Stabilization of active, selective, and regenerable Ni-based dimerization catalysts by condensation of ethene within ordered mesopores

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**Abstract**

This study reports the high and stable ethene dimerization turnover rates conferred upon Ni-based active sites at subambient temperatures by the condensation of liquid ethene reactants within ordered mesopores in Al-MCM-41. Such active and stable catalysts do not require the activators or co-catalysts essential for organometallic Ni-based catalysts and their robust porous framework allows their full regeneration by thermal treatments in inert or oxidizing environments when deactivation occurs. Dimerization rates (per Ni) are independent of Ni content below Ni2+/H+ exchange ratios of unity, consistent with isolated (Ni-OH)+ cations as active moieties, and with the formation of inactive NiO oligomers at higher Ni contents. Both CO and 2,6-di-tertbutylpyridine, used as titrants of Ni centers and protons, respectively, fully suppressed reactivity, indicating that the Ni2+ and OH− centers in (Ni-OH)+ are involved in stabilizing the kinetically-relevant C=C formation transition state. Deactivation constants decreased abruptly to undetectable values at those temperatures and ethene pressures that formed an extended liquid phase within the MCM-41 mesopores that confine the Ni active sites. This remarkable shift from rapid to undetectable deactivation reflects how intrapore liquids preferentially stabilize the late transition states that mediate the desorption of bound 1-butenes before subsequent isomerization and C=C bond formation events during one surface sojourn. Their preferential desorption inhibits the formation of regioisomers and larger oligomers, thus inhibiting deactivation while also leading to very high C4 selectivities among products. Such unprecedented stability and high selectivities allow accurate kinetic measurements and their rigorous mechanistic interpretation in terms of transition state formalisms of chemical dynamics in thermodynamic non-ideal media. Dimerization turnovers involve kinetically-relevant C=C bond formation between unbound ethene molecules and an ethene bound at low coverages on (Ni-OH)+ moieties. Such catalytic sequences lead to dimerization rates with a nearly second-order dependence in ethene fugacity, but with an effective rate constant that benefits from the stabilization of the C=C bond formation transition state as intrapore liquids form. The essential elimination of deactivation events and secondary reactions by such liquids leads to dimerization rates and 1-butene selectivities that are much higher at 240–260 K with liquid-filled mesopores than at 448 K, conditions that maintain all species in their gaseous form. In addition to their significant practical impact, these results provide compelling evidence for the ability of an extended liquid to create a thermodynamically non-ideal environment that markedly alters reaction pathways through the selective stabilization of specific transition states based on their location along the reaction coordinate for a given elementary step.

1. Introduction

The formation of C=C bonds via alkene dimerization provides attractive routes to fuels and chemicals. Ethene, in particular, is the predominant product of thermal cracking processes, especially with natural gas condensate as the feedstock, thus making it an attractive reactant in dimerization routes to larger alkenes [1,2]. Both Cossee-Arlman [3,4] and metallacycle [2] mechanisms have been proposed as plausible dimerization pathways on homogeneous catalysts; in contrast, the precise nature of the active sites on Ni-based solid catalysts remains uncertain, as is also the case for the extent to which the mechanistic details and site requirements proposed for homogeneous catalysts can be extended to...
Ni-based aluminosilicates, which do not require activators or co-catalysts [5-9]. Alkene oligomerization is also catalyzed by solid Brønsted acids (H+); their turnover rates (per proton) depend sensitively on acid strength, because stronger acids form more stable conjugate anions at ion-pair transition states, and on the nature of inorganic frameworks that provide voids of molecular dimensions and stabilize transition states through van der Waals contacts [10]. Solid acids typically operate at higher temperatures than Ni-based homogeneous catalysts; such temperatures lead to facile hydride and methyl shifts and to skeletal isomerizations and regioisomerizations at relative concentrations predominantly dictated by thermodynamics [11].

Ni-based metal organic frameworks (MOF) [12-14] and organometallic complexes [15,16] give higher oligomerization rates (per Ni center) and 1-alkene selectivities than solid Brønsted acids, but they require the use of aluminoxane activators or co-catalysts in large excess and the presence of solvents or reactants as a bulk liquid phase. These Ni-based systems also exhibit rapid deactivation and require complex regeneration protocols to avoid structural and catalytic degradation, thus limiting their use in practical large-scale oligomerization processes. Cationic Ni species dispersed on oxides (ZrO2, TiO2) and Ni2+ cations exchanged onto zeotypes [17-19] catalyze ethene oligomerization without the need for co-catalysts, but at lower rates (per Ni) than organometallic Ni complexes. NiO domains interacting with O-H groups on Brønsted acids (H+) at higher temperatures than Ni-organometallic catalysts [5-9]. Alkene oligomerization is also catalyzed by solid acids typically operating at higher temperatures than Ni-based heterogeneous catalysts; such temperatures lead to facile hydride and methyl shifts and to skeletal isomerizations and regioisomerizations at relative concentrations predominantly dictated by thermodynamics [11].

2. Methods section

2.1. Ni-MCM-41 catalyst synthesis

Ni-MCM-41 (0.1-14.7 wt% Ni; X= Ni2+/H+ = 99.99%) was prepared by contacting Ni(NO3)2·6H2O solutions (0.05-0.5 M; Sigma-Aldrich) in deionized water (resistivity ~0.06 μS cm−1) with Al-MCM-41 (0.01 g/cm3, Si/Al = 40, Sigma-Aldrich) while stirring for 24 h in a round-bottomed flask placed within an oil bath at 353 K. Solids were recovered by filtration, treated in ambient air at 393 K for 12 h, and treated in flowing air (ultra dry, Praxair; 0.5 cm3 g−1 s−1) by heating to 823 K at 0.083 K s−1 and holding for 3 h.

2.2. Ethene oligomerization rates and product selectivity

Ethene oligomerization rates were measured in a stainless steel tubular reactor (6.4 mm × 3 cm). Samples (10 mg: 125-180 μm aggregates) were digested with SiO2 (1:150 mass; Davisol-62, Sigma-Aldrich, treated in air, 1073 K, 8 h). Catalysts were treated in a flow of dry air (ultra dry, Praxair; 0.5 cm3 g−1 s−1) by heating to 823 K (0.083 K s−1, 0.5 h hold) and flushed with He (99.999%, Praxair) before cooling to reaction temperatures and introducing ethene (99.999%, Praxair) at 10-20 mol g−1 h−1. Temperatures were measured with a K-type thermocouple (K-type, Omega) and controlled electronically (Watlow 982). Subambient temperatures were maintained by balancing the flow of a cold N2 stream with resistive heating using electronic controllers. Pressure was maintained electronically (LF-1, Equilibar). Concentrations of reactant ethene and products were measured by flame ionization detection after chromatographic separation (Agilent 6890; HP-1 methyl silicone, 25 m, 0.32 mm diameter, 1.05 μm film).

2.3. Site titration methods

The number of accessible protons in the Al-MCM-41 sample (Si/Al = 40, Sigma-Aldrich) was measured by titration with 2,6-di-tert-butylpyridine (DTBP, >97%, Sigma-Aldrich). The Al-MCM-41 sample was treated using the same procedures to prepare Ni-Al-MCM-41 catalysts (as described in Section 2.1), using a HNO3 (Sigma-Aldrich, 70%, AR grade) solution of the same pH as the Ni precursor solutions (pH = 3.3–3.7). Solids were recovered by filtration and treated in flowing air as described in Section 2.1. Before titration, Al-MCM-41 (40 mg) was treated in flowing dry air (ultra dry, Praxair, 21.5% O2, 0.4 cm3 g−1 h−1) at 353 K. Solids were recovered by filtration and treated in flowing air as described in Section 2.1. Before titration, Al-MCM-41 (40 mg) was treated in flowing dry air (ultra dry, Praxair, 21.5% O2, 0.4 cm3 g−1 h−1) by heating the temperature from ambient to 823 K at 0.083 K s−1 and holding for 0.5 h, then flushed with He (99.999%, Praxair) at 100 cm3 min−1 g−1 and 823 K for 1 h and temperature set to 448 K. The H+ content of this Al-MCM-41 was measured by contact with DTBP (0.5 kPa, 0.01 mol DTBP g−1 h−1) in flowing He. DTBP was introduced as a n-hexane (99%, Sigma-Aldrich) solution (1:25 DTBP/n-hexane molar ratio) using a syringe pump (Cole Parmer, 60061 Series). All gas flows were metered using electronic flow controllers (Porter).

DTBP titrations at 448 K were also carried out during ethene dimerization on Ni-MCM-41 samples. Before titration experiments, Ni-MCM-41 samples were treated as described above. During titration, ethene (0.1 MPA, 20 mol g−1 h−1) was introduced to the reactor (0.01 mol g−1 h−1, as a solution in n-hexane). DTBP concentrations were measured by gas chromatography. DTBP flow was stopped after dimerization rates reached undetectable levels; no desorption of DTBP was detected in the effluent thereafter, indicative of irreversible adsorption. Titrations with CO were carried out during ethene reactions (243 K; 1.5 MPA ethene) on Ni-MCM-41 samples, containing Ni2+/H+ ratios of 0.1 and 0.8, by injection of 0.5 cm3 pulses of 1% CO/He (ultra dry, Praxair; 1.5 MPA) at
1 h intervals with concurrent measurements of dimerization rates using the chromatographic protocols described above.

2.4. Additional characterization methods

N₂ uptakes were measured at its normal boiling point using a volumetric physisorption unit (ASAP 2020, Micromeritics). As-synthesized catalysts were first degassed at 623 K (heating rate, 10 K min⁻¹) for 4 h in vacuum. Ni contents were measured using inductively-coupled plasma atomic emission spectrometry (ICP-AES; Galbraith Laboratories). Infrared spectra of chemisorbed CO and DTBP were collected in a Nicolet NEXUS 670 infrared spectrometer equipped with a Hg-Cd-Te (MCT) detector cooled with liquid N₂. Self-supported Ni-MCM-41 wafers (40 mg) were sealed within a quartz vacuum infrared cell fitted with NaCl windows. During CO chemisorption, samples were treated in flowing He within a quartz vacuum infrared cell fitted with NaCl windows. Infrared spectra of chemisorbed CO collected with 2 cm⁻¹ resolution in the 4000–400 cm⁻¹ spectral range by averaging 64 scans. During DTBP chemisorption, samples were pretreated at 673 K for 1 h in flowing He, cooled to 448 K and treated in 1 kPa DTBP in He for 0.5 h. The cell was evacuated before spectra were taken at 448 K.

3. Results and discussion

3.1. Identification of active species during ethene dimerization

Dimerization rates are reported here as the combined molar rates of formation rates of C₄ and C₅ alkene chains, which account for most (>99.5%) of the products formed. These rates (per mass) at 243 K and 1.5 MPa ethene increased linearly with increasing Ni²⁺/H⁺ ratios in Ni-Al-MCM-41 up to stoichiometric ratios of unity, and then reached nearly constant rates at higher ratios (Fig. 1; H⁺ from ambient to 823 K at 0.083 K s⁻¹ resolution in the 4000–400 cm⁻¹ spectral range by averaging 64 scans. During DTBP chemisorption, samples were pretreated at 673 K for 1 h in flowing He, cooled to 448 K and treated in 1 kPa DTBP in He for 0.5 h. The cell was evacuated before spectra were taken at 448 K.

CO interacts with Ni⁺ and Ni²⁺ sites of low coordination [7,21]. Exposing Ni-MCM-41 samples to 1 kPa CO at 263 K led to an infrared band at ~2200 cm⁻¹ (Fig. S3, SI), corresponding to Ni²⁺-(CO) [34]; these bands are not present in the H-form of Al-MCM-41. Fig. 4 shows dimerization rates (1.5 MPa; 243 K) as a ratio to that before contact with CO pulses as a function of the cumulative CO uptakes (introduced CO molecules per Ni atom) on Ni-MCM-41 samples with Ni²⁺/H⁺ ratios of 0.1 and 0.8, chosen here because they do not appear to contain the inactive bulk-like NiO domains prevalent at higher Ni contents and which may also be able to adsorb CO. The rate decrease as a function of cumulative CO per total Ni is similar for Ni-MCM-41 samples, leading to CO uptake (per Ni atom) that are similar at these two Ni²⁺/H⁺ ratios. The number of CO molecules that must be introduced in order to fully saturate nearly constant rates at higher ratios (Fig. 1; H⁺ from ambient to 823 K at 0.083 K s⁻¹ resolution in the 4000–400 cm⁻¹ spectral range by averaging 64 scans. During DTBP chemisorption, samples were pretreated at 673 K for 1 h in flowing He, cooled to 448 K and treated in 1 kPa DTBP in He for 0.5 h. The cell was evacuated before spectra were taken at 448 K.

Fig. 1. Ethene dimerization rates (per mass, ■); 1-butene selectivity in C₄ alkenes (S₁-butene, ▲); and C₅ alkenes within products (S₂C₅, ◀️) as a function of Ni surface density and Ni²⁺/H⁺ atomic ratio (based on fresh Al-MCM-41: 1.8 × 10⁻⁴ mol H⁺ g⁻¹) (243 K, 1.5 MPa ethene, 4–6% conversion). Ni contents (0.1–8.0% wt.) shown in brackets. Dashed curves denote trends.

suppress dimerization rates exceeds the expected 1:1 CO/Ni²⁺ stoiciometry, because not all molecules in each pulse can access Ni sites by diffusion through intrapore liquids during their passage through the catalyst bed. The fraction of each pulse that is retained by the sample cannot be determined because mass spectrometry cannot distinguish CO and ethene molecules because of their similar mass (28 amu).

The full suppression of rates by both DTBP (Fig. 3) and CO (Fig. 4) implicate the concerted involvement of OH⁻ and Ni²⁺ centers in dimerization turnovers and the presence of isolated (Ni-OH)⁺ species grafted onto the locations set by H⁺ in Al-MCM-41. Dimerization turnover rates at 258 K on such species (per Ni) are two orders of magnitude higher than on NiO domains in Al-MCM-41 [21] or isolated Ni²⁺ sites in zeolites [27,28] at around 390 K (Table 1); the poor reactivity of these latter materials appears to reflect their tendency to form Ni²⁺ monomers (type III, Fig. 2), which would require their reduction to Ni⁺ in H₂ for the formation of a vicinal proton; leading to inactive Ni⁺ and to a proton that is much less active than isolated (Ni-OH)⁺ centers.

3.2. Stabilization of active Ni-based sites by the formation of liquid ethene within MCM-41 mesopores

Ethene dimerization rates (r_red) remain constant with time at an ethene pressure of 1.5 MPa and 243 K (Fig. 5). These rates decrease by a factor of 2.5 when ethene pressures are decreased from 1.5 MPa to 0.9 MPa, consistent with rates that are approximately second-order in ethene pressure. Deactivation becomes immediately evident upon this decrease in ethene pressure. The curved nature of the semilogarithmic rate plots in Fig. 5 reflect deactivation rate constants (given by the local slopes of these curves) that decrease with time, as deactivation occurs and ethene conversion, and thus the concentration of oligomerization products, concomitantly decrease. These trends are consistent with site blockage by larger oligomers, which prevail at the higher conversions characteristic of earlier reaction times. The prevalence of these longer chains at higher conversions is also evident from higher C₆/C₄ ratios, however, also increase with ethene pressure; yet and surprisingly at first glance, dimerization rates are stable and deactivation becomes undetectable at higher pressures, in seeming contradiction to the expected blockage of active centers by longer alkenes (Fig. 5). The deactivation observed at lower pressures can be fully reversed by thermal treatments at 823 K in either an inert (He) or oxidizing (O₂) environment, indicative of desorption as the restoring mechanism and of species that chemisorb reversibly at high temperatures (but not at those of dimerization catalysis).

First-order deactivation constants (k_d) are used here to define the stability of the active Ni sites in samples from:

\[
\frac{r_{red}(t)}{r_{red}(t_0)} = \exp\left[-k_d \cdot (t - t_0)\right]
\]

where \(r_{red}(t)\) and \(r_{red}(t_0)\) represent ethene dimerization rates at each time \(t\) and at the initial time \(t_0\). Fig. 6 shows deactivation rate constants (k_d, Eq. (1)) as a function of ethene pressure at 243 and 253 K (more details on rate-time data are included Figs. S4 and S5, SI). The k_d values in Fig. 6 show an abrupt increase as the ethene pressure decreases below 1.2 MPa at 243 K and below 1.8 MPa at 253 K. These k_d values are shown in Fig. 7 (left axis) as a function of ethene pressure (P/ P_sat), the ratio of the ethene pressure to its saturation vapor pressure (P_sat) at each temperature. These threshold pressures are slightly lower than the ethene saturation pressures (P/ P_sat = 0.6–0.7) at each temperature (1.94 MPa at 243 K; 2.55 MPa at 253 K), indicating that stability may coincide with the condensation of ethene within small MCM-41 cylindrical pores of nearly uniform

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**Fig. 2.** Ni species on Al-MCM-41 (Si/Al = 40) that could form upon with Ni(NO₃)₂ 6H₂O solutions, prepared as described in Section 2.1. Ni species are defined as isolated hydroxylated Ni⁴⁺ monomers (I), Ni⁴⁺ dimers (II) derived upon thermal treatment (Δ) of type I species, Ni⁴⁺ monomers exchanged on two H⁺ sites (III), or bulk nickel oxide (IV). Similar species have been shown to form in crystalline aluminosilicates upon contact with Cu²⁺ (aq.) [31].

**Fig. 3.** Ethene dimerization rates at 448 K, 0.1 MPa ethene and an ethene molar rate of 20 mol g⁻¹ h⁻¹ for 0.1 Ni²⁺/H⁺ (□) and 0.8 Ni²⁺/H⁺ (■) samples on stream (left panel, before titration) and with respect to cumulative titrant per initial H⁺ content (1.8·10⁻⁴ mol H⁺ g⁻¹) after addition of 0.5 kPa of 2,6-di-tert-butylpyridine (DTBP, right panel). Titration experiments conducted at 448 K on stable dimerization rates and by injecting 0.5 kPa DTBP and 12.5 kPa n-hexane at 0.01 mol DTBP·s⁻¹·h⁻¹. A rate decrease towards a DTBP/H⁺ ratio of unity indicates the titration of residual H⁺ from Ni species on Al-MCM-41 and OH⁻ from Ni-OH⁺ (type I, Fig. 2), which would require their reduction to Ni⁺ in H₂ for the formation of a vicinal proton; leading to inactive Ni⁺ and to a proton that is much less active than isolated (Ni-OH)⁺ centers.

**Fig. 4.** Ratio of rates after each pulse referenced to the rates measured before CO introduction (per Ni) as a function of introduced CO molecules per Ni atom after each pulse (1% CO/He pulses) for 0.1 Ni²⁺/H⁺ (40 mg, □) and 0.8 Ni²⁺/H⁺ (10 mg, ■) at 243 K, 1.5 MPa ethene and at an ethene molar rate of 20 mol g⁻¹ h⁻¹. Each pulse corresponds to 2.5 CO molecules per Ni atom.
Table 1
Ethene dimerization rates (per mass, per Ni-atom), C4 and 1-butene selectivities.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Support</th>
<th>Ni (%wt.)</th>
<th>Pressure (MPa)</th>
<th>Temperature (K)</th>
<th>Ethene dimerization</th>
<th>Butenes selectivity</th>
<th>1-Butene selectivity in C4</th>
<th>Mean life 1/kd (h)</th>
<th>(Al/Ni)ref</th>
<th>Ref.</th>
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<td>5.6</td>
<td>308</td>
<td>–</td>
<td>59,000</td>
<td>–</td>
<td>94</td>
<td>–</td>
<td>100</td>
<td>15</td>
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<td>1.0</td>
<td>303</td>
<td>–</td>
<td>61,000</td>
<td>77</td>
<td>–</td>
<td>–</td>
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<td>157</td>
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<td>92 (91)</td>
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<td>3.0</td>
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<td>8700</td>
<td>98 (96)</td>
<td>93 (92)</td>
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a Homogeneous Ni (II)-α-Diimine; batch reactor, toluene solvent; modified methylaluminoxane (MAO) activator. Butenes selectivity corresponding to α olefins.
b Nickel complexes containing P,N-Chelating Ligands; complex 16c in reference; batch reactor toluene; in the presence of AlEtCl2.
c NU-1000-hpy-NiCl2 (Ni-MOF) with Et2AlCl; flow reactor.
d Ni-(Fe)MIL-101 MOF with Et2AlCl; iron (III) octahedral trimers linked by 2-aminoterephthalates; batch reactor, n-heptane solvent.
e Ni-MFU4 with MAO; batch reactor, toluene solvent.
f Homogeneous and supported co-catalysts with NiCl2(PBu3)2; batch reactor, toluene solvent; diethylaluminum chloride as co-catalyst on DEAC-MCM-41.
g 5.7%wt Ni/AlM41; flow reactor, no solvent. No deactivation detected over 8 h on stream.
h Batch reactor, n-heptane solvent. 1-butene and cis/trans 2-butene in equilibrium.
i Ni-exchanged Na-FAU zeolite (Si/Al = 3); flow reactor, no solvent. 100% conversion.
j Commercial H-BEA (Si/Al = 12); flow reactor, no solvent. No deactivation detected over 8 h on stream.
k Ni-exchanged Al/MCM-41 (Si/Al = 40); flow reactor, no solvent at 5% (or 40%) conversion.
l Butenes (%mol) among products.
m 1-butene (%mol) among butenes.
n Reciprocal first-order deactivation rate constant (1/kd).
(1.0–2.2 nm diameter). The fraction of total pore volume in MCM-41 filled with ethene is shown in Fig. 7 (right axis). N$_2$-physorption uptakes (Fig. S6, SI) were used to determine the fraction of mesopores filled with liquid ethene at dimerization conditions. The similar BET surface areas obtained for porous adsorbents using N$_2$ and ethene as the physisorbed probe molecules [36] and their similar ratios of physisorption to liquid condensation enthalpies (the $c$ constant in the BET equation [37]) allows the rigorous use of N$_2$ uptakes to determine the extent or pore filling by liquid ethene.

Fig. 8 shows the pore diameter of Ni-Al-MCM-41 (Ni$^{2+}$/H$^+$ = 5.0) as a function of fraction of pore volume filled with ethene; the inset shows the differential pore volume distribution as a function of the pore diameter, obtained from N$_2$ uptakes at 77 K (Fig. S6, SI). Such distribution shows that the fraction of the total pore volume that represents complete filling of the ordered mesoporous channels in MCM-41 (1.0–2.2 nm diameter) is 0.62. These values correspond to the relative ethene pressures (P/P$_{sat}$ = 0.6–0.7) that lead to undetectable deactivation in Ni-Al-MCM-41 samples, indicating that the presence of an extended liquid phase in 1.0–2.2 nm pores in contact with the Ni-based active sites leads to their unprecedented stability during ethene dimerization.

3.3. Kinetic and mechanistic analysis of ethene dimerization pathways

Fig. 9 shows the values of second-order dimerization rate constants ($k_d$, Eq. (1)) as a function of ethene pressure at 448 K and can be described with a constant value of $\alpha$:
can no longer be considered to behave as a thermodynamically ideal system, and any treatment of chemical dynamics must rely on transition state formalisms that rigorously account for such non-idealities and for the preeminence of chemical potentials and fugacities as the relevant kinetic driving forces for chemical reactions.

The effects of ethene pressures (or fugacities) on dimerization rates are consistent with the kinetic relevance of step 1.2 (Scheme 1; $k_b$), which forms a $\text{C}-\text{C}$ bond between a gaseous and a bound ethene present at low coverages on Ni centers (Step 1.1, $k_a$).

Transition state (TS) theory formalisms would then describe dimerization rates ($r_{ed}$, per unit volume) in terms of the number of transition-state complexes ($C^z$) that convert to products in the time scale of a molecular vibration of frequency $\nu_b$ corresponding to the mode that causes the bond to form or cleave (in this case the symmetric vibration of the $\text{C}-\text{C}$ bond being formed) [38]:

$$r_{ed} = \nu_b \cdot C^z \quad (3)$$

These TS treatments are based on thermodynamic constructs that naturally incorporate thermodynamic non-idealities in terms of the chemical potential and fugacity ($f_E$) of ethene [32,33]. The relevant concentration of transition state structures require, in turn, their activity coefficient ($\gamma^E$) within intrapore liquids. Dimerization rates ($r_{ed}$) under non-ideal solutions [38–40]:

$$r_{ed} = \left(\frac{k_B T}{h}\right) \cdot e^{-\Delta G^z / RT} \cdot \frac{T^z}{\gamma^E} \quad (4)$$

where $k_B$ is the Boltzmann constant; $h$, the Planck constant, and $f_E$ is proportional to $P_E$ through a fugacity coefficient ($\phi_E$). $\Delta G^z$ is the Gibbs free energy difference between the $C^2$ and $G^z$ in step 1.2 in its thermodynamically ideal state and two ethene molecules as an ideal (2$G_E$): $\Delta G^z = G^1 - 2G_E$.

The corrections to the ethene pressure values dictated by the non-ideal character of the extrapore gas phase (e.g., $\nu_E = 0.80$ at 243 K, 1.99 MPa; from Eq. (S1), Section S8 [41]) give $f_E$ values that describe rates ($r_{ed} \sim f_E^1$, Fig. 10) with a slightly stronger effect of fugacity than prescribed by Eq. (4) when the TS structures bound at Ni sites are considered to be ideal (i.e. $\gamma^E = 1$) (solid line, Fig. 10) at 243 K. These rate enhancements reflect the solvation of the dimerization TS by the intrapore liquids ($\gamma^E < 1$), which render such structures also different from those in contact with an ideal gas phase. The non-ideal character of this TS was treated by estimating the activity coefficients for dilute 1-butene in liquid ethene ($\gamma^B$), used as a proxy for the bimolecular TS ($\gamma^E$) (UNIFAC model with group contributions [42]; Section S9, Table S1), as a function of ethene pressure. Such estimates give a $\gamma^E$ value of 0.80 at 243 K, with negligible effects of ethene pressure in the pressure range required to form intrapore liquids in MCM-41. These $\gamma^E$ values account for the deviations from ideal systems as channels are filled by a denser liquid phase. They accurately capture the rate enhancements observed relative to the ideal systems ($\gamma^E = 1$), as prescribed by Eq. (4) (dashed curve; Fig. 10) and indicative of the stabilization of the dimerization TS relative to its ideal state by the intrapore liquids. The rate enhancements at 253 K are also well described by Eq. (4) ($\gamma^E = 0.79$) (Fig. 10), while conditions that do not lead to intrapore liquids and to ideal gas behavior by ethene

$$\text{C}_2\text{H}_4(g) + \text{C}_2\text{H}_4* \underset{90}{\overset{90}{\rightleftharpoons}} \text{C}_2\text{H}_4* \underset{90}{\overset{90}{\rightleftharpoons}} (\text{C}_2\text{H}_4-\text{C}_2\text{H}_4)^{\dagger} \rightarrow \text{C}_4\text{H}_8 + * \quad (K_{C2}; 1.1)$$

$$\text{C}_2\text{H}_4(g) + \text{C}_2\text{H}_4* \underset{90}{\overset{90}{\rightleftharpoons}} \text{C}_2\text{H}_4* \rightarrow \text{C}_4\text{H}_8 + * \quad (k_E; 1.2)$$

Scheme 1. Ethene dimerization elementary steps (*: a Ni active center).

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Fig. 9. Second-order ethene dimerization rate constants ($\alpha$), after correction with ethene pressure, as a function of ethene pressure on Ni-Al-MCM-41 (Ni$^{2+}$/H$^+$ = 5.0) at an ethene molar rate of 20 mol g$^{-1}$ h$^{-1}$. Filled symbols at 243 K ($\bullet$) and 253 K ($\square$) represent ethene liquid-filled pores and empty symbols at 243 K ($\circ$), 253 K ($\triangle$) and 448 ($\diamondsuit$) denote conditions where pores $\leq$ 2.2 nm are empty (as inferred from N$_2$ pore filling models in Figure S6). Dimerization rate data obtained from immediate rate changes (as required to evaluate kinetic responses) after change in ethene pressure. Dashed lines used as trends.

Fig. 10. Dimerization rates (symbols), trends for ideal thermodynamics ($\gamma^E = \phi_E = 1$; 243 K; solid line) and rates predicted by Eq. (1) (dashed lines) as a function of the square of ethene fugacity on Ni-Al-MCM-41 (Ni$^{2+}$/H$^+$ = 5.0). Dimerization rate data at 243 and 253 K obtained from immediate rate changes (as required to evaluate kinetic responses) after change in ethene pressure in Figs. 9 and 55, respectively. Rates at 448 K measured after 5 h (Fig. 5). Ideal rates from slope of rates at 0.8 MPa$^2$ at 243 K. Symbols ($\bigcirc$) and ($\blacklozenge$) denote conditions leading to intrapore gas and liquid, respectively.

$$r_{ed} = \alpha \cdot P_E^2 \quad (448 K) \quad (2)$$

At subambient temperatures, however, $\alpha$ values increase with ethene pressure (Fig. 9) as conditions approach the condensation point of ethene molecules. At such conditions, the ethene gas phase

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(e.g. 448 K, and open symbols at 243–253 K; Fig. 10) can be described, as expected, by $c/C_2$ and $u_E$ values of unity. The slight increase in rates with temperature (243 K to 253 K) at conditions that prevent deactivation reflect the small values of dimerization activation barrier; while the lower rate observed at higher temperatures (448 K, Fig. 10) is a consequence of very rapid initial deactivation at the momentary high conversion conditions expected at such higher temperatures and the concomitant loss of a significant fraction of the Ni active sites (Fig. 5).

3.4. Mechanistic interpretations of primary and secondary reactions during Ni-catalyzed ethene dimerization

The sole formation of 1-butene at very short residence times and low ethene conversions (243 K; Fig. 11a) reflects its direct formation as the sole primary dimerization product, defined here as that formed after a single surface sojourn and without intervening desorption and readsoption events. The selectivity to other regioisomers increases as conversion increases, but these selectivity values and trends are identical for catalysts with a broad Ni content ($Ni^{2+}/H^+ = 0.1–5.0$); such data indicate that Ni sites, instead of residual protons from Al-MCM-41, account for any secondary isomerization events of primary 1-butene products at these low temperatures (243 K, Fig. 11a). Similar trends with conversion are evident at 448 K (after 5 h on stream), but 1-butene selectivities are much lower than those at 243 K for all ethene conversions. These temperature effects predominantly reflect the lower values of primary 1-butene selectivities (evident by extrapolation to zero ethene conversion; Fig. 11a), which decrease as the Ni content decreases, apparently as a result of the isomerization reactivity of residual protons; such secondary reaction rates become comparable to those of ethene dimerization as the $H^+/Ni^{2+}$ ratio increases with decreasing Ni content. In fact, C4 regioisomers reach equilibrium compositions on the sample with the largest number of protons ($H^+/Ni^{2+}=10$), even at <5% conversion ($K_{eq} = 5.4$ for trans-2-butene/1-butene; $K_{eq} = 2.9$ for cis-2-butene/1-butene; at 448 K). These high regioisomer selectivities even at very short residence times and low conversions at 448 K give the impression that residual H+ sites from Al-MCM-41 can form isomers of the 1-butene molecules that form on (Ni-OH)+ sites. These high regioisomer selectivities reflect instead the very fast nature of double-bond isomerization events on residual H+ sites at these higher temperatures [11,43], which cause these rearrangements to occur as 1-butene isomers egress via diffusion from a given catalyst aggregate and before they enter the flowing fluid phase in the reactor.

The nearly exclusive formation of C4 molecules at 243 K and short residence times (Fig. 11b) indicates that only one C–C bond forms during each reactive sojourn at Ni sites and that desorption can occur before subsequent reactions of bound 1-butene species.

Scheme 2. Alkene oligomerization ($k_E$ and $k'_E$) and isomerization ($k_{12}$ and $k_{21}$) reactions on Ni-MCM-41.
with another ethene molecule. Larger chains (C₄+) form only via readsorption onto (Ni-OH)⁺ sites (instead of H⁺ sites) at these temperatures, as shown by the identical C₄ selectivities obtained at all Ni²⁺/H⁺ ratios, including those with sub-stoichiometric Ni contents and a significant number of residual H⁺ sites on the Al-MCM-41 support. These trends with conversion and Ni content are also evident at 448 K (Fig. 11b) and at 243 K (Fig. S12) in the absence of intrapore liquids, but the primary C₄ selectivities are 93% and 98%, respectively (instead of 100% on all catalysts at 243 K with intrapore liquids) (Fig. 11b), indicating that more than one C–C bond can form before butenes desorb from Ni sites and that the extended intrapore liquid phase favors the desorption of bound primary butene isomers over their subsequent regioisomerization and oligomerization, thus leading to higher selectivities to primary 1-butene products.

In the reaction sequence depicted in Scheme 1, 1-butenes can desorb from Ni sites (Scheme 1, step 1.2) (k₄₁, k₄₂; k₄₃ is the lumped desorption constants for all butene regioisomers) but can also isomerize or grow, either before desorption or after readsorption, to form bound regiosomers of C₄ alkenes ([k₁₂, k₃₁] or C₄ alkenes [k₁₂, k₃₂], which can also desorb, isomerize, or grow. The primary selectivities to 1-butene and C₄ chains depend on the ratios of (k₄₁/k₁₂) and (k₄₂/k₃₂), respectively. Both kinetic ratios increase as pores fill with liquid ethene (Fig. 11), apparently because of the preferential solvation of the late product-like TS structures that mediate endothermic processes, such as desorption events. Such late transition states reside more fully within, and therefore are more effectively solvated by, the intrapore liquids than the more tightly bound and earlier transition states that mediate the isomerization and growth of bound 1-butene chains formed in primary dimerization events. The readsorption of alkenes, mediated by the same TS as that for their desorption, is similarly favored by intrapore liquids, leading to residence time effects on selectivities that do not depend on temperature or on density of the intrapore fluids (Fig. 11).

3.5. Regeneration of deactivated Ni-Al-MCM-41 catalysts by thermal treatments

Fig. 12 shows the effects of thermal treatments in inert He (623 K, 823 K) on the recovery of dimerization rates of deactivated Ni-MCM-41 (Ni²⁺/H⁺ = 5.0; 448 K, 1.5 MPa ethene). Deactivation events that occur rapidly in the absence of intrapore liquids (0.9 MPa ethene at 243 K, Fig. 5; 1.5 MPa ethene at 448 K, Fig. 12) can be fully reversed by treating samples in He at 823 K. The slightly lower rates (relative to initial rates) observed after treatment in He at 823 K (Fig. 12) reflect the formation of some refractory dehydrogenated species at 448 K, which in contrast, with other blocked sites, cannot be recovered by desorption. The ability to reverse the deactivation by a thermal treatment in an inert environment indicates that Ni sites can be unblocked by the mere desorption of species, instead of only via chemical reduction or oxidation, but that such desorption events require temperatures well above those of dimerization catalysis. Such thermal treatments, whether in inert or chemical environments, would cause irreversible degradation of the structure and catalytic reactivity of organometallic or Ni-MOF catalysts [12–14].

4. Conclusions

This work reports the synthesis and reactive properties of stable and selective ethene dimerization catalysts consisting of Ni active sites dispersed within ordered Al-MCM-41 mesopores, as well as their robustness during thermal regeneration treatments. These catalysts convert ethene to 1-butene with very high selectivity (98% butenes in products; 93% 1-butene in butenes) and turnover rates (>10 s⁻¹; per Ni atom) even at subambient temperatures (243–258 K); they do not exhibit detectable deactivation at these conditions or require aluminoxane activators, essential for homogeneous and Ni-MOF catalysts. Such unique reactivity, selectivity and stability are conferred by an extended ethene liquid phase within MCM-41 channels. We suggest that such liquids preferentially solvate the transition states that mediate desorption of adsorbed products, thus preventing their isomerization and growth, and the formation of stranded oligomers that block Ni sites. Such stability allows to identify kinetically relevant isolated Ni sites, exchanged at H⁺ sites on Al-MCM-41 pores.

The application of Ni-based catalysts for oligomerization seems feasible at ambient temperature and pressures leading to alkene condensation. This work provides one of the most novel demonstrations of the role of intrapore liquids in altering reaction pathways through the selective stabilization of specific transition states, and aims to expand this concept to other reactions studying the consequences of intrapore solvation on reactivity and active-site stability.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2017.06.025.

References