



The role of catalyst environment on CO₂ hydrogenation in a fixed-bed reactor



Matthew J. Bradley^a, Ramagopal Ananth^b, Heather D. Willauer^{c,*}, Jeffrey W. Baldwin^d, Dennis R. Hardy^e, Felice DiMascio^f, Frederick W. Williams^g

^a ASEE Postdoctoral Research Associate, Naval Research Laboratory, Materials Science & Technology Division, Washington, DC 20375, United States

^b Naval Research Laboratory, Chemistry Division, Washington, DC 20375, United States

^c Naval Research Laboratory, Materials Science & Technology Division, Washington, DC 20375, United States

^d Naval Research Laboratory, Acoustics Division, Washington, DC 20375, United States

^e NOVA Research Inc., 1900 Elkin Street, Alexandria, VA 22308, United States

^f Office of Naval Research, Arlington, VA 22203, United States

^g Emeritus, Naval Research Laboratory, Chemistry Division, Washington, DC 20375, United States

ARTICLE INFO

Article history:

Received 12 August 2016

Received in revised form 17 October 2016

Accepted 29 October 2016

Available online 16 November 2016

Keywords:

Carbon dioxide (CO₂)

GHSV (gas hourly space velocity)

Selectivity

Kinetics

Modeling

ABSTRACT

To reduce the negative impact that water formation has on the catalyst environment during CO₂ hydrogenation reactions in a fixed-bed reactor, a start-up solvent, (mineral oil) was added to the reactor as a pretreatment. A Macrolite[®]-supported iron-based catalyst was used as the model catalyst to determine the impact of pretreatment with mineral oil on product selectivity, CO₂ conversion, and catalyst stability over a range of reaction temperatures (280 °C, 300 °C, and 320 °C). At the lower reaction temperatures (280 °C, 300 °C), CO₂ conversion and C₂-C₅+ yield was increased by as much as 17% and 25% respectively by addition of start-up solvent. The characterization of the catalyst showed the formation of an iron manganese oxide phase, in the absence of the start-up solvent. Modeling and kinetic analysis of the data suggested that the start-up solvent decreased oxidation of the catalyst phase by reducing water adsorption, thereby increasing the Fischer-Tropsch reaction rate. This led to an increase in hydrocarbon yield in the presence of mineral oil.

Published by Elsevier Ltd.

1. Introduction

The US Department of Defense (DoD) used an average of 3 billion gallons of jet fuel a year between fiscal years (2006–2016) [1,2]. As the single largest buyer and consumer of petroleum derived middle-distillate fuel in the world, DOD's budget is heavily influenced by changes and fluctuations in global fuel prices. In the last 10 years the DOD experienced the largest change in fuel price during fiscal year (FY) 2008 [1,2]. During that fiscal year the price of fuel rose from approximately \$2.33/gallon for JP-5 jet fuel to \$4.09/gallon. The Defense Logistics Agency Energy (DLA-Energy) reports a current fuel price of \$2.64/gallon for JP-5 (FY2016) [1]. Considering the long term projected rise in fuel cost due to

increases in global demand and the variability in supply, DOD has invested in energy alternatives to provide greater energy security while having a minimal impact on the environment [3]. Producing “drop-in” replacements for petroleum-derived operational fuel at or near the point of use translates into “Freedom of Action for the Warfighter” and potential long term cost savings and strategic advantages for the DOD.

In an effort to synthesize operational fuel at the point of use, this research utilizes a carbon source that is readily available in seawater. Carbon dioxide (CO₂) in the form of bicarbonate is 140 times more concentrated in seawater than air on a weight per volume basis (w/v) and is about a third of the concentration of a stack gas (w/v) [4–6]. One of the difficulties of using CO₂ as the carbon source for operational fuel synthesis *via* thermochemical methods is the high energy barrier for hydrogenation and the essential need of hydrogen for the process [7–11]. A recent review by Porosoff et al. [12] addresses the need to identify new cost-effective, stable, and highly selective CO₂ hydrogenation catalysts, and to reduce the cost of CO₂-free hydrogen to make large scale hydrocarbon production processes from CO₂ economically feasible.

* Corresponding author.

E-mail addresses: matthew.bradley.ctr@nrl.navy.mil (M.J. Bradley), ramagopal.ananth@nrl.navy.mil (R. Ananth), heather.willauer@nrl.navy.mil (H.D. Willauer), jeff.baldwin@nrl.navy.mil (J.W. Baldwin), kashardy@gmail.com (D.R. Hardy), felixdim@aol.com (F. DiMascio), fredsshadwell@gmail.com (F.W. Williams).

In addition to the importance of the catalyst composition, the role that the catalyst environment has on product selectivity, mass transfer, and conversion in hydrogenation reactions has been well documented [13,14]. Initial studies using CO₂ hydrogenation catalysts in a continuously stirred tank/thermal reactor (CSTR) reported CO₂ conversion levels as high as 50% with an olefin/paraffin ratio of 4.4 and a C2–C5+ hydrocarbon selectivity of 62.4% at a GHSV of 0.0015 L/g-s [15]. The CSTR simulates conventional slurry phase reactors that are used for large scale industrial applications [13,16]. The physical size and nature of the slurry phase reactor are not ideal for producing operational fuel at sea or in remote locations. Thus the challenge remains to find low cost modular chemical reactor solutions that are scalable and provide efficiencies and the operational ability to be used for off-shore and remote synthetic fuel production applications. Companies at the forefront of developing these systems are using fixed-bed design concepts [17,18].

To simulate these reactor systems at the laboratory scale, CO₂ hydrogenation catalysts were evaluated in a fixed-bed reactor. Moving from a CSTR to a fixed-bed reactor had a significant impact on the catalytic activity of the Fe promoted CO₂ hydrogenation catalyst at similar GHSV and temperature. Hydrocarbon selectivity was reduced from 62.4% (CSTR) to 30.5% (fixed-bed reactor) [15,19]. Kinetic and modeling analysis indicated this change in catalyst activity observed in a fixed-bed reactor environment may be attributed to the increased interaction between water and the catalyst surface as water accumulates along the fixed catalyst bed during the hydrogenation reaction [19]. Due to the nature of the CSTR, water vapor formed during the reaction leaves the catalyst suspended in the mineral oil and does not accumulate in the CSTR unlike in the fixed-bed reactor. Water formed under typical Fischer-Tropsch (FT) conditions is known to influence catalyst activity primarily by re-oxidizing the catalyst [20–24]. Since *in-situ* water removal in the fixed-bed reactor is not ideal or practical, mineral oil was added as a start-up solvent to simulate the chemical/solvent environment of the slurry phase reactor [23,25,26].

Though there is extensive FT literature that has established relationships between catalyst activity/selectivity and start-up solvents [23,25,26,33,34], CO₂ hydrogenation reactions occur under fundamentally different kinetic and mechanistic conditions than FT and very little is reported on how start-up solvents effect these reactions. Even though CO₂ is formed in FT reactions as a small by-product due to the water gas shift (WGS) reaction, the effects of solvent on the hydrocarbon formation and reverse water gas shift (RWGS) can be different when CO₂ is used as the primary reactant. Specifically, the findings of this paper show the effects of solvent on suppressing catalyst oxidation through fixed-bed reactor studies, which measure product selectivity, CO₂ conversion, and catalyst stability as a function of temperature. Spectroscopic and diffraction techniques indicate start-up solvent and catalyst support change the surface characteristics of the catalyst and thus the overall catalytic performance. Experimental results are used to develop and validate a three dimensional packed catalyst bed model to include transport and kinetics of CO₂ hydrogenation.

The model includes mass transport due to diffusion and fluid dynamics occurring within the porous structure of the catalytic bed. Gas flow through the porous medium under pressure is calculated using the Brinkman equation and is coupled to the reactive-transport equations for each reactant and product species. The model is an advancement over the kinetics model of Willauer et al. [19] and Riedel et al. [27], who assumed infinite rate species diffusion and ideal plug flow, which neglects transport limitations. Including the finite rate transport into the present model is important in view of the significant measured differences in the

yield and conversion between CSTR and fixed-bed reactors as discussed above. Because the contents of the CSTR are well mixed, the CSTR is expected to have minimal transport limitations compared to a fixed-bed reactor, where significant gradients in species concentrations are predicted by the model. The model is used to explain the observed solvent effect on CO₂ hydrogenation based on the hypothesis that the addition of the start-up solvent (mineral oil) creates a non-polar environment that reduces water adsorption onto the catalyst.

2. Experimental methods

2.1. Catalyst preparation

Macrolite[®] engineered ceramic media (M2) (Fairmount Water Solutions) having a bulk density of 73 lbs/ft³ was used as the support material. Macrolite[®] is aluminosilicate that primarily consists of nepheline syenite spherical particles with an average diameter of 55 micrometers. In a 100 mL beaker, the metal precursor solution containing (Fe(NO₃)₃·9H₂O, KMnO₄, and KNO₃) was prepared by dissolving 50% of the metal salts into approximately 50 mL of deionized water. The beaker was placed on a stirring plate where the contents were mixed using a stirring rod until all of the metal salts were dissolved. The metal precursor solution was applied to the M2 support using a hand sprayer. The solution was poured into the sprayer and the precursor solution discharged as a fine mist on the M2 while the mixer was rotating. When the entire volume of precursor solution was discharged, the 'wet' M2 was placed on a tray and into the dryer where dry air was passed over it. Wearing a muffle glove, a titanium crucible was filled with the dried impregnated M2 and carefully placed in the muffle oven set at 650 °C for 4 h. The catalyst was removed from the muffle oven and placed in a glass tray to cool. Once cooled (approximately one hour), the catalyst was returned to the rotary mixer the process was repeated with the remaining 50% of metal salts. The final catalyst loaded into the CO₂ hydrogenation reactor had the composition iron/manganese/potassium/Macrolite[®] 3.93/2.36/3.23/100 by weight. This ratio is defined 3.93 g of elemental Fe, 2.36 g Mn, and 3.23 g of K as for every 100 g of M2 used as support.

2.2. Catalyst testing and characterization

All CO₂ hydrogenation reactions with the catalyst described herein were conducted in a 12" long stainless steel tube (3/8" ID, 1/2" OD). The catalyst bed occupies 10" length of the stainless steel tube with 0.5" inlet and 0.5" outlet for gas flow. After completion of the hydrogenation reactions, the catalyst was unloaded from the reactor, rinsed with hexanes, vacuum dried, than characterized by a series of techniques (XRD, SEM, XPS, and BET).

2.3. Fixed-bed reactor set-up

In a typical CO₂ hydrogenation experiment, 20 g of catalyst was loaded into the fixed-bed reactor. In the experiments where heavy mineral oil (Sigma Aldrich product# 330760-1L, Lot# MKBH0096 V, density 0.862 g/ml, kinematic viscosity > 20.5 mm²/s) was added to the catalyst bed inside the reactor, the reactor was filled by alternating between layers of catalyst (approximately 2 g) and mineral oil (approximately 1 mL) totaling 20 g of catalyst and 10 mL of mineral oil. The catalyst (with and without mineral oil) was reduced *in-situ* by flowing 100 mL/min H₂ at 300 °C and 20 bar for 18 h.

Three mass flow controllers (Brooks Instruments, USA) were used to control the flows of CO₂, H₂, and N₂ into the reactor. The reactor was operated vertically with the gases flowing from the top

Download English Version:

<https://daneshyari.com/en/article/6456284>

Download Persian Version:

<https://daneshyari.com/article/6456284>

[Daneshyari.com](https://daneshyari.com)