Mechanistic Investigations of Ethene Dimerization and Oligomerization Catalyzed by Nickel-Containing Zeotypes

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The shift in feedstock for U.S. steam crackers, from petroleum-derived naphtha to shale gas-derived ethane, results in an abundance of ethene and a deficit of heavier alkenes and aromatics. Dimerization is an entry step in oligomerization and chain growth pathways to convert ethene into chemical intermediates, aromatics and liquid fuels. Nickel cations supported on various inorganic supports are reported to catalyze ethene dimerization and oligomerization in the absence of externally supplied activators or co-catalysts, unlike most homogeneous nickel complexes. Efforts to probe the reaction mechanism and kinetics, however, are complicated by catalyst deactivation, the non-requirement of the activators, concurrent reactions (e.g. oligomerization, isomerization) on residual H^+ sites in the case of aluminosilicate zeolites and different Ni structures proposed as precursors to the dimerization active sites.

In this work, ethene dimerization (453 K) was studied on Ni^{2+} cations exchanged onto Beta zeotypes, while suppressing contributions from residual H^+ sites, by selectively pre-poisoning them with Li^+ cations and using a zincosilicate support containing H^+ sites of weaker strength. Beta zeolites with only H^+ sites formed linear butene isomers (1-butene, cis-2-butene, trans-2-butene) in thermodynamically-equilibrated ratios in addition to isobutene, and thus isobutene serves as a kinetic marker for double-bond isomerization at H^+ sites. After residual H^+ sites on Ni-zeotypes deactivate during initial reaction times, linear butene isomers are formed in non-equilibrated ratios that are invariant with ethene site-time, reflecting primary butene double-bond isomerization at Ni^{2+}-derived active intermediates. Further, *in situ* X-ray absorption spectroscopy shows that Ni cations retain their 2+ oxidation state during ethene dimerization catalysis. Also, butene site-time yields measured at dilute ethene pressures (<0.4 kPa) show an activation (induction) transient during initial reaction times, that is eliminated at higher ethene pressures (≥0.4 kPa) and while co-feeding H_2. This behavior is consistent with ethene-assisted *in situ* formation of $[Ni(II)\text{-}H]^+$ intermediates, as verified by H/D isotopic scrambling and H_2-D_2 exchange experiments that quantify the number of $[Ni(II)\text{-}H]^+$ intermediates formed. Taken together, these findings provide unambiguous evidence for the coordination-insertion pathway as the dominant mechanism for alkene dimerization on Ni containing zeotypes.

The prevalence of the coordination-insertion cycles at Ni^{2+} cations provides a framework to interpret the kinetic consequences of the structure of Ni^{2+} sites that are precursors to the dimerization active sites. The butene site-time yields (453 K) were measured on Beta zeotypes predominantly containing either exchanged Ni^{2+} cations or grafted Ni^{2+} cations, as verified by CO infrared, UV-vis and X-ray absorption spectroscopies. The deactivation transients for butene site-time yields on exchanged Ni^{2+} cations indicate two sites are involved in each deactivation event, while those for grafted Ni^{2+} cations indicate involvement of a single site. Next, the butene site-time yields were extrapolated to initial time, and then further extrapolated to zero ethene site-time to rigorously determine the initial ethene dimerization rates (453 K, per Ni). The initial dimerization rates show a first-order dependence in ethene pressure (0.05-1 kPa) implying the β-agostic $[Ni(II)\text{-ethyl}]^+$ complexes within the coordination-insertion mechanism to be the most abundant reactive intermediates and their formation from $[Ni(II)\text{-ethyl-ethene}]^+$ intermediates as the sole kinetically-relevant step. The apparent first-order dimerization rate constant was two orders of

magnitude higher for the exchanged Ni^{2+} cations than for the grafted Ni^{2+} cations, reflecting differences in ethene adsorption energies or dimerization transition state free energies at these two Ni precursor sites.

The presence of residual H^+ sites on aluminosilicate zeotypes, in addition to the Ni^{2+} sites, causes formation of saturated hydrocarbons and oligomers that are heavier than butenes and those containing odd numbers of carbon atoms. The reaction pathways on Ni^{2+} and H^+ sites were systematically probed on a model Ni-exchanged Beta catalyst that forms a 1:1 composition of these sites *in-situ*. The quantitative determination of apparent deactivation orders for the decay of product space-time yields provides insights into the site origins of the products formed. Further, Delplot analysis systematically identifies the primary and secondary products in the reaction network. This strategy shows linear butene isomers to be primary products formed at Ni^{2+}-derived sites, while isobutene is formed as a secondary product by skeletal isomerization at H^+ sites. In addition, propene is formed as a secondary product, purportedly by cross-metathesis between linear butene isomers and the reactant ethene at Ni^{2+}-derived sites. Also, ethane is a secondary product that forms by hydrogenation of ethene at H^+ sites, with the requisite H_2 generated *in-situ* likely by dehydrogenation and aromatization of ethene at H^+ sites.

The predominance of the coordination-insertion mechanism at Ni^{2+}-derived sites implies kinetic factors influence isomer distributions within the dimer products, providing an opportunity to influence the selectivity toward linear and terminal alkene products of dimerization. In the case of bifunctional materials, reaction pathways on the Ni^{2+} and H^+ sites dictate the interplay between kinetically-controlled product selectivity at Ni sites and thermodynamic preference of product isomers formed at the H^+ sites. In summary, through synthesis of control catalytic materials and rigorous treatment of transient kinetic data, this work presents a detailed mechanistic understanding of the reaction pathways at the Ni^{2+} and H^+ sites, stipulating design parameters that have predictable consequences on the product composition of alkene dimerization and oligomerization.