

Steering linear 1-alkene, propene or gasoline yields in ethene oligomerization via the interplay between nickel and acid sites



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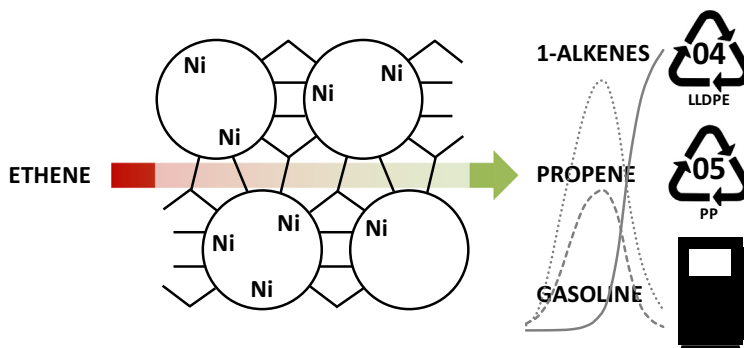
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HIGHLIGHTS

- The acid and nickel sites interplay during ethene oligomerization was quantified.
- 2 catalyst descriptors suffice to adequately reproduce data on different catalysts.
- Reaction pathway analyses provided guidelines for in-silico catalyst design.
- In-silico tuning of product yields via the interplay between acid and nickel sites.
- Product inhibition occurred by alkylates, resulting in a lower catalyst activity.

GRAPHICAL ABSTRACT



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ABSTRACT

The ethene oligomerization performance of heterogeneous, Ni-based acid catalysts has been assessed by combining experimental measurements and Single-Event MicroKinetic (SEMK) modelling. In addition to the independently determined physisorption parameters, two catalyst descriptors, i.e., the ethene coordination enthalpy on the Ni-ion sites and the alkene protonation enthalpy on the acid sites, sufficed to adequately describe experimental data acquired on 1.8 wt% Ni-SiO₂-Al₂O₃ and 4.9 wt% Ni-Beta zeolite.

While Ni-sites ensure ethene dimerization, further alkylation, isomerization and cracking reactions occur on the acid sites. Unavoidably, alkylated species lead to product inhibition by hindering the accessibility of active Ni-ion sites for ethene. Very pronounced product physical adsorption was demonstrated to even result in reduced ethene conversion and, hence, catalyst activity.

Through extensive reaction pathway analyses, guidelines for rational catalyst design for heterogeneous, Ni-based acid catalysts were proposed which are simulated to lead to selectivities of 60% towards 1-alkenes, 50% towards gasoline and 25% towards propene.

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1. Introduction

The pursuit of so-called ‘sustainable’ fuels and chemicals has never assumed such a global character as today. With increasing

environmental concerns and corresponding legislation, as well as with crude oil depletion, alternative feedstocks and processes are screened for their economic potential while accounting for their environmental impact as well. Shale gas and oil, tar sands and stranded gas are all hydrogen and carbon sources which have gained significant popularity today, but which do not eliminate the need for more sustainable processes based on renewable feedstocks in the long term. Moreover, shale gas processing leads to a

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Nomenclature

Roman symbols

$a_{C,j}$	the number of carbon atoms in component j (-)
\underline{b}	estimated parameter vector
C_j	molar concentration of component j ($\text{mol kg}_{\text{cat}}^{-1}$)
E_a	activation energy (J mol^{-1})
F_j	molar flow rate of component j (mol s^{-1})
ΔH	enthalpy change (J mol^{-1})
i, j	counter
k	reaction rate coefficient (variable)
k	single-event rate coefficient (variable)
K	equilibrium coefficient (variable)
n_{alk}	number of alkenes (-)
n_e	number of single events (-)
n_{exp}	number of experiments (-)
n_{par}	number of parameters (-)
n_{resp}	number of responses (-)
r	reaction rate ($\text{mol s}^{-1} \text{kg}_{\text{cat}}^{-1}$)
R_j	net rate of formation of component j ($\text{mol s}^{-1} \text{kg}_{\text{cat}}^{-1}$)
S_j	selectivity towards component j (mol s^{-1}) (mol s^{-1}) $^{-1}$
X_j	conversion of component j (mol s^{-1}) (mol s^{-1}) $^{-1}$
$Y_{i,j}$	observed value for response j at experiment i (variable)
$\hat{Y}_{i,j}$	calculated value for response j at experiment i (variable)
w_i	weighing factor of response i during regression (-)
W	catalyst mass (kg_{cat})

Greek symbols

α	stoichiometric coefficient (-)
β	real parameter vector
σ_{ii}^2	covariance of response i (-)

Subscripts

C_2	ethene
ref	reference
t	total

Superscripts

0	inlet
alk	alkylation
as	alkylshift
β_s	β -scission
c	coordination of ethene at a nickel-alkene species
ins	insertion
iso	isomerization
pcp	pcp branching
phys	physisorption
pr	protonation
ter	termination
+	carbenium ion

product slate primarily composed of ethene rather than propene, hence, impacting on the polypropene production and that of other propene derivatives (Swift and Moore, 2013). The development of a process which transforms the ethene excess into propene would be a valuable asset. Moreover, if that process can adapt its product spectrum to a varying market demand, i.e., from fuels such as gasoline, to chemicals such as propene and 1-alkenes, the exploitation of non-conventional and renewable hydrocarbon containing sources becomes economically more attractive.

Natural gas is considered to be stranded when its commercial exploitation is impeded by excessive investment and operation costs. For such, typically smaller, reservoirs several projects have been and still are investigating the application of so-called 'Gas-To-Liquid' (GTL) technologies. One of these projects is OCMOL, which is the acronym for 'Oxidative Coupling of Methane followed by the Oligomerization to Liquids' (<http://www.ocmol.eu/>, 2014). In the first step of this proposed integrated process, methane originating from stranded gas or biogas is oxidatively coupled to ethene. In the subsequent step, the latter is oligomerized and transformed further into liquid fuels, e.g., gasoline, or chemicals such as linear 1-alkenes and propene. Additionally, heterogeneous catalysts are used in order to improve the process sustainability by eliminating the need for environmentally unfriendly solvents as well as the energy requirements for solvent recuperation in its homogeneously catalyzed implementation (Anastas et al., 2001).

Ethene is typically converted into longer alkenes via homogeneous catalysis, e.g., trialkylammonium and nickel complexes (Ullmann's Encyclopedia of Industrial Chemistry, 2014; Spivey et al., 1999). The use of heterogeneous catalysts such as zeolites, would result in a 'greener' process. Ethene is not susceptible to acid catalyzed reactions under relatively mild reaction conditions, i.e., below 523 K, because of the pronounced instability of the primary carbenium ions that would be involved. In the presence of Ni-ions, however, ethene is readily dimerized to butene which, in turn, can undergo further acid catalyzed steps more easily via more stable secondary carbenium ions.

A lot of experimental work has already been performed with respect to ethene oligomerization on Ni containing bifunctional, heterogeneous catalysts, i.e., on amorphous Ni-SiO₂-Al₂O₃ (Heveling et al., 1991, 1998; Toch et al., 2015), Ni-Beta (Martinez et al., 2013), Ni-MCM-22 (Lallemand et al., 2008), Ni-MCM-36 (Lallemand et al., 2008), Ni-MCM-41 (Hulea and Fajula, 2004; Lallemand et al., 2011) and Ni-Y zeolite (Lallemand et al., 2006). Fundamental kinetic models simulating the experimental observations in an adequate manner are scarce. In our previous work, a Single-Event MicroKinetic (SEMK) model was successfully developed (Toch et al., 2015). An experimental data set acquired on an amorphous 1.8 wt% Ni-SiO₂-Al₂O₃ was used to determine the kinetic and catalyst descriptors related to Ni-ion catalyzed oligomerization (Toch et al., 2015).

In the present work, ethene oligomerization is investigated on an alternative bifunctional, heterogeneous catalyst, i.e., Ni-Beta zeolite. Under mild operating conditions, Ni-Beta zeolite has been shown to exhibit stable ethylene oligomerization behavior, leading to highly branched liquid products (Martinez et al., 2013; Moussa et al., 2016). The branching degree of these liquid oligomers has been directly related to the Brønsted acid site concentration and strength (Moussa et al., 2016). The nature of the Ni sites at reaction conditions remains unclear, but most probably, Ni²⁺ species are responsible for the ethene dimerization (Martinez et al., 2013; Moussa et al., 2016). In case of butene oligomerization, at higher temperatures, i.e., >478 K, and high 1-butene partial pressures, i.e., 1.4–2.9 MPa, the conversion rate is controlled by oligomer diffusion in the beta zeolite framework (Wulfers and Lobo, 2015).

Our experimental results indicate the participation of acid catalyzed reactions such as isomerization, alkylation and cracking in the reaction mechanism as evident from the formation of odd carbon numbered alkenes, e.g., propene and pentene. For modeling purposes, the SEMK model for Ni-ion catalyzed ethene oligomerization (Toch et al., 2015) has been extended to account for these acid catalyzed elementary steps. The SEMK model demonstrated how the positive effect of having both Ni and acid sites is

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