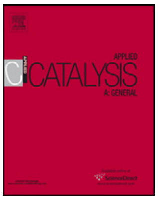
Applied Catalysis A: General 445–446 (2012) 35–41

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Autothermal reforming of butanol to butenes in a staged millisecond reactor: Effect of catalysts and isomers

Hui Sun, Samuel Blass, Edward Michor, Lanny Schmidt*

Department of Chemical Engineering and Materials Science (CEMS), University of Minnesota, 432 Amundson Hall, 421 Washington Avenue SE, Minneapolis, MN 55455, USA

ARTICLE INFO

Article history:
Received 10 May 2012
Received in revised form 27 July 2012
Accepted 29 July 2012
Available online 3 August 2012

Keywords:
Biomass
Butanol
Butene isomers
Dehydration
Isomerization
Autothermal

ABSTRACT

Dehydration and isomerization of butanol is studied in an autothermal short contact-time reactor containing a 1 wt% Pt stage followed by a zeolite or γ-Al_2O_3 stage downstream to convert butanol into butenes with up to 95% yield at residence times on the order of 100 ms. CH_4 is fed as a sacrificial fuel to the Pt stage and butanol is fed between the stages to avoid undesired oxidation and reforming reactions of butanol over Pt. The energy released by CH_4 catalytic partial oxidation drives downstream butanol dehydration and isomerization.

The effect of catalyst is studied by comparing the performance of HZSM-5, HFER, and γ-Al_2O_3 catalysts. Higher yields (20%) of butenes were obtained with γ-Al_2O_3 and HFER than with HZSM-5. The absence of Br⌀nsted acid sites in γ-Al_2O_3 and the small pore structure of HFER lead to reduced yields of large side products such as higher hydrocarbons that promote oligomerization reactions. A 95% butene yield is obtained with HFER at temperatures ranging from 280–350 °C and a 95% yield with γ-Al_2O_3 at temperatures between 320 and 350 °C. Only a 75% butene yield was obtained with HZSM-5 at 230 °C.

The effect of hydrocarbon structure on product formation is studied by comparing conversions of each butanol isomer using a heated tube reactor at temperatures between 200 and 400 °C. The reactivity of butanol follows as: *t*-butanol > 2-butanol > iso-butanol > 1-butanol. *trans*-2-Butene and *cis*-2-butene are primarily formed from linear butanol isomers, while isobutene forms from branched butanol isomers. Conversions and product distributions of butanol isomers formed over HZSM-5 in a staged reactor are comparable (<10% difference across all species) with data using a heated tube reactor at similar temperatures.

We successfully demonstrate an alternative pathway to dehydrate butanol into butenes with an autothermal staged reactor compared to conventional methods for applications in small-scale biomass utilization. The largest advantage of this reactor is the integration of highly exothermic autothermal stage and endothermic alcohol dehydration stage which provides an alternative processing technique to maintain the bed temperature.

1. Introduction

Significant research has focused on the development of processes to convert biomass to fuels and chemicals with the goal of decreasing dependence on fossil fuels. The production of butanol from biomass has recently attracted both industrial and academic interest [1,2]. Various processes for producing butanol isomers from biomass are described in the literature. 1-Butanol can be produced by traditional ABE fermentation process with a production ratio of 3:6:1 of acetone:butanol:ethanol. Recently, Liao and coworkers [3] demonstrated that iso-butanol can be produced by yeast or micro-organism from sugar, such as glucose or cellulose. A biosynthetic pathway reported by Atsumi et al. [4] achieved a high yield, high-selectivity production of iso-butanol from glucose.

Butenes are currently priced lower than butanol and thermal conversion results in inevitable process inefficiencies. However, deoxygenation of butanol is investigated as a means of increasing energy density for potential use as a transportation fuel or chemical precursor in addition to a fuel additive. In addition, dehydration of butnaol into butenes has a potential application on improving market acceptance of alcohols. In spite of a lot of efforts, alcohols have rarely gained acceptance beyond their inclusion as blending components in the fuel. The conversion of butanol into butenes overcomes this obstacle and results in the production of material that is valuable as fuel intermediate and as petrochemical intermediate.

Previous studies have focused on the mechanisms of butanol dehydration over solid-acid catalysts [5–7], and skeletal isomerization of linear butene into branched butenes [8–11]. Butene can

---

* Corresponding author. Tel.: +1 612 625 9391; fax: +1 612 626 7246.
E-mail addresses: schmi001@umn.edu, schmi001@maroon.tc.umn.edu (L. Schmidt).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2012.07.039