Propene oligomerization over Ni-exchanged Na-X zeolites

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ABSTRACT

The oligomerization of propene was investigated over a series of nickel ion-exchanged Na-X zeolites with varying Ni loadings. Catalyst characterization by temperature-programmed reduction, elemental analysis, and XANES indicates that all of the exchanged Ni is present as Ni^{2+} that charge-compensates two exchange sites. The selectivity to propene oligomers remained greater than 98% for all Ni–Na-X catalysts with dimers being the main product. In contrast, the activity of Ni–Na-X was determined to depend strongly on Ni loading. At low to intermediate Ni loadings, the catalyst activates, reaches a maximum activity, and then deactivates with further time on stream. The rates of activation and deactivation are functions of the Ni content in the zeolite and both increase with increasing Ni loading. Stable activity was achieved for low Ni loadings (<0.6 wt%) by rapidly activating and deactivating the catalyst in propene at elevated temperature. The rate of propene dimerization measured under steady state conditions is first order in propene and characterized by an activation energy of 45 kJ mol^{-1}. Activation of Ni–Na-X is attributed to migration of the Ni^{2+} cations from hexagonal prisms of the zeolite into the supercage where the cations form a catalytically active Ni^{2+}–olefin complex. Deactivation is proposed to occur via the reaction of two nearby Ni–olefin complexes leading to the deactivation of both sites. A model for the dynamics of activation and deactivation and for the dimerization of propene to hexene is proposed. This model provides a satisfactory description of the effects of propene partial pressure and Ni loading on the rate of propene dimerization as a function of time on stream.

1. Introduction

Oligomerization of light olefins, C_2–C_5, is of substantial interest as a means for producing high-volume hydrocarbons including gasoline and diesel fuels [1,2]. Heterogeneous Brønsted acid catalysts, including zeolites, are known to catalyze olefin oligomerization at moderate temperature and pressure; however, the selectivity to oligomers is low as the Brønsted acid sites are also active for product cracking and aromatization under operating conditions [2–4]. Furthermore, although the Brønsted acid catalysts are highly active for C_3–C_5 olefin oligomerization, the oligomerization of ethene is more difficult and requires higher temperatures to reach meaningful conversions [2].

A number of authors have considered Ni-based catalysts as an alternative to Brønsted acids because such catalysts are highly selective to oligomers and active for ethene oligomerization [2,5–9]. These catalysts have been shown to be highly active for olefin oligomerization at lower temperatures but higher pressures than those required for Brønsted acid catalysts. For example, it has been shown that Ni-exchanged aluminosilicates can realize 99% ethene

conversion with 97% selectivity to oligomers at 393 K and 35 bar [9].

Although numerous Ni-exchanged aluminosilicates, including zeolites, have been shown to be active catalysts for olefin oligomerization, there is little consensus regarding how the catalysts function. Ni catalysts have been reported to possess an activation period when the olefin is first introduced to the catalyst [9–11], but the cause of the activation period is not known. It has also been reported that the catalyst can deactivate with time on stream, which has been attributed to site blocking by the formation of long oligomers [6,12,13] or to the irreversible reduction of the Ni site to inactive Ni^0 [14], but neither of these mechanisms explain the long-term catalyst stability observed at higher pressure [9]. There is also disagreement concerning the nature of the active site, with various authors having reported it to be Ni^{2+} [11,15], Ni^+ [10,11,15], or a pair of Ni and H^+ sites [13,16,17]. Lack of agreement between the active site and an understanding of the causes of catalyst activation and deactivation make elucidating the mechanism for olefin oligomerization challenging.

The goal of this study was to establish the causes of catalyst activation and deactivation during low pressure olefin oligomerization of propene in Ni-exchanged zeolites as well as the state of the active site through these transformations. A series

of Ni-exchanged Na-X zeolites were synthesized with varying Ni weight loadings to probe the effects of Ni loading on the activity and catalyst selectivity. The Ni weight loading of the catalyst was determined to influence both the time required to activate and deactivate the catalyst. Comparison between the Ni–Na-X zeolite and a catalyst containing isolated Ni cations on SiO$_2$ shows that the activation period is due to the zeolite framework and is consistent with migration of Ni from the hexagonal prisms of the zeolite to the supercage. The deactivation of the catalyst was determined to be hyperbolic with time on stream and suggests that the loss of activity is caused by a two-site deactivation mechanism. A model of the reaction kinetics was developed and shows that the proposed activation and deactivation mechanisms are consistent with the experimental results. The oxidation state of the Ni cations was explored using in situ XANES experiments and has shown that Ni remains Ni^{2+} after synthesis and during reaction with propene suggesting that stable steady state activity is due to isolated Ni^{2+} complexes.

2. Methods

2.1. Catalyst preparation

Ni–Na-X was prepared by aqueous ion exchange of 5 g of Na-X (Sigma–Aldrich, 13X, powder) with 100 mL of 1–100 mM Ni(NO$_3$)$_2$ (Sigma–Aldrich, 99.999% trace metals basis, hexahydrate) solution. The exchange was performed at 343 K for 16 h in a round-bottomed flask equipped with a Teflon coated stir bar and a water-cooled condenser. The exchanged zeolite was filtered, washed with deionized water (Millipore), and dried before being rewashed, and dried to remove residual nickel nitrate. The catalyst was placed in a quartz boat and heated in a horizontal quartz tube furnace to 773 K at 2 K min^{-1} under 100 cm^3 min^{-1} air (Praxair, zero-grade) and held at 773 K for 3 h to remove the nitrate groups and residual water. After calcination, the samples were stored in a desiccator to limit the readsorption of water vapor. Ni–Na–MOR was prepared using the same procedure with 5 g of Na–MOR (Zeolyst, Si/Al = 6.5) and 100 mL of 5 mM Ni(NO$_3$)$_2$ solution.

A Ni–SiO$_2$ catalyst was synthesized as follows: 390 mg of Ni(NO$_3$)$_2$·6H$_2$O and 405 mg of H-EDTA (Sigma–Aldrich, 99%) were added to 15 mL of water (Millipore) to create a solution with an approximately 1:1 molar ratio of Ni to H-EDTA. The mixture was then heated to 343 K for 6 h to dissolve most of the H-EDTA and resulted in the solution changing color from deep green to blue, suggesting the formation of a Ni–EDTA complex [18]. Incipient wetness impregnation of 2.30 g of solution into 2.00 g of Silicycle silica (average pore diameter = 150 Å; surface area = 300 m^2 g^{-1}) followed by calcination at 773 K under 100 cm^3 min^{-1} of air to remove the EDTA ligands produced the 0.6 wt% Ni–SiO$_2$ catalyst. After calcination, the catalyst was stored in a desiccator to limit readsorption of water vapor.

2.2. Catalyst characterization

Catalysts were characterized by a number of different techniques. Ni, Na, Si, and Al contents were determined using inductively coupled plasma optical emission spectroscopy conducted at Galbraith Laboratories in Knoxville, TN. Micropore volume measurements were obtained using the t-plot method with N$_2$ (Praxair, 99.999%) adsorption and were collected using a Micromeritics Gemini VII BET instrument. Prior to carrying out the BET experiments, samples were outgassed overnight at 393 K under vacuum to remove residual adsorbed water. X-ray diffraction (XRD) data were obtained by immobilizing the catalyst powder on a XRD sample plate using Vaseline. The sample was then analyzed with a

Siemens D5000 diffractometer using Cu Kα radiation and a scintillation counter detector. Data were digitally recorded from 7° to 35° 2θ with a step size of 0.015°. Temperature-programmed reduction (TPR) experiments were carried out by loading 7–30 mg of sample into a quartz U-tube, which was then attached to a Quantasorb TPR instrument. The sample was heated at 10 K min^{-1} to 1048 K in 1% H$_2$ diluted in argon (Praxair, certified standard), and the consumption of H$_2$ was monitored using a thermal conductivity detector.

Transmission electron microscopy (TEM) was performed at the Electron Microscopy Laboratory of the University of California, Berkeley. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were taken using a FEI Tecnai F20 microscope operated at an accelerating voltage of 200 kV and equipped with an electron-gun monochromator. Samples were prepared by sonicating 50 mg of sample in 10 mL of isopropyl alcohol to create a suspension that was then dropped onto a carbon-coated copper grid and dried in ambient air.

Ni K-edge X-ray absorption data were collected at the Advanced Photo Source at Argonne National Lab on beamline 10-BM. Sample pellets were pressed into a sample holder that was then placed in a horizontal quartz tube between two ionization chamber detectors. A Ni reference foil was placed after the second ionization chamber allowing the collected sample spectra to be aligned to the foil. In situ experiments were carried out by placing the sample tube in a furnace located between the ionization chambers where the sample was heated to 773 K in 100 cm^3 min^{-1} of air and held at temperature for 1 h to remove moisture. The cell was then cooled to the reaction temperature of 453 K and purged with 100 cm^3 min^{-1} of helium for 15 min before switching to 30 cm^3 min^{-1} of propene and holding at 453 K for 8 h. Data were analyzed using the Athena program of the IFEFFIT software package [19,20].

2.3. Measurement of reaction rates

Measurements of catalyst activity were performed using a ½″ stainless steel reactor that was pinched in the middle to allow for the creation of a fixed bed. Quartz wool was placed inside the reactor followed by 200 mg of catalyst diluted with 100 mg of Silicycle silica. Additional quartz wool was placed on top of the catalyst to create a fixed bed. A K-type thermocouple was then inserted directly into the fixed-bed to monitor the temperature. The reaction pressure was controlled digitally using a Tescom back-pressure regulator.

Prior to each experiment, samples were calcined in situ in 100 cm^3 min^{-1} of flowing air. The sample temperature was raised to 773 K at 2 K min^{-1} and held for 3 h to remove water that had readsorbed while preparing the reactor. Samples were then cooled to reaction temperature at 2 K min^{-1}, flushed with 100 cm^3 min^{-1} helium for 5 min, and then contacted with 30 cm^3 min^{-1} of propene (Praxair, 99.9%) while increasing pressure to reaction conditions. Products were analyzed using an Agilent 7890A gas chromatograph equipped with a gas-sampling valve, a 30 m HP-Plot Q column, and a flame ionization detector.

3. Results

3.1. Catalyst characterization

The catalyst Ni loading and degree of site exchange, determined from elemental analysis, are shown in Fig. 1 for each catalyst used in this study. For Ni(NO$_3$)$_2$ concentrations between 1 and 50 mM, the Ni loading increases linearly with the concentration of Ni(NO$_3$)$_2$, as expected for complete exchange of two Na$^+$ cations by one Ni^{2+} cation. The only data point that lies below this line is for the sample prepared using the 100 mM Ni(NO$_3$)$_2$ exchange solution, indicating