



Zinc inclusion to heterogeneous nickel catalysts reduces oligomerization during the semi-hydrogenation of acetylene



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ABSTRACT

Isotopic labeling and density functional theory (DFT) were used to determine the mechanism for acetylene hydrogenation and oligomerization on well-defined intermetallic nickel–zinc catalysts. The primary benefit of adding zinc to nickel is a reduction in oligomeric species formation which leads to higher ethylene selectivity. The production of ethane is not highly dependent on zinc content; therefore, ethane production is not a good descriptor of ethylene selectivity since acetylene may also be converted to higher molecular weight products. Analysis using DFT and Langmuir–Hinshelwood kinetics shows that the large decrease in the adsorption energy of acetylene on intermetallic NiZn compared to pure Ni is responsible for the observed increase in ethylene selectivity. The adsorption energy of acetylene appears to be a descriptor for carbon–carbon bond formation since a high adsorption energy leads to an increased coverage of C₂ species and an increased rate of carbon–carbon bond formation.

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1. Introduction

The catalytic semi-hydrogenation of acetylene to produce ethylene is a common method for the removal of trace acetylene (0.5–2% by volume) in ethylene feed streams destined for ethylene polymerization [1]. Acetylene impurities in ethylene produced from naphtha, responsible for the deactivation of the polymerization catalyst, must be reduced to a level of 5 ppm prior to polymerization [2]. A good catalyst for this reaction converts all of the acetylene to ethylene without further converting any ethylene to ethane such that there is a net increase in the amount of ethylene. Well-dispersed palladium supported on metal oxides exhibits high activity for acetylene removal, but limited selectivity as a result of over-hydrogenation to ethane and limited long-term stability as a result of oligomer (“green oil”) accumulation [3,4]. The addition of silver to palladium catalysts results in a higher ethylene selectivity due to a decrease in hydrogen coverage and a reduction in the hydrogenation of gas-phase ethylene [4–12]. More recently, intermetallic Pd–Ga compounds demonstrated high ethylene selectivity and long-term stability due to isolation of the Pd active sites in a

well-defined intermetallic structure [13–17]. Isolated Pd atoms reduce the ability of the catalyst to over-hydrogenate ethylene to form ethane, produce oligomerization products, and form coke on the catalyst surface. However, there exists room for catalyst improvement, particularly in terms of cost.

Intermetallic NiZn was identified as a low-cost replacement for Pd–Ag catalysts by Studt et al. using a density functional theory (DFT) scaling analysis across alloys of late 3D transition metals [18,19]. Nickel–zinc catalysts were subsequently synthesized by co-impregnation of nickel and zinc nitrates on a MgAl₂O₄ support, reduced at 400 °C, and tested for the catalytic hydrogenation of acetylene in the presence of ethylene [18]. Structural characterization, however, was not included in the study of Studt et al. to prove the existence of intermetallic NiZn [18]. Furthermore, it has since been shown that nickel–zinc catalysts synthesized by the method of Studt et al. do not contain intermetallic NiZn [20]. A temperature of 400 °C is not sufficient for the reduction of ZnO (which is present after calcination of zinc nitrate) such that the catalyst contains a mixture of Ni and ZnO phases after reduction [20–23]. An additional shortcoming in previous studies of nickel–zinc catalysts is the measure of ethylene selectivity. Studt et al. used ethane concentration as a descriptor for ethylene selectivity where a low ethane concentration was related to a high ethylene selectivity

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[18]. However, it is well known that acetylene oligomerizes on Ni-based hydrogenation catalysts and that ethane is only one of many products of the reaction [24–28]. In addition, acetylene may dissociatively adsorb to ZnO, depositing carbon atoms on the surface [29,30]. Thus, it is important to measure ethylene formation directly rather than inferring the concentration based on ethane formation.

Scheme 1 summarizes the possible pathways for the reaction of a mixture of acetylene, ethylene, and hydrogen on Ni-based catalysts. According to **Scheme 1**, acetylene and ethylene competitively adsorb to the catalyst surface, where adsorbed species are denoted with an asterisk (*). Acetylene that has been partially hydrogenated may either react with another adsorbed hydrogen to form adsorbed ethylene or react with an adsorbed acetylene to form oligomers [11,26] (leading eventually to “green oil”), the simplest of which is butadiene (C₄H₆). Previous work has suggested that C₂H₃* and adsorbed acetylene are the precursors for oligomer formation [26]. Finally, adsorbed ethylene may either desorb to form gas-phase ethylene (desired product), or further hydrogenate to form ethane. During catalysis, ethane produced from ethylene is indistinguishable from ethane produced from acetylene. In addition, it is impossible to quantify the ethylene that is produced from ¹²C acetylene when the reaction is run with excess ¹²C ethylene.

Herein, we employ a bulk synthesis method to create intermetallic nickel–zinc compounds with well-defined structures. We use isotopic labeling of the carbon atoms in acetylene, where the reactant mixture consists of ¹³C₂H₂, ¹²C₂H₄, and H₂. Isotopic labeling has been used previously to elucidate the mechanism for acetylene hydrogenation on Pd and Pt catalysts [31–34]. To the best of our knowledge, there are no previous reports of isotopic labeling for acetylene hydrogenation on Ni catalysts. We use isotopic labeling in a batch reactor to evaluate each of the pathways proposed in **Scheme 1** and provide an overall measure of ethylene selectivity. Ethylene selectivity is defined as the net ethylene production per acetylene removal (Eq. (1)).

$$\text{Ethylene selectivity} = \frac{P_{^{13}\text{C}_2\text{H}_4,t} - P_{^{12}\text{C}_2\text{H}_6,t}}{P_{^{13}\text{C}_2\text{H}_2,i} - P_{^{13}\text{C}_2\text{H}_2,t}} \quad (1)$$

The ethylene produced from acetylene is directly measured as the amount of ¹³C₂H₄. The gas-phase ethylene that reacts to form ethane is measured as the amount of ¹²C₂H₆. Then, the net ethylene production is defined as the amount of ¹³C₂H₄ formed minus the amount of ¹²C₂H₆ formed. Acetylene removal is quantified by taking the difference between the initial and final amounts of acetylene in the reactor. Eq. (1) gives the expression for ethylene selectivity, where P_X is the partial pressure of component X, i is the initial time, and t is the time at which the selectivity is being measured. By this definition, the maximum in ethylene selectivity is 1 and ethylene selectivity may be negative, which corresponds to a net decrease in the amount of ethylene. Acetylene conversion is defined as the decrease in partial pressure of acetylene at time, t , divided by the initial partial pressure of acetylene (Eq. (2)). Selectivity for all other products of the reaction is defined in Eq. (3), where N_X is the

number of carbon atoms in component X. The term $N_X/2$ normalizes the data with respect to the number of carbon atoms in acetylene.

$$\text{Acetylene conversion} = \frac{P_{^{13}\text{C}_2\text{H}_2,i} - P_{^{13}\text{C}_2\text{H}_2,t}}{P_{^{13}\text{C}_2\text{H}_2,i}} \quad (2)$$

$$S_X = \frac{P_{X,t} \frac{N_X}{2}}{P_{^{13}\text{C}_2\text{H}_2,i} - P_{^{13}\text{C}_2\text{H}_2,t}} \quad (3)$$

We use density functional theory (DFT) methods to generate the reaction energy diagram for hydrogenation and oligomerization pathways on pure Ni and intermetallic NiZn. A comparison is made between the selectivities of Ni and intermetallic NiZn using Langmuir–Hinshelwood kinetics. The reaction energy diagram for acetylene hydrogenation on intermetallic NiZn has been previously calculated [18], but neither a microkinetic analysis nor a comparison with pure Ni was made. In this manuscript, we apply experimental and theoretical methods for determining the effect of Zn content on the selectivity of Ni catalysts for the semi-hydrogenation of acetylene.

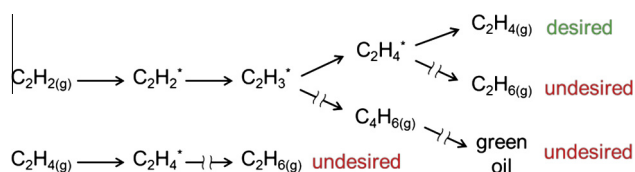
2. Experimental methods

2.1. Synthesis of bulk intermetallic compounds

Bulk intermetallic Ni–Zn compounds were synthesized by solid-state diffusion in quartz tubes evacuated to a pressure of ~30 mTorr. Ni powder (Sigma Aldrich, <150 μm particle size, 99.999%) and Zn granules (Sigma Aldrich, 3 mm diam, 99.99%) were added with the correct stoichiometry to an alumina crucible (LSP Ceramics, 13 mm i.d.) and sealed in an evacuated quartz tube. NiZn and Ni₅Zn₂₁ were heated to 700 °C at a ramp rate of 10 °C/min, held for 24 h, and cooled to RT at a ramp rate of 1 °C/min. Ni₄Zn was heated to 900 °C at a ramp rate of 10 °C/min, held for 24 h, and cooled to RT at a ramp rate of 3 °C/min. Pure Ni was also subjected to an identical treatment to Ni₄Zn. The samples were removed from the quartz tubes and loaded into a stainless steel ball mill (SPEX Mixer/Mill, 8001 sample container) along with 1 mL of 1,1,1,2,2,3,4,4,5,5,5-decafluoropentane (Vertrel XF, Dupont) per gram of sample within an argon-filled glove box (<1 ppm oxygen). The samples were removed from the glove box in the sealed milling container and milled for 4 h in an argon atmosphere. After milling, the samples were placed in the glove box and the decafluoropentane was allowed to evaporate at room temperature. Samples were stored in the glove box prior to catalytic measurements.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) data were collected on a PANalytical Empyrean X-ray diffractometer using Cu Kα (λ = 1.5418 Å) radiation. Samples were prepared for analysis by filling the cavity of a silicon zero background holder and leveling the surface with a glass slide. The Empyrean has a diffractometer radius of 240 mm and is equipped with a PIXcel detector using scanning line mode (1D) detection. The incident beam optics had the following configuration: ½° antiscatter slit, 10 mm beam mask, ¼° fixed divergence slit, and 0.04 rad sollar slits. The diffracted beam optics had the following configuration: 0.04 rad sollar slits, Ni beta-filter, and ¼° antiscatter slit. Data were acquired with a 0.025° 2θ step size from 20° to 90° 2θ. Rietveld refinement was performed within Jade (version 2.2.0 (2010) Materials Data Incorporated) to determine the unit cell parameters from the X-ray diffraction data. A 5th order polynomial background function and the default peak shape parameters were used within Jade for the Rietveld refinement. Visualization of the unit cells was performed with Materials Studio.



Scheme 1. Proposed reaction routes during the hydrogenation of acetylene in the presence of ethylene. Adsorbed species are denoted with an asterisk (*) and solid arrows denote elementary steps.

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