

available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/chnjc

Article

Influence of supports for selective production of 2,5-dimethylfuran via bimetallic copper-cobalt catalyzed 5-hydroxymethylfurfural hydrogenolysis

Sanjay Srivastava, G. C. Jadeja, Jigisha Parikh *

Department of Chemical Engineering, Sardar Vallabhbhai National Institute of Technology, Surat-395007, Gujarat, India



ARTICLE INFO

Article history:

Received 16 December 2016

Accepted 10 January 2017

Published 5 April 2017

Keywords:

5-Hydroxymethylfurfural

Hydrogenation

Hydrogenolysis

Copper-cobalt

Bimetallic

Biofuels

ABSTRACT

The hydrogenolysis of carbon–oxygen bonds is an important model reaction in upgrading biomass-derived furanic compounds to transportation fuels. One of these model reactions, namely conversion of 5-hydroxymethylfurfural (HMF) to the gasoline additive 2,5-dimethylfuran (DMF), is especially attractive. In this study, bimetallic Cu-Co catalysts supported on CeO₂, ZrO₂, and Al₂O₃ were used for the selective hydrogenolysis of HMF to DMF. The structures of the fresh and used catalysts were studied using X-ray diffraction, the Brunauer-Emmett-Teller method, transmission electron microscopy, temperature-programmed reduction by H₂, temperature-programmed desorption of NH₃, and CHNS analysis. The structures were correlated with the catalytic activities. The Cu-Co/CeO₂ catalyst produced mainly 2,5-bis(hydroxymethyl)furan via reduction of C=O bonds on large Cu particles. The Cu-Co/Al₂O₃ catalyst gave the best selectivity for DMF, as a result of a combination of highly dispersed Cu, mixed copper–cobalt oxides, and suitable weak acidic sites. Cu-Co/ZrO₂ had low selectivity for DMF and produced a combination of various over-hydrogenolysis products, including 2,5-dimethyltetrahydrofuran and 5,5-oxybis(methylene)-bis(2-methylfuran), because of the presence of strong acidic sites. The reaction pathways and effects of various operating parameters, namely temperature, H₂ pressure, and time, were studied to enable optimization of the selective conversion of HMF to DMF over the Cu-Co/Al₂O₃ catalyst.

© 2017, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Energy crises, depletion of fossil fuel reserves, and global warming have increased interest in the production of biobased materials [1]. In confronting these challenges, biorefined materials have emerged as an alternative to industrial carbon. In biorefining, lignocellulosic biomass is transformed into value-added chemicals and fuels [2]. The hydrogenation/hydrogenolysis of furans such as furfural (FAL) and 5-hydroxymethylfurfural (HMF) has been widely studied for the production of biobased fuels such as 2-methylfuran (2-MF),

2-methyltetrahydrofuran, pentane, and 2,5-dimethylfuran (DMF) [3–6]. HMF is a valuable chemical because it can be converted to a variety of chemicals such as 2,5-bis(hydroxymethyl)furan (BHMF), 2-hydroxymethyl-5-methylfuran (5-MFOL), DMF, and 2,5-dimethyltetrahydrofuran (DMTHF) (Scheme 1) [7–9]. DMF is an important compound because it has potential use in gasoline blends and can be converted to *p*-xylene through a Diels-Alder reaction with ethylene [10–12].

Precious metals, i.e. Pt, Pd, Rh, Ru, and Au, are the main metals with potential uses in the hydrogenation of HMF to

* Corresponding author. Tel: +91-261-2251689; E-mail: jk_parikh@yahoo.co.inDOI: 10.1016/S1872-2067(17)62789-X | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 38, No. 4, April 2017

DMF; Pd and Ru have been reported to give the best selectivities for DMF [9,13–17]. The first reported catalyst for hydrogenation of HMF to DMF was CuRu/C, which gave 71% yields of DMF from two different starting materials [9,18]. It was reported that the activity of this catalyst gradually decreased because of deactivation of active centres and/or the presence of chloride ions [9]. Thananathanachon and Rauchfuss reported the conversion of HMF to DMF using Pd/C as a catalyst and formic acid as an additive [8]. An excellent yield, i.e. 93%, with 99% HMF conversion was achieved, but only when formic acid and H₂SO₄ were used. However, because of their highly corrosive nature and environmental concerns, the use of both formic acid and H₂SO₄ is restricted. Luijckx et al. [19] used a combination of Pd/C and HCl to reduce HMF to DMF; The results were similar to those reported by Rauchfuss et al. [8]. Zu et al. [15] used Ru/Co₃O₄ as a catalyst for the selective conversion of HMF to DMF at 130 °C and 0.7 MPa; they clearly identified the roles of Ru and CoO_x, which are responsible for reduction and hydrogenolysis of carbonyl and hydroxyl groups, respectively.

Because of the high cost of noble metals, research on precious-metal-free catalysts which can effectively convert HMF to DMF is needed. Yang et al. [20] obtained a 76% yield of DMF over Ni/Co₃O₄ catalysts; the roles of Ni and CoO_x were similar to those reported for Ru and CoO_x by Zu et al. [15]. Cu/ZnO, Cu–Zn alloy, Cu/MgO/Al₂O₃, Ru-modified Cu/MgO/Al₂O₃, and Cu–PMO catalysts have been examined in the hydrogenation of HMF to DHMF and DMF [21–23]. However, the development of low-cost and environmentally benign robust catalytic systems for this reaction is still in progress.

Recently, supported bimetallic Cu–Co nanoclusters have emerged as versatile catalytic systems for hydrogenation/hydrogenolysis reactions because of the presence of Cu(0), CoO_x species, and mixed oxide phases [24–34]. It has been reported that early-transition-metal oxides such as CoO_x, ReO_x, and MoO_x can effectively split C–O and O–H bonds [15,19,35,36]. A combination of Cu metal and CoO_x could

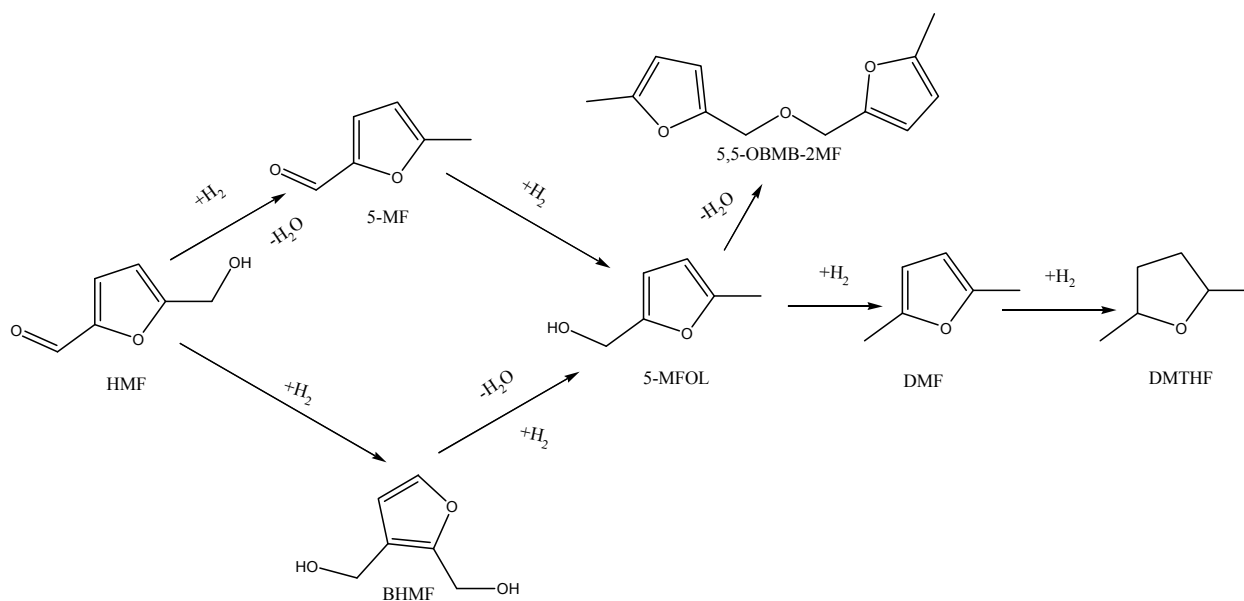
therefore be effective in the production of DMF by hydrogenation/hydrogenolysis of HMF. In our previous work, we hydrogenated FAL to 2-MF over bimetallic Cu–Co catalysts supported on SiO₂, H-ZSM-5, and Al₂O₃ [29]. Cu–Co/Al₂O₃ was the best hydrogenolysis catalyst because of the presence of small Cu particles and Cu–Co_x mixed phases, and synergies among Cu, Co, and Al₂O₃.

The present work was undertaken based on the background described above. In this study, instead of using SiO₂ and H-ZSM-5 as supports, materials which stabilize metal dispersion and improve oxygen storage (e.g. CeO₂ and ZrO₂) were examined and compared with Al₂O₃ as supports for Cu–Co bimetallic catalysts. The structures of these synthesized catalysts were studied using X-ray diffraction (XRD), the Brunauer–Emmett–Teller (BET) method, transmission electron microscopy (TEM), temperature-programmed desorption of NH₃ (NH₃-TPD), temperature-programmed reduction by H₂ (H₂-TPR), and CHNS analysis. The activities and selectivities of these catalysts in the hydrogenolysis of HMF to DMF were investigated. Cu–Co/Al₂O₃ catalysts were best for the hydrogenolysis of biomass-derived HMF to DMF; DMF was selectively obtained in 78% yield under mild conditions. The HMF conversion and DMF selectivity were optimized based on the reaction pathways and effects of the reaction parameters, namely temperature, H₂ pressure, and time.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF), HMF, and all the products shown in Scheme 1 (all GC grade) were purchased from Sigma-Aldrich, Mumbai, India. The supports, i.e. CeO₂, ZrO₂, and Al₂O₃ (purity 99%), were purchased from Sterling Chemical Pvt., Ltd., Surat, India. Bimetallic Cu–Co catalysts with Cu:Co molar ratios of 1, 2, and 4 were synthesized on CeO₂, ZrO₂, and Al₂O₃ at fixed Cu



Scheme 1. Reaction pathway in DMF synthesis from HMF.

Download English Version:

<https://daneshyari.com/en/article/6505948>

Download Persian Version:

<https://daneshyari.com/article/6505948>

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