Journal of Catalysis 320 (2014) 198–207

Contents lists available at ScienceDirect

Journal of Catalysis

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

Investigation of the reaction kinetics of isolated Lewis acid sites in Beta zeolites for the Meerwein–Ponndorf–Verley reduction of methyl levulinate to γ-valerolactone

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ARTICLE INFO

Article history:
Received 29 August 2014
Accepted 19 October 2014
Available online 11 November 2014

Keywords:
Liquid-phase transfer hydrogenation
γ-Valerolactone
Lewis acids
Zeolites
Reaction kinetics

ABSTRACT

We investigate the reaction kinetics of the Meerwein–Ponndorf–Verley (MPV) reduction of methyl levulinate (ML) to 4-hydroxypentanoates and subsequent lactonization to γ-valerolactone (GVL) catalyzed by Lewis acid zeolites. Reaction kinetics studies show a first-order dependence on ML and 2-butanol, confirm that the hydride shift is the rate-limiting step, and support a dual-binding mechanism on a single Lewis acid site. All catalysts generate GVL with selectivities >97%, with Hf-Beta exhibiting the highest activity in the temperature range of 393–453 K. Sn-, Zr-, and Hf-Beta show apparent activation energies of ca. 52 kJ mol^{-1}, which is significantly lower than that of Ti-Beta (69 kJ mol^{-1}). Secondary alcohols consistently exhibit higher reaction rates than primary alcohols with lower apparent activation energies. Increasing polarity of the hydrogen donor leads to a decrease in reaction rates. The experimental data are used to build a kinetic model for the MPV reaction in a tubular packed-bed reactor.

1. Introduction

Biomass conversion to sustainable chemicals and fuels requires the development of efficient catalytic processes capable of converting highly complex and oxygenated precursors to platform molecules. Ideally, selective deoxygenation and hydrogenation must occur under mild conditions while simultaneously minimizing unit operations. Transfer hydrogenations are versatile reactions that avoid the use of high pressures of molecular hydrogen by using molecules capable of donating hydrogen atoms in the liquid phase [1–5]. In particular, the Meerwein–Ponndorf–Verley (MPV) reaction, wherein an alcohol donates a hydride to an aldehyde or ketone, has shown promising results in several biomass-relevant reaction schemes. Examples include the conversion of the following: crotonaldehyde to crotyl alcohol [6]; 5-(hydroxymethyl) furfural to 2,5-bis(ethoxymethyl)furan [7]; levulinates to γ-valerolactone [8,9]; and intramolecular hydride transfers in hexoses, pentoses, and other sugars [10–19].

Traditionally, homogenous Lewis acids catalyze the MPV reaction as shown for aluminum alkoxides [20,21] in an isopropanol/ketone system, for lanthanide complexes in the reduction of aryl ketones [22], and more recently for actinide isopropoxides [23]. The reaction mechanism involves a cyclic six-membered transition state where the carbonyl and the alcohol are both coordinated to the same metal center. The reaction proceeds through a direct hydride shift where the hydrogen on the C-1 position of the alcohol is directly transferred to the carbonyl carbon of the ketone/aldehyde. To overcome the problems associated with using homogenous catalysts, such as expensive separations and moisture sensitivity, many heterogeneous catalysts have been studied for the MPV reaction. These include metal oxides [24,25], hydrotalcites [26,27], and zeolites [28–32]. In particular, zeolites containing Lewis acid centers have shown very high activity and selectivity under mild reaction conditions [33–36]. Lewis acidic metal centers tetravalently incorporated into a silicate framework can coordinate with and polarize carbonyl functional groups [37,38]. It is proposed that these metal centers coordinate the ketone and alcohol to form the same six-membered transition state as that formed with homogenous MPV catalysts. Various Lewis acid zeolites are capable of catalyzing the MPV reaction including Al-, Ti-, Sn-, and Zr-containing zeolites.

Recently, we reported on the one-pot conversion of xylose-derived furfural into γ-valerolactone (GVL) using the combined action of zeolites featuring Lewis and Brønsted acid sites [8]. GVL is a versatile platform molecule that has the functionality and reactivity to be upgraded to fuel additives, fuels, and commodity chemicals [39–43]. GVL is stable, non-toxic and has shown promise as an effective solvent for sugar production by breaking down

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http://dx.doi.org/10.1016/j.jcat.2014.10.010
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lignocellulosic biomass [44]. In our domino-like reaction sequence, furfural was reduced to furfuryl alcohol (FA) via an MPV reaction with 2-butanol catalyzed by a Lewis acid; next, FA was converted to levulinic acid (LA) through a hydrolytic ring opening catalyzed by a Brønsted acid; finally, LA was reduced via a second MPV step to 4-hydroxypentanoate (4HP), which underwent a spontaneous lactonization to form GVL and water. GVL selectivity values always exceeded 94%, but it was observed that Ti-, Sn-, and Zr-Beta catalysts featured drastically different turnover rates for the second MPV step, with Zr-Beta having the highest activity. Assary et al. showed with computational techniques that stronger Lewis acids better stabilize the six-membered transition state for the rate-limiting hydride shift step [45]. Indeed, changing the identity of the framework heteroatom can alter the Lewis acid character of the zeolite; however, Lewis acidity is also highly dependent on the nature of the solvent and reacting molecules. A difficult challenge exists in correctly predicting which catalyst will be optimal for a specific substrate/solvent combination. For example, Boronat et al. showed that while Sn-Beta is more active for the reduction of cyclohexanone in 2-butanol, Zr-Beta is more active for the reduction of benzaldehyde in 2-butanol under identical reaction conditions [46]. The nature of the hydrogen donor also had a dramatic impact on the reaction rates. As such, establishing a robust kinetic framework that describes the governing parameters of the ML to GVL transformation over a wide range of conditions is of great relevance to understand, and ultimately predict, the performance of Lewis acid zeolites in transfer hydrogenation reactions.

In this work, we present an experimental study aimed at extracting relevant kinetic parameters that describe the catalytic performance of Lewis acid catalysts during the reduction of ML to form GVL. We propose a set of elementary steps, derive a rate expression for the overall reaction, and perform reactivity measurements to confirm reaction orders and identify the rate-limiting step in the mechanism. We quantitatively compare the kinetic parameters of Ti-, Sn-, Zr-, and Hf-Beta catalysts over a wide range of temperatures and find that Hf-Beta has the highest activity of all catalysts. We also study the effect of varying the hydrogen donor by determining the kinetic parameters when using primary and secondary alcohols with varying carbon chain lengths.

2. Experimental methods

2.1. Catalyst synthesis

Lewis acid zeolites with the Beta topology were synthesized in fluoride media following the procedure outlined by Corma et al. [47], using different heteroatom metal precursors. For example, Hf-Beta was prepared as follows: 27.16 g of tetraethylammonium hydroxide (Sigma–Aldrich, 35% (w/w) in water) and 23.97 g of tetraethylorthosilicate (Sigma–Aldrich, $\geqslant$99% (w/w)) were added to an open Teflon jar. The mixture was magnetically stirred at room temperature for 90 min. An additional 15 ml of deionized water was added and the mixture was cooled in an ice bath. Then, 0.37 g of hafnium(IV) chloride (Sigma–Aldrich, 98% (w/w)) was dissolved in 2 ml of ethanol, and this solution was added dropwise to the mixture while stirring on ice. The solution was left uncovered while stirring to complete the hydrolysis of TEOS, evaporate the ethanol, and reach approximately 2 g of water above the target water content. Then, 2.62 g of hydrofluoric acid (Sigma–Aldrich, 48% (w/w) in water) was added dropwise and the mixture was homogenized using a PTFE spatula, resulting in a thick paste. Next, 0.36 g of previously-made Hf-Beta was sonicated in 2 ml deionized water and added into the mixture as seeds. The mixture was homogenized and allowed to evaporate to a final weight of 33.96 g. The final molar composition of the gel was 1 SiO_2/0.01 $HfCl_4$/0.56 TEAOH/0.56 HF/7.5 H_2O. The thick paste was transferred to a Teflon-lined stainless steel autoclave and heated to 413 K in a static oven for 20–40 days. The solids were recovered by filtration, washed extensively with water and ethanol, and dried at 373 K overnight. The solids were calcined at 923 K for 10 h with a 1 K/min ramp and 1 h stops at 423 K and 623 K at a flow rate of 300 ml min^{-1} of dry air (Airgas, ultra zero grade) to remove the organic content in pores of the crystalline material. After calcination, the solid yield was 80–90%. The other metal precursors used were as follows: tin(II) chloride dihydrate (Sigma–Aldrich, 99.99% (w/w)), zirconium(IV) oxychloride octahydrate (Sigma–Aldrich, 99.5% (w/w)), and titanium(IV) isopropoxide (Sigma Aldrich, 99.999% (w/w)). All the catalysts were synthesized to achieve a silicon/metal ratio of ca. 100.

2.2. Catalyst characterization

The crystal structures of Beta zeolite catalysts were determined from powder X-ray diffraction (PXRD) patterns collected using a Bruker D8 diffractometer using Cu Kα radiation (40 kV, 40 mA). Nitrogen adsorption and desorption isotherms were measured on a Quantachrome Autosorb iQ apparatus at liquid nitrogen temperature (77 K). Prior to the adsorption analysis, all samples were pelleted and degassed under vacuum for 12 h at 623 K. Micropore N_2 uptake was recorded at $P/P_0 = 0.01$, and total pore volume was recorded at $P/P_0 = 0.95$. Ultraviolet–visible (UV–vis) spectra were recorded using a Cary 5000 (Varian) instrument equipped with a Praying Mantis diffuse-reflectance accessory (Harrick Scientific Products) on calcined samples using a barium sulfate blank. Reflectance measurements were converted to absorbance using the Kubelka–Munk function. Elemental analysis was performed with a CCD-based inductively coupled plasma (ICP) atomic emission spectrometer (Activa-S, HORIBA Scientific). Samples were dissolved in 48% HF and diluted into 3% HNO_3 before analysis. A 5-point calibration curve was built using the following ICP standards: 1000 ppm Zr in 3% HNO_3/trace HF, 1000 ppm Sn in 10% HCl, 1000 ppm Ti in 2% HNO_3/trace HF, 1000 ppm Hf in 5% HNO_3/trace HF (all TraceCERT$^{®}$) on the following spectral lines: 327.305 nm Zr line, 189.989 nm Sn line, 339.978 nm Hf line, 336.121 nm Ti line.

Fourier transform infrared (FT-IR) spectra were collected with a Bruker Vertex 70 spectrophotometer equipped with an Hg–Cd–Te (MCT) detector. Each spectrum was recorded by averaging 128 scans at 2 cm^{-1} resolution in the 4000–400 cm^{-1} range. Zeolite-beta catalysts were pressed into self-supporting wafers (8–10 mg cm^{-2}) that were sealed within a high temperature cell (Harrick Scientific) with ZnSe windows. Zeolite wafers were calcined in flowing air (Airgas, zero grade, 25 ml min^{-1}) at 773 K for 8 h, evacuated at 573 K for 3 h (<0.01 Pa, dynamic vacuum, Edwards' T-Station 75 Turbopump), and cooled to 298 K in vacuum. A reference spectrum was acquired before dosing with excess CD_3CN (Sigma Aldrich, 99.8% (atom D)) vapor under static vacuum. Once dynamic vacuum was re-established, the difference spectrum was acquired.

2.3. Kinetic studies of MPV reduction of levulinates

Flow reactions were conducted in a 0.46 cm I.D. tubular stainless steel reactor mounted inside a 30 cm long aluminum block within an insulated single-zone furnace (Applied Test Systems Series 3210, 850W/115 V). The catalyst was pelleted and sieved to obtain 75–150 μm particles. The catalyst particles were then diluted into 5 times their weight in inert α-aluminum oxide (Sigma Aldrich, >99% (w/w)) with the same particle size range, creating a bed approximately 2.5 cm long. The bed was loaded between glass wool plugs and supported by additional α-aluminum oxide. The reaction temperature was monitored by a K-type thermocouple (Omega, inconel) placed inside the bed and a PID temperature controller