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Short communication

Oligomerization of 1-butene over carbon-supported CoO_x and subsequent isomerization/hydroformylation to n-nonanal

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ABSTRACT

A two-step process was demonstrated for the conversion of 1-butene to n-nonanal with an overall reaction selectivity of 70.8%. The process consists of a dimerization step over a heterogeneous carbon-supported cobalt oxide catalyst to a mixture of oligomers, consisting primarily of internal linear octenes. After product distillation, the olefinic mixture was converted to C_9 aldehydes with a normal/isomeric (N/I) ratio of 3.8 over a homogeneous Rh/BIPHEPHOS catalyst. This work demonstrates a new route to produce linear aldehydes from light olefins.

1. Introduction

Light olefins (C_2-C_4) are precursors for numerous chemicals in the petrochemical industry. Recent increases in the supply of ethane from natural gas extraction has stimulated research in processes for the conversion of light olefins towards fuels and value-added chemicals. Oligomerization represents one potential route for valorising these light olefins to produce longer-chain oligomers such as linear alpha olefins (LAOs) or transportation fuels [1, 2]. LAOs have significantly higher value than fuels due to their application as co-monomers for linear low-density plastics production and as precursors for the lubricant, surfactant and detergent industry. Several efforts have focused on identifying selective heterogeneous catalysts for oligomerization to compete with homogeneous catalysts [3, 4]. One major limitation of current heterogeneous oligomerization catalysts is the limited uses for reaction side products, which include branched and internal olefin isomers. The ability to employ a heterogeneous oligomerization catalyst to selectively upgrade light olefins to value-added chemicals would be desirable.

Common catalysts for commercial oligomerization processes include homogeneous systems such as a nickel-phosphine complex used in the Shell Higher Olefin Process (SHOP) process [5], or triethyl aluminum Ziegler catalysts used in the INEOS and Gulf process [6]. Known heterogeneous olefin oligomerization catalysts include many forms of solid acids and supported metals and metal oxides [7]. It is well known that Brønsted acids can be used to produce gasoline-range fuels, but the rapid skeletal isomerization leads to a highly-branched product distribution [8, 9]. Recently, many authors have identified Ni-based catalytic systems as potential candidates for the heterogeneous oligomerization of ethylene. A few examples include Ni-exchanged SiO_2-Al_2O_3 [10, 11], zeolites [12–14] and MOF frameworks [15, 16]. While these Ni-based systems produce linear oligomers from 1-butene oligomerization, the highest reported yields were approximately 10% [11].

A series of publications by Schultz et al. [17, 18] highlighted the exceptional linear selectivity of a “doubly-ammoniated cobalt oxide on carbon” catalyst for the oligomerization of light olefins. Recently, our group has reported on a heterogeneous, ammonia-treated carbon-supported cobalt oxide catalyst (2A-CoO_x/N-C) based on the work of Schultz et al. [19–21] that is capable of oligomerizing 1-butene to straight-chain dimers with high selectivity (82.9%) with the remainder of the dimerization products consisting entirely of mono-branched olefins. To the best of our knowledge, 2A-CoO_x/N-C is the most selective heterogeneous catalyst for the dimerization of light olefins into linear oligomers. While selectivity towards straight-chain oligomers is high, double-bond isomerization is facile and oligomerization products approach thermodynamic equilibrium with internal C_8 olefins being the primary oligomers and only trace amounts of terminal C_8 olefin produced.

In this work, we demonstrate how the oligomers produced from the 2A-CoO_x/N-C catalyst can be selectively converted into linear C_9 aldehydes with a tandem isomerization/hydroformylation catalyst as shown in Scheme 1 [22–24]. We expect that this technology could be

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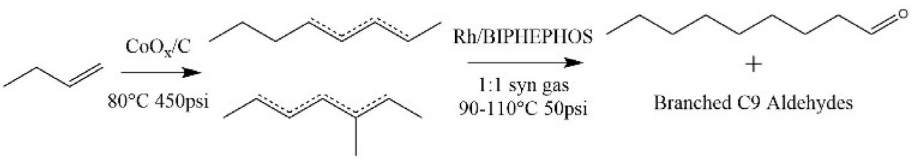

Scheme 1. Catalytic reaction route to produce n-nonanal from 1-butene by first oligomerizing the terminal olefin to an equilibrium mixture of linear and mono-branched isomers followed by the tandem isomerization/hydroformylation to the corresponding aldehyde. Double-bond positions of the major C_8 products are shown as dotted lines. Branched C_9 aldehydes were not drawn for simplicity but reported in the Electronic Supporting Information (ESI) (see Table S1).

combined with other olefins (C_nH_{2n}, where n = 2–6) [25] to produce the corresponding linear aldehyde ($C_{2n+1}H_{4n+2}O$) of the dimerization product. The analyzed route from light olefins to longer-chain aldehydes could be further coupled with other reactions such as hydrogenation, oxidation or reductive amination to produce alcohols, carboxylic acids or amines of different functionalities, respectively [26]. Specifically, C_8 and C_9 oxo alcohols are used in plasticizers for polyvinylchloride (PVC) production [7].

2. Experimental

Relevant information about instrumental analysis of reaction products and catalyst characterization is provided in the Electronic Supporting Information.

2.1. Catalyst preparation

Oligomerization catalysts were prepared by the incipient wetness impregnation (IWI) of 4.2 M cobalt nitrate solution on an activated carbon support (Norit Darco MRX) to obtain a loading of ~12 wt% cobalt. Detailed synthesis and characterization of this catalyst are reported elsewhere [20]. After IWI, the catalyst was dried at 125 °C in air.

Hydroformylation catalyst solutions were prepared in a nitrogen glove box with Schlenk techniques. Anhydrous solvents and BIPHEPHOS (Sigma-Aldrich) were used as received. For each reaction, rhodium dicarbonyl acetylacetonate (0.0178 g; 250 ppm Rh) and BIPHEPHOS (0.1623 g, 3 mol/mol Rh) are combined with the solvent (30 ml); 1 ml tetraglyme ($\geq$99%) was added as internal standard for GC analyses.

2.2. Catalytic measurements

Catalytic oligomerization reaction studies were carried out in a fixed bed up-flow reactor. Details of the experimental setup are described elsewhere [20]. Prior to reaction, the catalyst was pre-treated in flowing helium (100 ml/min) at 230 °C (5 °C/min ramp, 2 h hold). The reactor was then cooled to reaction temperature, pressurized to 450 psig with He, then 1-butene (99.9%) was flowed via a high-pressure syringe pump (Teledyne Isco). Liquid-phase reaction products were collected and drained from a chilled collection vessel placed after the reactor into a chilled n-hexane solution with a n-heptane internal standard. Products were analyzed by 2D-GC–MS system. C_4 isomerization products were analyzed by sampling a He sweep gas flowing through the headspace of the collection vessel at the exit of the reactor with GC (Fig. S1, ESI). The skeletal composition of the C_8 isomers products was determined by GC analysis of the hydrogenated liquid products. Reaction mixtures were hydrogenated with the H_2 carrier gas of the GC passed over a Pd/C catalyst packed in the GC liner. Reaction products collected for hydroformylation experiments were distilled to produce a feed that consisted of primarily C8 olefins (4% C_4, 94.2% C_8, 1.8% C_{12}). GC conditions can be found in Table S2 (ESI).

For hydroformylation reaction studies, catalyst solutions were charged to the reactor and heated to the reaction temperature with stirring under a ~ 50 psig gaseous mixture of H_2 and CO with a molar ratio of 1:1 (syngas) for 30 min. The mixed C_8 olefin was then added via pressure-lok syringe (3 ml). A charge sample was taken for GC and target reaction pressure was established with 1:1 syngas (CO/H_2). The pressure was held constant by using Brooks 5150 mass flow meters. Gas uptake was measured with a Brooks totalizer. Samples were taken periodically for GC analysis to determine conversion and product selectivity. The total reaction time was set to 6 h.

2.3. Scanning transmission electron microscopy (STEM)

STEM images were obtained with an aberration-corrected FEI Titan microscope. Catalyst samples were suspended in ethanol with sonication, then deposited on a carbon-coated copper grid (EMS) and plasma cleaned for 15 min prior to analysis with an aberration-corrected FEI Titan STEM.

3. Results and discussion

3.1. Oligomerization process step

In the first step of this process, 1-butene was converted in a flow reactor over 2A-CoOx/N-C catalyst. This catalyst is active for both the isomerization of 1-butene to its internal double-bond stereoisomers and for the oligomerization to longer chain lengths without the addition of a co-catalyst. The ability to operate without a co-catalyst activator, such as methylaluminoxane (MAO), represents a significant processing advantage as both homogeneous and heterogeneous catalytic oligomerization systems commonly employ these pyrophoric materials in stoichiometric excess to alkylate the active metal sites and initiate the catalytic cycle [27]. Fig. 1a shows the rate of isomerization, oligomerization and linear octene distribution as a function of time. The 1-butene conversion to oligomers in these experiments was between 2 and 10%. An analysis of the detailed dimerization product composition as a function of conversion can be found elsewhere [19]. At the chosen reaction conditions, catalyst deactivation resulted in the simultaneous decrease in isomerization and oligomerization activity. We suspect that both isomerization and oligomerization occur on the same catalytic site, as the deactivation profile is identical for each reaction regardless of WHSV. From surface area measurements, Xu et al. [21] proposed that deactivation can be attributed to either pore filling of the carbon support or accumulations of heavy oligomers on the active sites. Nanoparticle sintering and leaching were ruled out by small-angle x-ray scattering (SAXS) and elemental chemical analysis (ICP) of the fresh and spent catalysts. Control experiments showed minimal isomerization activity (< 5%) and no oligomerization activity on the ammonia-treated carbon support. Regeneration in an inert atmosphere was tested and partially recovers some of the lost activity. The investigation of additional methods for reducing catalyst deactivation, such as removal of oligomers from the spent catalyst or support pore modification in order to increase the transport of heavy oligomers out of the catalyst pore system, remains an important topic for future studies.

Work by Xu et al. [21] which analyzed product compositions from various starting molecules suggested that oligomerization over 2A-CoO_x/N-C occurs via a Cossee-Arlman mechanism, where the catalytic cycle is characterized by an initial insertion step of the olefin into a metal hydride followed by successive olefin insertion steps. The active metal hydride is regenerated by β-hydride elimination. Double-bond isomerization of both 1-butene and the oligomer products occurs concurrently through the reversible insertion/elimination into the metal hydride bond. It is noteworthy that no activation period was observed with our system. Recently, a DFT study by Brogaard and Olsbye [12]