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To be cited as: *ChemCatChem* 10.1002/cctc.201800650

Link to VoR: http://dx.doi.org/10.1002/cctc.201800650

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ChemCatChem 10.1002/cctc.201800650

Ethylene oligomerization to select oligomers on Ni-ETS-10

Jay Thakkar, Xinyang Yin, and Xueyi Zhang*[a]

Abstract: The oligomerization of short alkenes (ethylene and propylene) can be used for producing commodity chemicals. Various catalysts have been used for alkene oligomerization, among which ordered microporous catalysts are thermally and mechanically stable, and are already established for large-scale industrial applications. In this work, we demonstrate ethylene oligomerization reaction on a microporous titanosilicate ETS-10 (Engelhard Titanosiliate-10) exchanged with Ni^{2+} (Ni-ETS-10). We demonstrate a template-free and fluoride-free ETS-10 synthesis method that does not produce impurities commonly seen in hydrothermal ETS-10 synthesis. Ni-ETS-10showed high C_2 conversion rate, high selectivity to C_4 and high stability comparing to other microporous catalysts investigated in this work for ethylene oligomerization reaction.

Oligomerization reaction of ethylene has been studied on various heterogeneous catalysts such as, metal oxides and sulfates,[1-5] micro and mesoporous aluminosilicates,[1,6-17] and metal organic frameworks (MOFs).[18-23] Compared to other solid catalysts for ethylene oligomerization reaction, nickel (Ni^{2+}) containing microporous materials (such as zeolites and MOFs) offer the opportunity to control and optimize reaction rate and selectivity of these reactions.[6-23] ETS-10 (Engelhard Titanosilicate-10) is a thermally stable microporous crystalline titanosilcate (Si/Ti=5) containing [TiO_6] units, which generate a -2 charge (due to Ti^{4+}),[24,25] capable of loading significant amounts of divalent cations for ion exchange and water treatment applications.[26,27] Since ETS-10 is capable of loading a broad spectrum of divalent transition metal cations,[26,27] this versatile ion-exchange capability of ETS-10 was therefore exploited in this study, and Ni^{2+} was exchanged into the framework for ethylene oligomerization. The framework structure of ETS-10 consists of periodic large 12-member ring pores (7.6Å x 4.9Å) and aperiodic 18-member ring pores (14.3Å x 7.6Å) due to stacking faults.[24,25,28] Additionally, ETS-10 can be synthesized using a template-free procedure which eliminates the need of sacrificing the organic structure-directing agents by calcination.[28] To the best of our knowledge, although there have been numerous attempts at utilizing zeolites and MOFs for ethylene oligomerization, gas phase ethylene oligomerization reaction in continuous mode on Ni^{2+} exchanged ETS-10 (Ni-ETS-10) has not been studied before.[1,6-23,29] In order to investigate the catalytic outcomes of Ni-ETS-10, two other similar microporous materials that can load divalent transition metal with significant amount – CIT-6[30] and MOF-74[31] were chosen. Zeolite CIT-6 has *BEA topology, but contains Zn^{2+}as heteroatoms, where the framework Zn atoms generate a -2 charge per Zn.[30] The -2 charge can be used for loading Ni^{2+} for oligomerization, similar to ETS-10.[30] Ni-MOF-74 contains a significant amount of coordinatively unsaturated Ni^{2+} which can potentially be utilized for ethylene oligomerization reaction.[31]

In this work, we present the synthesis and catalytic behaviors of Ni-ETS-10. We demonstrate a template-free and fluoride-free synthesis method that produces ETS-10 without impurities commonly seen in other systems. Ni-ETS-10 is shown to be more active for ethylene oligomerization, and has shown higher stability and higher selectivity to C_4 than other microporous catalysts (Ni-CIT-6 and Ni-MOF-74) compared in this study.

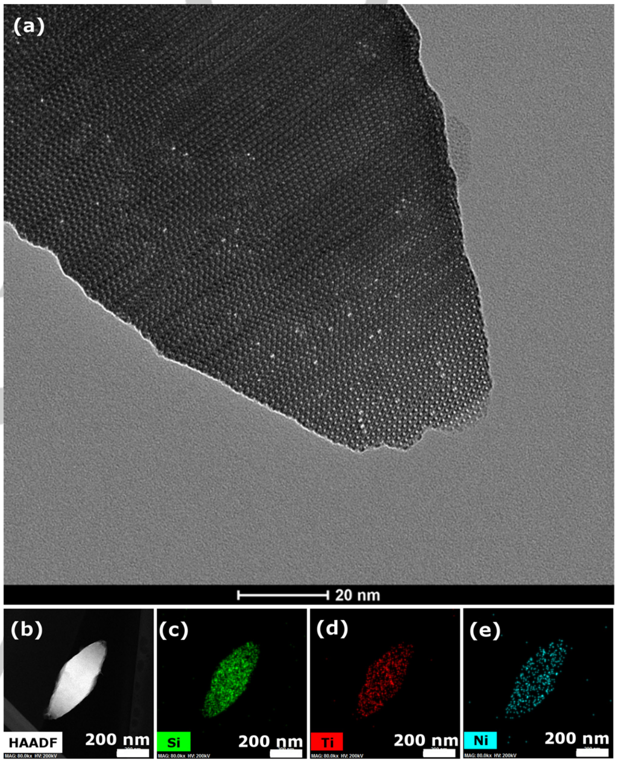

Figure 1. (a) TEM image of ETS-10 particles synthesized using $3.4Na_2O$: $1.5K_2O$: $1TiO_2$: $5.5SiO_2$: 6.95 HCl: 140.7 H_2O, where both 12-member rings and 18-member rings (from stacking faults) are visible in the TEM image; (b-e) Element maps of Ni(6.85wt%)-ETS-10 samples showing uniform distribution of elements.

Previous reports have shown that the final OH^-concentration (or pH value) of the ETS-10 synthesis gel plays an important role in the final product purity.[28] Therefore, a set of experiments were carried out to minimize the impurities and maximize the mass fraction of active catalyst. A molar composition of $3.4Na_2O$: $1.5K_2O$: $1TiO_2$: $5.5SiO_2$: 6.95HCl: $140.7H_2O$ was shown to produce the highest purity, where the impurities (quartz and other dense SiO_2 phases) were undetectable from powder X-ray diffraction (Figure S1). The ETS-10 with the least impurity (x=6.95, where x is the moles of HCl) was used for subsequent characterization, ion exchange, and catalytic reactions. The as-synthesized ETS-10 nanoparticles have a square bipyramidal morphology and a size of less than 500nm (figure S2a). High-

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resolution TEM image of the ETS-10 nanoparticle provides further evidence of its crystallinity (figure 1a), where the typical stacking faults of ETS-10 and the resulting 18-member rings are visible. Elemental analysis shows that a Si/Ti ratio of 5.03 was obtained from the as-synthesized ETS-10 (Table S1). ETS-10 particles with size greater than ~2.5µm were also synthesized in order to study the effect of crystallite size on the activity of catalyst in ethylene oligomerization reaction (Ni(4.12wt%, 2.5µm)-ETS-10).[32,33] Two different ion-exchange procedures were used to obtain different levels of Ni^{2+} loading. After ion-exchange with Ni^{2+}, three samples with Ni/Ti molar ratios of 0.36, 0.35 and 0.56 were obtained, corresponding to Ni mass percentages of 3.90%, 4.12% and 6.85%, respectively. There is a uniform distribution of framework elements (Si, Ti) and exchanged Ni^{2+} ions in Ni-ETS-10 as is evident from STEM-EDS (Ni loading 6.85wt%, figures 1b-1e).

There has been no previous report of using Ni-ETS-10 for gas-phase ethylene oligomerization. The catalytic performance of Ni-ETS-10 was compared with two other ethylene oligomerization catalysts with comparable particle sizes, Ni-CIT-6 and Ni-MOF-74. Figure 2a shows that Ni-ETS-10 is a promising catalyst for ethylene oligomerization with the obtained maximum turnover frequency of 688.96 $mol_{C2}/(mol_{Ni}\ h)$, when the Ni loading was 3.9wt%. This rate is greater than those obtained from previously-reported microporous catalysts such as Ni-CIT-6 (with a comparable Ni loading of 3.3wt%) and Ni-MOF-74 (figure 2a). The Ni-ETS-10 nanoparticles exhibited higher ethylene conversion rates than Ni-CIT-6 and Ni-MOF-74 over the entire time-on-stream range investigated. Since the catalyst particles have comparable particle sizes (figures S2a, c, and d), the higher rate on Ni-ETS-10 may not be due to diffusion limitation, but due to the property of the active sites. Ni-ETS-10 with lower loading (Ni(3.90wt%)-ETS-10) showed higher initial TOF than Ni-ETS-10 with higher Ni loading (Ni(6.85wt%)-ETS-10). However, the ethylene TOF on Ni(3.90wt%)-ETS-10 reduced over time on stream, and the TOF stabilized at a lower value than that of Ni(6.85wt%)-ETS-10. On the other hand, the TOF on Ni(6.85wt%)-ETS-10 did not significantly change as the reaction progressed, indicating that a higher Ni loading is desirable for catalyst stability. Ethylene oligomerization reaction performed on pure, as synthesized ETS-10 (i.e. without Ni^{2+} ions) as a control experiment exhibited no catalytic activity – indicating that the obtained activity for ethylene oligomerization on Ni-ETS-10 is solely from exchanged Ni^{2+} cations. The effect of ETS-10 particle size on ethylene oligomerization reaction was also studied (figure 2a), which indicates that large particle size resulted in lower turnover frequency. The obtained C_4 selectivities over a period of 6 hours for catalysts are also shown in figures 2(b and c) and figure S4. Ni(6.85wt%)-ETS-10 sample showed the highest C_4 selectivity, especially after the reaction stabilized. Conventional aluminosilicate zeolites (such as zeolite Beta normally have strong Brønsted acid sites,[34-36] which lead to reduced C_4 selectivity. Therefore, the high C_4 selectivity on ETS-10 may be attributed to the lack of strong Brønsted acid sites.[29,34-41] This catalyst sample (Ni(6.85wt%)-ETS-10) also showed higher 1-butene selectivity over the entire period of 6 hours when compared to Ni(3.9wt%)-ETS-10 and Ni-MOF-74 (figure S4). The higher 1-butene selectivity however decayed

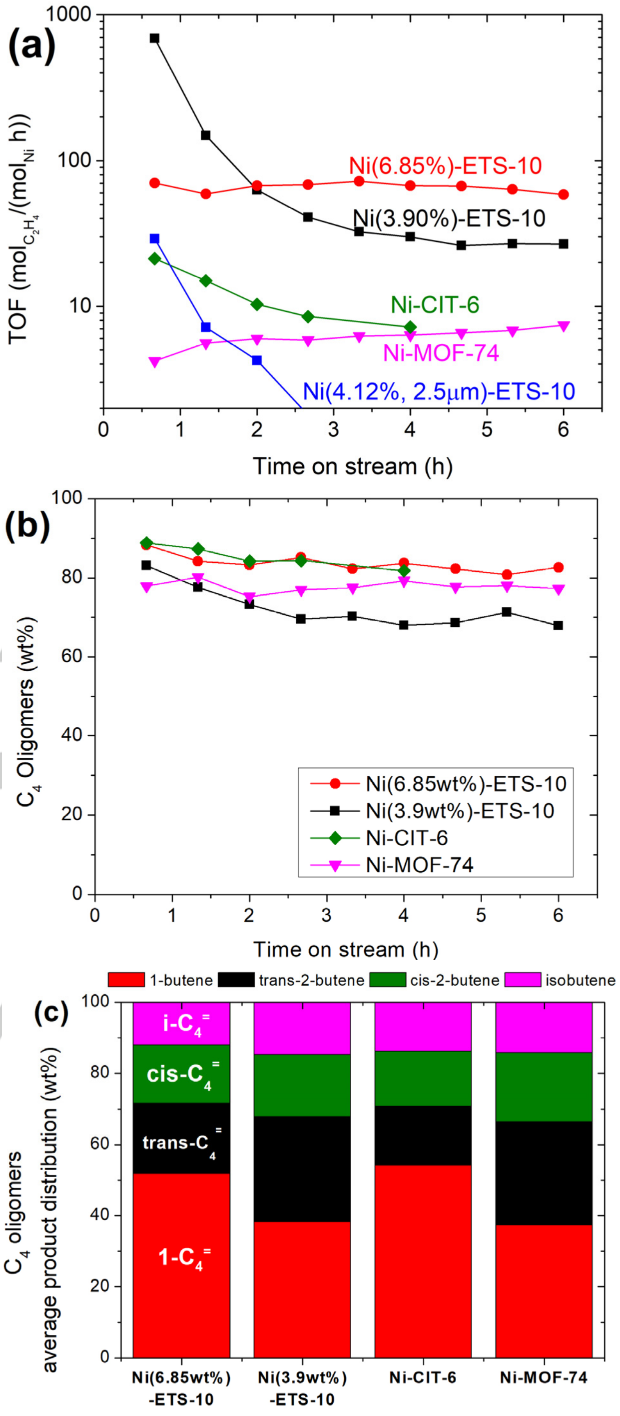

Figure 2. Catalytic behavior of four Ni^{2+}-containing catalysts (Ni-ETS-10, Ni-CIT-6, and Ni-MOF-74) with time on stream:(a) Turnover frequency (TOF) based on total C_2 consumed and total Ni loading; (b) C_4 selectivity; (c) C_4oligomer product distribution (all C_4 alkenes normalized to 100%, averaged over the entire TOS range).

continuously over time, while the selectivity of trans- and cis-2-butene increased over time (figure S4a), indicating that the generated 1-butene product oligomer might be undergoing isomerization. Ni(6.85wt%)-ETS-10 also showed the lowest C_6 selectivity over the entire period of 6 hours (figure S5). Overall, the above observations indicate that Ni(6.85wt%)-ETS-10 is a stable catalyst for ethylene oligomerization to C_4 and that Ni-ETS-10 is a promising catalyst for ethylene oligomerization.

In conclusion, we exploited the ion-exchange capability of ETS-10 for catalytic reactions, where Ni^{2+} was exchanged into ETS-10for ethylene oligomerization. The Ni-ETS-10 catalyst was active for ethylene oligomerization, which shows higher rate (based on total Ni) than other microporous catalysts. Ni-ETS-10 also showed highest selectivity to C_4 and higher stability than other microporous catalysts investigated in this work.

Experimental Section

Catalyst synthesis and characterization

Microporous nanoparticle ETS-10 was synthesized using conventional hydrothermal method based on a previous report.[28] NaOH (EMD Millipore), KOH (EMD Millipore), TiO_2 (P25, Acros Organics), sodium silicate solution (EMD Millipore), and 37wt%HCl aqueous solution (Sigma-Aldrich) were used without further purification. DI water (resistivity=18.2Ω m) was used in the synthesis and subsequent washing of the final products. The NaOH, KOH, sodium silicate solution, and P25 were sequentially added into DI water at ambient temperature, into which HCl solution was added dropwise while stirring at 500 rpm. A thick gel was formed at the end of the addition of HCl solution. The following molar ratio of the components, $3.4Na_2O$: $1.5K_2O$: $1TiO_2$: $5.5SiO_2$: xHCl: (116.7+3.45x) H_2O (x=6.6-8.1) was achieved in the end. The gel was then heated in a convection oven at 230ºC for 72 hours. The product was washed with DI water until the pH of the supernatant is 9-10. Micron-sized ETS-10 particles were synthesized according to the synthesis method based on a previous report (SEM images in figure S2b).[32,33]

In order to exchange the Na^+, K^+ ions present in the microporous ETS-10 with Ni^{2+} ions, the as-synthesized ETS-10 was stirred in a 0.25 mol/L $Ni(NO_3)_2$ aqueous solution for 18 hours at ambient temperature (or for 3 hours at 80ºC twice for higher Ni^{2+} loading), washed with DI water and calcined at 500ºC for 5hrs.

Other catalysts, Ni-CIT-6, and Ni-MOF-74, were also used in order to compare the catalytic outcomes from Ni-ETS-10. Ni-CIT-6[30] and Ni-MOF-74[31] were synthesized and pretreated using previous reported methods. XRD patterns in figure S3 show the crystallinity of the Ni-CIT-6 and the Ni-MOF-74 synthesized and used in this study. SEM images of the Ni-CIT-6 particles and the Ni-MOF-74 are shown in figure S2c and figure S2d, respectively.

Catalyst Characterization

Powder XRD patterns were obtained using PANalytical Empreyean diffractometer (40mA, 45kV), Cu Kα radiation (λ=1.54Å). TEM, STEM, and STEM-EDS micrographs were collected on an FEI Talos F200X at 200kV. Bruker Esprit software was used to collect the element maps. SEM images of the synthesized ETS-10 catalyst were taken using FEI Helios NanoLab 660 FESEM and Thermo Fisher Scios 2 at 2kV. Elemental analysis (ICP) was performed by Galbraith Laboratories, Inc.

Packed-bed reactor with online gas chromatograph

A packed-bed reactor was used for testing the catalysts for ethylene oligomerization reaction in an isothermal, continuous gas flow mode. 50 mg of catalyst was diluted with pre-calcined (1000ºC, 24h) 13.5g silica gel in order to eliminate local hot-spots and temperature gradients across catalyst bed during reaction. Heated flow lines (170ºC) were used to eliminate condensation of large oligomeric reaction products.

Catalysts were treated in-situ in helium flow at 180ºC for 16 hours before performing the reactions. (ETS-10 catalysts were additionally pretreated in-situ under dynamic vacuum (2 mmHg absolute) for 12 hours at 450ºC before helium treatment.) The reactions were carried out at 180ºC, 5atm ethylene pressure and 90 $g_{C2}/(g_{catalyst}h)$ space velocity (conversion <1% for all catalysts, figure S6). Rates and selectivities were quantified continuously using an online gas chromatograph.

Acknowledgements

The authors acknowledge the financial support from the Department of Chemical Engineering and the Institute for Natural Gas Research (INGaR) at the Pennsylvania State University. X.Z. acknowledges financial support from the John J. and Jean M. Brennan Clean Energy Early Career Professorship. Materials characterization was performed at the Materials Characterization Laboratory, which is a partner in the National Nanotechnology Infrastructure Network (NNIN) and the Materials Research Facilities Network (MRFN), supported by the U.S. National Science Foundation (award DMR-1420620). A U.S. patent application by X.Z. and J.T. was filed on March 5, 2018 (Application No. 62/638,366).

Keywords: catalysts • ETS10 • ethylene • heterogeneous • oligomerization

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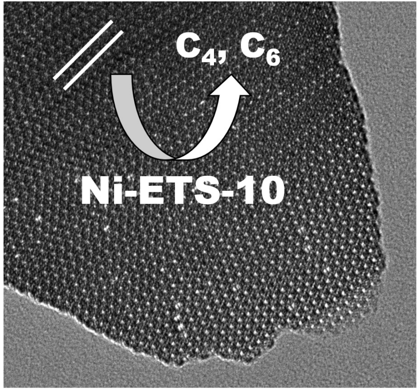
ETS-10 loaded with Ni^{2+} is shown to be active and stable for ethylene oligomerization. Ni-ETS-10 showed high C4 selectivity among microporous catalysts for ethylene oligomerization.



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