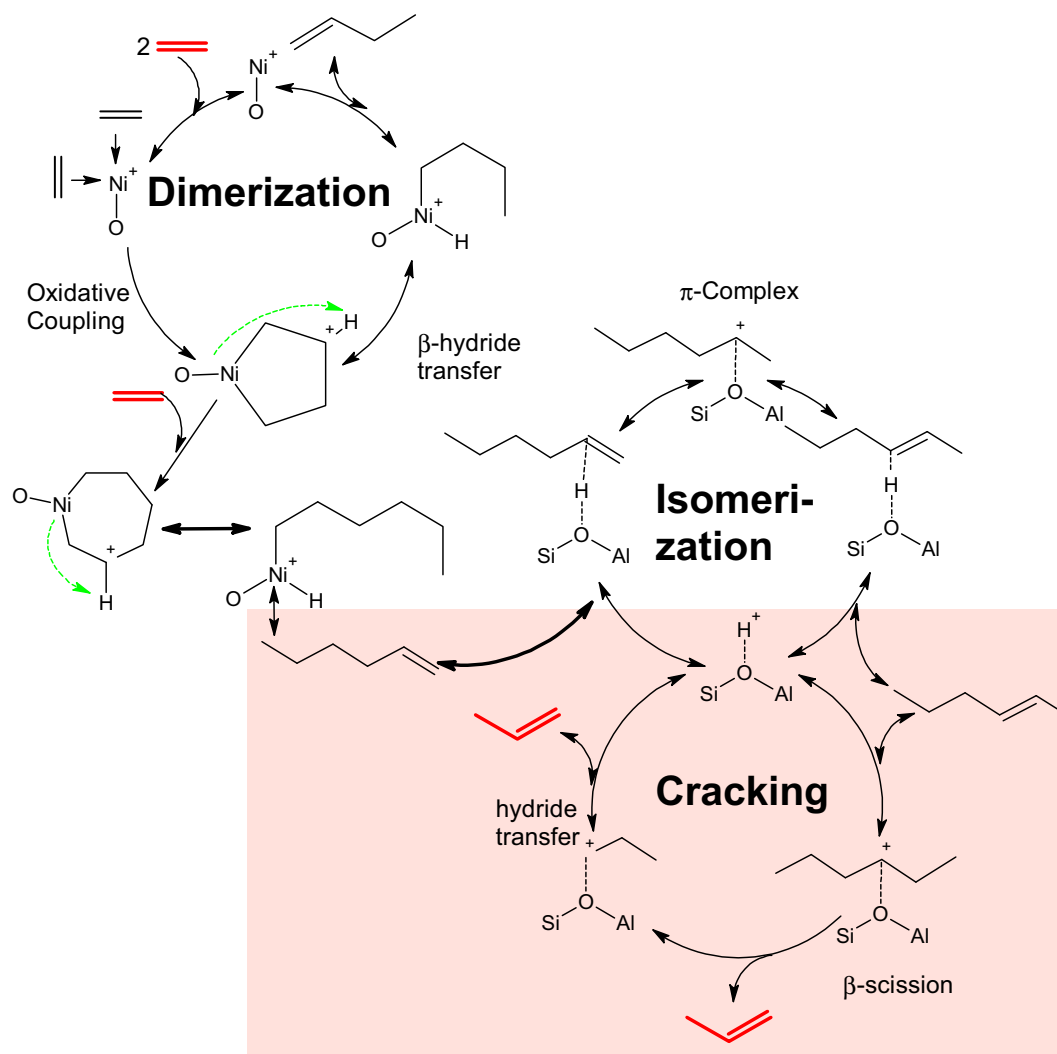
Fig. 3. Proposed catalytic mechanism for the propene production from ethene, modifying the mechanism based on the proposal by Iwamoto (Fig. 1), considering oligomerization and cracking steps.

4.3. Stability of the catalytic system

From the previous investigations, a severe deactivation was observed with time on stream (Alvarado Perea et al., 2013, 2017). For the base case of 10% ethene feed and a weight-to-flow ratio of 500 kg$_{Kat}$·s/m^3 an experiment lasting 24 h was performed using the HTKR. The change in conversion and yield (Fig. 4a), as well as selectivity of the measured products (Fig. 4b), are pronounced and illustrated below.

The graphs show that with time on stream the conversion of ethene decreases severely from 28% to values below 5%. Also, the yields of the products decrease. However, the selectivity is kept constant for the entire reaction time. This indicates that the active catalytic sites are inhibited, mainly by coke like residues, but the characteristics of those sites are not changed. Therefore, under the chosen reaction conditions a simple blocking of the catalyst seems to be ongoing, without any poisoning, discharge or sintering.

The catalyst provided reproducible results for more than 2000 h of total reaction time with continuous regeneration. However, detailed investigations for the regeneration conditions are still pending. Identification of substances accumulating on the catalyst should be possible via investigating the residues and their burn-off

characteristics. As shown in Fig. 5, the darkened catalyst due to coke deposits can be fully regenerated with the appropriate oxygen concentration and regeneration time.

A regeneration model with its kinetic parameters is needed to optimize an overall process (Fig. 6). Such processes consist of a production phase, with reaction and simultaneous deactivation, and regeneration phases, where no product is obtained. The resulting time, of both the deactivation and regeneration phase, gives the cyclic time for the process. A necessity is knowledge regarding the kinetics of deactivation and regeneration. Both detailed information benefits one to optimize each step and the overall process according to the desired performance parameter, by choosing optimal stoppage criteria.

A plot summarizing the results of all 120 runs performed is shown in Fig. 7. Exploiting periodically the described reactivation the Ni/(Al)MCM-41 (Si/Al = 60) a similar activity could be maintained over the whole measurement range of conditions. The entity of all performed experiments can be separated into 4 sections. In the first section, named "Feed + Temp", the limits of the experimental setup and the catalyst were evaluated. In this timeframe, the regeneration strategy was optimized. Therefore, not all experiments are suitable for consideration. Even though for some
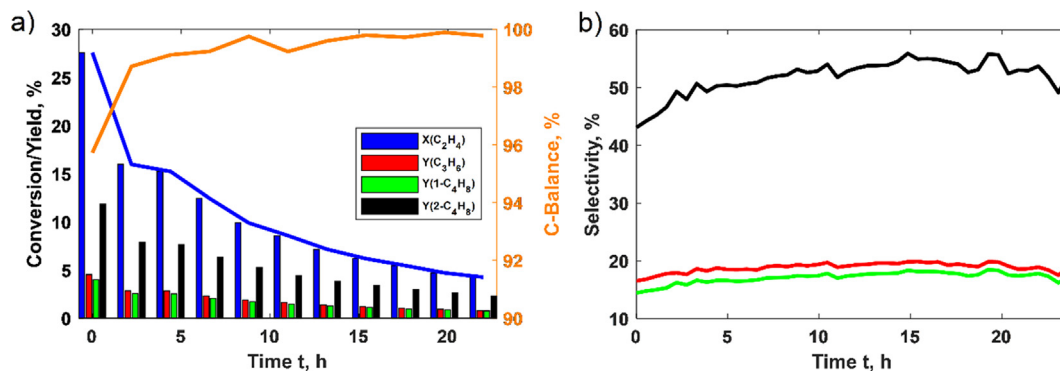
Fig. 4. (a) Time-dependent values of conversion and yield of the observed products with time on stream and the change in the C-Balance. (b) Selectivity of the observable products as a function of time on stream for a reaction of 10% ethene feed at 350 °C, with a W/F = 500 kg$_{Kat}$·s/m^3.

- ➢ Fresh Catalyst
- ➢ After Experiment
- ➢ Reg. 3h with 2.5% O_2
- ➢ Reg. 3h with 5% O_2
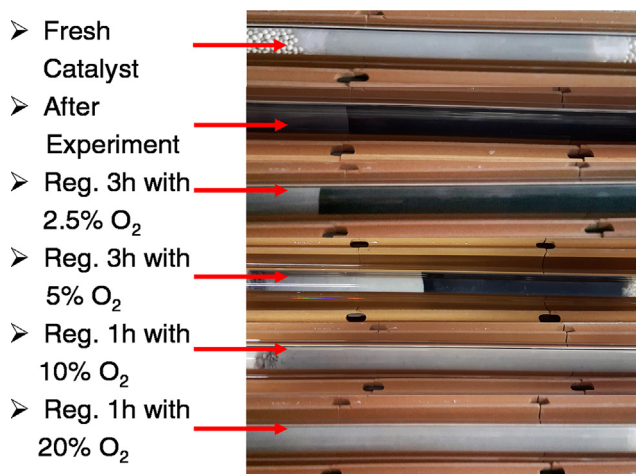- ➢ Reg. 1h with 10% O_2
- ➢ Reg. 1h with 20% O_2

Fig. 5. Dependency of the deactivated catalyst bed with varying regeneration time and oxygen concentration.
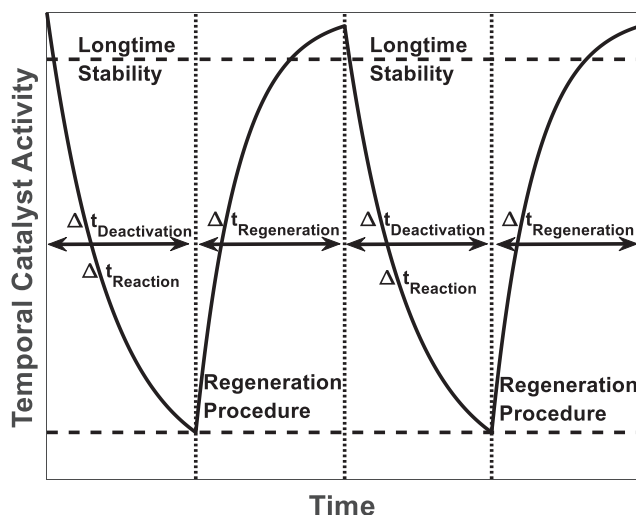

Fig. 6. Exemplified cyclic operation of a reactor setup, with distinct reaction and deactivation, subsequently followed by regeneration, with stoppage criteria as low and high activity, initializing the following process step.

experiments not all of the preliminary activity could be regained, as shown in Fig. 5, a prolonged regeneration allowed for an increase to the initial activity.

In the second section, named "Temp", the longtime stability of the catalytic system was evaluated, while repeating similar experiments. A steady value for propene selectivity is observed. Even though the conversion showed a slight decrease, only from 700 to 1000 h, thus, an active and productive catalytic system was observed. With the application of pre-treatment and pro-longed regeneration condition, the catalytic activity could be restored. Additionally, it becomes clear from Fig. 7, that the reaction temperature is a major factor for the propene synthesize in the complex reaction network and deactivation. At temperatures lower than 300 °C almost no reactant is converted. Regarding the desired product propene, a lower feed concentration appears beneficial. This is due to decreased side reactions, of enhanced dimerization/oligomerization and interaction of the feed the main product, the butenes.

For the third section, the "Feed" concentration was varied from 2,5 to 25% of ethene for constant temperatures of 250, 300 and 350 °C. The temperature has a significant influence on the performance of the catalyst. Only low conversion and almost no selectivity to propene are seen below 300 °C. For varying inlet concentration two counter behaviors are monitored. Higher inlet concentration of ethene increases side reactions, therefore the selectivity of propene decreases. At the same time, the conversion of ethene increases, because of these side reactions, which enhances the effect of lower propene selectivity.

The last section of "Validation" presents a series of repetition experiments under constant conditions. A reproducible saw tooth profile is obtained for conversion, while selectivity is rather constant. These results show that the catalyst is still active after 2000 h of time on stream. Its morphology and properties are unchanged and give constant product distribution and quality.

5. Conclusions

The heterogeneously catalyzed synthesis of propene from ethene was studied for a Ni/(Al)MCM-41 catalyst with a Si/Al ratio of 60. A large set of experiments was performed, with varying feed concentration and catalyst weight-to-flow ratios, to identify and quantify the ongoing reactions. At first, an extended mechanistic cycle for the established reaction network suggested by Iwamoto (2008), consisting of dimerization, isomerization and metathesis steps was applied. In an attempt to obtain a better representation of the experimental data, a modified reaction network was assumed in which catalytic cracking was considered, rather than a metathesis step for propene production. This allowed for an improved description and explanation of the observed product spectrum. It will be of interest to derive detailed mechanistically explanatory kinetic models, based on the catalytic cycles proposed.

Furthermore, deactivation behavior and its dependent kinetics were observed. Based on these observations a strategy for the
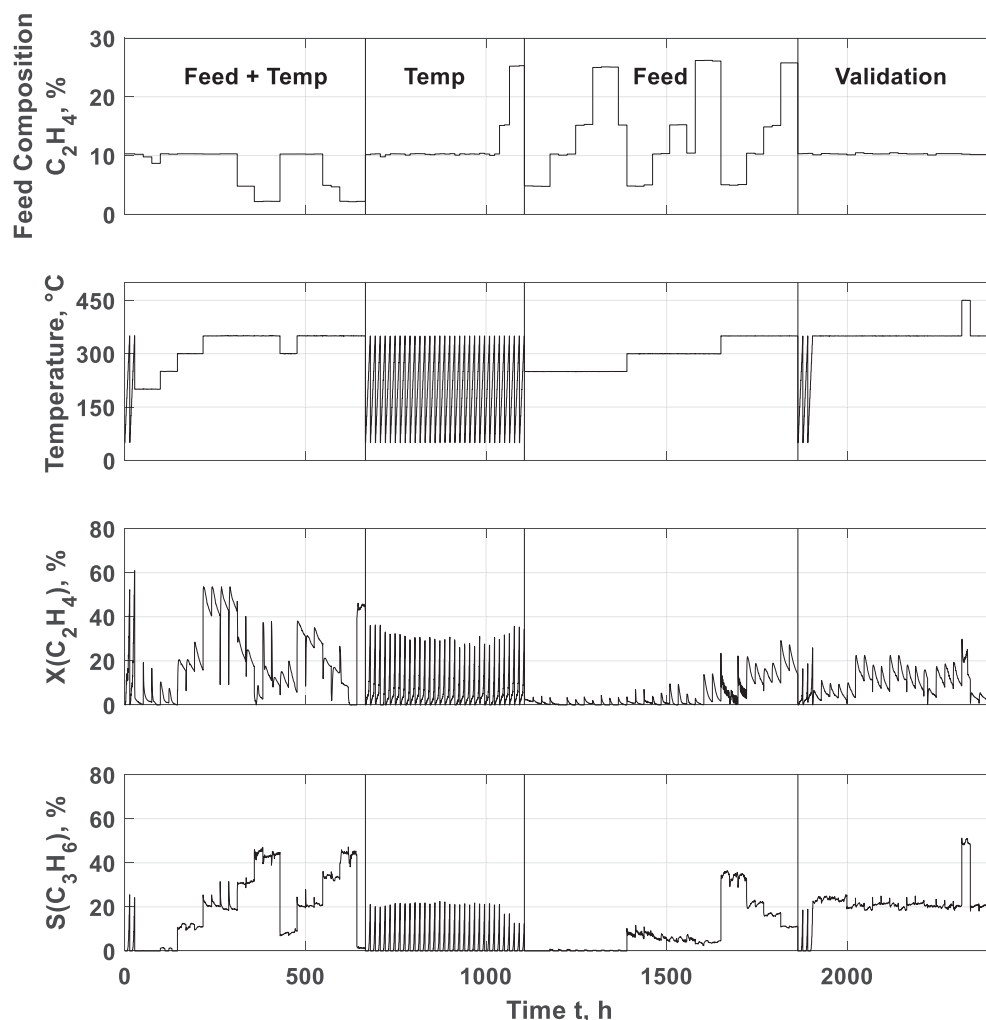
Fig. 7. Summary of the conditions and corresponding performance criteria for the set of the Nex = 120 sequentially carried out experiments using an identical sample of a (Ni/(Al)MCM-41) catalyst, concentration was varied from 2,5 to 25% of ethene, temperature was varied from 50 to 350 °C and W/F was changed between 250 and 2000 $kg_{Kat} \cdot s/m^3$.

catalyst regeneration was developed, implemented and successfully tested. This allowed operation of over 2000 h for a single catalyst bed with attractive stability.

In further work, a quantitative kinetic model for the applied catalytic system will be derived and evaluated. Further, parameters for the deactivation and regeneration have to analyzed and optimized to enhance the efficiency of the overall process ($t_{Dead}/t_{Reaction}$), exemplified in Fig. 6.

Author contributions

The manuscript was written through contributions of all authors./All authors approved the final version of the manuscript.

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.

Acknowledgements

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ces.2019.115246.

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