



# Study of mesoporous catalysts for conversion of 2,3-butanediol to butenes



Quanxing Zheng<sup>a</sup>, Jason Grossardt<sup>a</sup>, Haider Almkhelfe<sup>a</sup>, Jiayi Xu<sup>a</sup>, Brian P. Grady<sup>b</sup>, Justin T. Douglas<sup>c</sup>, Placidus B. Amama<sup>a</sup>, Keith L. Hohn<sup>a,\*</sup>

<sup>a</sup> Department of Chemical Engineering, Kansas State University, Manhattan, KS 66506, USA

<sup>b</sup> Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, OK 73019, USA

<sup>c</sup> Nuclear Magnetic Resonance Laboratory, University of Kansas, Lawrence, KS 66045, USA

## ARTICLE INFO

### Article history:

Received 25 April 2017

Revised 9 August 2017

Accepted 17 August 2017

Available online 9 September 2017

### Keywords:

Cu/Al-MCM-48

Cu/Al-SBA-15

Mesoporous catalyst

Hierarchical zeolite

2,3-Butanediol

Butene

Cracking

Oligomerization

## ABSTRACT

In this study, three different types of mesoporous materials (Al-MCM-48, Al-SBA-15 and hierarchical ZSM-5 (meso-ZSM-5) where mesoporosity was introduced into ZSM-5 by sodium hydroxide treatment) were loaded with ~20 wt% CuO and investigated in the conversion of 2,3-butanediol to butenes. The results showed that the introduction of mesopores on the catalysts (Al-MCM-48 and Al-SBA-15 types) could decrease the production of cracking products, especially C<sub>3</sub> and C<sub>5</sub>–C<sub>7</sub> by comparison to the catalyst with ~20 wt% CuO loaded on HZSM-5; meanwhile, the selectivity of C<sub>8</sub> from oligomerization of butenes was found to increase with increasing pore size of the catalysts. In addition, Cu/meso-ZSM-5 catalyst has a performance with similarities to both Cu/ZSM-5 catalyst and mesoporous copper catalysts (Cu/Al-MCM-48 and Cu/Al-SBA-15) since both micropores (diameter of ~0.55 nm) and mesopores (pore size of ~23 nm) exist on meso-ZSM-5. Therefore, Cu/meso-ZSM-5 showed high activity for both cracking reactions (C<sub>3</sub> and C<sub>5</sub>–C<sub>7</sub>) and oligomerization (C<sub>8</sub>).

© 2017 Published by Elsevier Inc.

## 1. Introduction

Over the past few decades, renewable bio-based chemicals have attracted considerable attention due to the threat of petroleum depletion [1,2]. 2,3-Butanediol (2,3-BDO) has significant potential as a platform chemical for production of renewable fuels and chemicals since it can be produced with high productivity via fermentation [3–7] and provides a C<sub>4</sub> building block for further synthesis. Some researchers have investigated dehydration of 2,3-butanediol to 1,3-butadiene and methyl ethyl ketone (MEK) over thoria [8], scandium oxide [9], alumina [10], phosphate catalysts (BP, AlP, TiP, ZrP and NbP) [11] and HZSM-5 [12]. The obtained product 1,3-butadiene can then be dimerized to produce the aromatic intermediate styrene (Diels-Alder reaction) [13], while MEK is widely used as liquid fuel additive or organic solvent as well as a precursor for MEK peroxide [14–16]. More recently, Bell and coworkers developed novel pathways to convert biomass-derived methyl ketones (including MEK) to produce C<sub>12</sub>–C<sub>45</sub> hydrocarbons, which can serve as potential jet fuels (C<sub>12</sub>–C<sub>21</sub>) and synthetic lubricants (C<sub>33+</sub>), by self- and cross-condensation reactions over basic

Mg–Al–O or acidic Nb<sub>2</sub>O<sub>5</sub> catalysts [17,18]. Harvey et al. developed a pathway to selectively convert 2,3-butanediol with the acid catalyst Amberlyst-15 to a complex mixture of 2-ethyl-2,4,5-trimethyl-1,3-dioxolanes and 4,5-dimethyl-2-isopropyl dioxolanes, which can be used as a gasoline-range fuel and diesel oxygenate due to an anti-knock index of 90.5, high combustion value, low solubility in water and full miscibility with both gasoline and diesel fuel [19]. Our previous work has shown that bifunctional catalyst Cu/ZSM-5 can convert 2,3-butanediol to butenes with high selectivity (~70%) [20]. This offers a potential route to renewable fuels, since butene can be oligomerized to fuel-range hydrocarbons [21].

Conversion of 2,3-butanediol to butene involves a complicated reaction scheme, but the primary reaction pathway involves dehydration of 2,3-BDO to MEK and 2-methylpropanal, hydrogenation of these MEK and 2-methylpropanal to butanol, and dehydration of butanol to butene (a mixture of isomers). In addition to these pathways, butene can be oligomerized to form C<sub>8</sub> hydrocarbons, which can be further cracked to form a mixture of olefins. Our previous research showed that the acidity of support plays an important role in determining which products are formed. Cu/ZSM-5 catalysts with a variety of silica/alumina ratios were used to convert 2,3-butanediol to butene. The best results were noted for the highest silica/alumina ratio, which corresponds to the weakest

\* Corresponding author.

E-mail address: [hohn@ksu.edu](mailto:hohn@ksu.edu) (K.L. Hohn).

acidity. Lower silica/alumina ratios deactivated quickly by coking, producing low selectivities to butene after a few hours of reaction [20].

While the importance of support acidity has been investigated, the role of the pore structure of the support has not. Pore structure may play an important role in 2,3-BDO chemistry, favoring certain pathways while preventing others. A number of recent papers have indicated that the presence of mesopores can substantially enhance oligomerization reactions. For instance, Bertrand-Drira and coworkers investigated the catalytic oligomerization of pentene over mesoporous mordenites where mesoporosity was introduced by NaOH treatment, and they found that the introduction of mesopores resulted in high stability and high selectivity of the products C<sub>15</sub>–C<sub>30</sub> oligomers from pentene [22]. Grigor'eva and his coworkers reported that the introduction of mesopores on the regular zeolite Y could enhance the oligomerization of 1-octene with a selectivity of 65% of octene oligomers and 100% conversion of the monomer [23]. Deng et al. reported that the introduction of mesopores on the regular ZSM-5 treated by NaOH could enhance the oligomerization of endo-dicyclopentadiene to get dimer (exotricyclopentadiene) with a selectivity of 79.3% [24]. Corma et al. studied the oligomerization of light olefins (propene and 1-pentene) to high-quality liquid fuels over alkali-treated ZSM-5 (hierarchical ZSM-5), and they figured out that the Brønsted acid site density was determinant for propene oligomerization, while the presence of the mesoporosity was crucial for oligomerization of 1-pentene since the initial conversion and catalyst life can be improved greatly [25]. In addition, Mlinar et al. investigated the gas-phase oligomerization of propene over mesoporous aluminosilicate Ni-Na-MCM-41, Ni-Na-MCM-48 and Ni-Na-SBA-15, and they found out that the propene oligomerization turnover frequency was increased with increasing size of the pores in the support and independent of the pore connectivity [26]. It is well known that MCM-41 is a mesostructured material with one-dimensional hexagonal *p6mm* symmetry, having uniform mesopore size in the range of 2–10 nm [27,28], and MCM-48 is mesoporous aluminosilicate with three-dimensional interconnected cubic network (space group *la3d*), the average pore size of which is similar to MCM-41 [29–32], SBA-15 has highly ordered hexagonal arrays of mesopores with one-dimensional channels, indicating a two-dimensional hexagonal (*p6mm*) mesostructure with uniform pore size of 5–30 nm [33–35]. Hence, Mlinar et al. figured out that Ni-Na-SBA-15 exhibited higher catalyst activity than Ni-Na-MCM-41 (~2.5 nm) and Ni-Na-MCM-48 (2.05 nm) since it had larger pore size of 5.74 nm, indicating that there was a strong relationship between the catalytic activity and the pore size of the support [26]. Additionally, Andrei studied the oligomerization of ethylene over Ni-exchanged Al-SBA-15 mesoporous catalysts with diameter of 7.9 nm, and they demonstrated that the catalysts showed high activity on conversion of ethylene into C<sub>4</sub>–C<sub>10</sub> olefins due to the network of interconnected mesopores [36]. For this reason, our study focuses on the impacts that the presence of mesopores can have on 2,3-BDO conversion on bifunctional copper catalysts.

In this study, three different types of mesoporous materials (Al-MCM-48, Al-SBA-15 and hierarchical ZSM-5) were loaded with ~20 wt% CuO and tested in the conversion of 2,3-butanediol to butenes. It is found that the presence of mesopores can substantially impact product selectivities and improve catalyst lifetime.

## 2. Experimental

### 2.1. Synthesis

All Al-MCM-48 materials were prepared by a room temperature synthesis as reported in the literature [31,32]. Tetraethoxysilane

(TEOS, 99.9%, Fisher Scientific) and aluminum isopropoxide (>98.0%, Fisher Scientific) were used as Si and Al sources, respectively, and hexadecyltrimethylammonium bromide (CTAB, >99%, Fisher Scientific) was used as the template. Typically, a 2.4 g aliquot of CTAB (6.6 mmol) and different amount of aluminum isopropoxide (in order to obtain SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios of 23, 50, 100 and 200) were dissolved in 100 g of deionized water and 50 mL of ethanol (100%, 200 proof, USP, 0.87 mol), and 12 mL of aqueous ammonia (30 wt%, certified ACS Plus, 0.20 mol) was added to the surfactant solution. The solution was then stirred (450 rpm) until the Al precursor and the template were dissolved and then 3.4 g of TEOS (16 mmol) was added at one time. After stirring for 5 h at room temperature, the obtained solid was recovered by filtration, washed with deionized water, and dried in air at ambient temperature. The template was removed by calcination at 550 °C in air for 6 h with a heating rate of 1 °C/min. The obtained aluminosilicate materials are designated as Al-MCM-48(n), where n stands for SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio. The reference sample MCM-48 was prepared by the same method without adding aluminum isopropoxide. [Al]-MCM-48 represents the mesoporous materials including the purely siliceous MCM-48 and Al-MCM-48.

Al-SBA-15 materials were synthesized by using the pH-adjusting method [33]. TEOS and aluminum isopropoxide were used as Si and Al sources, respectively, and nonionic triblock copolymer surfactant Pluronic P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, where EO = ethylene oxide, PO = propylene oxide; molecular weight of 5800; BASF Corp.) was utilized as a template. Typically, 4 g of P123 was dissolved in 125 mL of HCl solution (2 M). Next, 8.5 g of TEOS and the required amount of aluminum isopropoxide (based on the desired SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 23, 50, 100 or 200) were added, and the resulting mixture was continuously stirred at 40 °C for 24 h and subsequently hydrothermally treated without stirring at 100 °C for an additional 48 h and then cooled down to room temperature. The pH was adjusted up to 7.5 by adding aqueous ammonia (30 wt%, certified ACS Plus) dropwise at room temperature and the obtained mixture was finally aged again at 100 °C for another 48 h. The solid was recovered by filtration, washed with deionized water, and dried in air at ambient temperature. The template was removed by calcination at 550 °C in air for 6 h with a heating rate of 1 °C/min. The final aluminosilicate materials are denoted as Al-SBA-15(n), where n stands for the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio in the initial gel. The control sample SBA-15 was prepared by the same method without adding aluminum isopropoxide. It should be noted that [Al]-SBA-15 represents the mesoporous materials including SBA-15 and Al-SBA-15.

The hierarchical ZSM-5 was prepared by a simple alkaline treatment method reported in the literature [37–42]. 6.6 g of parent ZSM-5 zeolite was vigorously stirred in 200 mL of NaOH solution (0.2 M) at a temperature of 70 °C for 30 min. The slurry was then quenched immediately, using an ice-water bath. The resultant solid was recovered by filtration, fully washed with deionized water until a neutral pH and finally dried at 100 °C overnight. After this step, the H-form zeolite was obtained by three consecutive ion-exchanges of the alkaline-treated sample with 1 M NH<sub>4</sub>NO<sub>3</sub> solution (10 mL/g) at 80 °C for 3 h, followed by calcination in air at 550 °C for 5 h. The obtained sample was named as meso-ZSM-5(n), where n stands for the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the parent zeolite.

The copper catalysts were prepared by an ammonia evaporation hydrothermal (AEH) method as reported [43–45]. The details of the synthesis were shown in the [Supplementary material](#). The content of CuO was determined by the inductively coupled plasma (ICP) method. The copper catalysts were named: Cu/Al-MCM-48(n), Cu/Al-SBA-15(n) and Cu/meso-ZSM-5(n), where n is the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio.

Download English Version:

<https://daneshyari.com/en/article/6455511>

Download Persian Version:

<https://daneshyari.com/article/6455511>

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