



# Mechanism and kinetics of 1-dodecanol etherification over tungstated zirconia



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## ABSTRACT

Growing interest in finding renewable alternatives to conventional fossil fuels and petroleum-derived specialty chemicals has motivated the investigation of biomass-derived alcohols to make ethers as diesel additives or lubricants. To optimize the direct etherification of long chain alcohols in the liquid phase, it is necessary to develop an understanding of the kinetics and mechanism of etherification and dehydration reactions. In this study, tungstated zirconia was identified as a selective solid-acid catalyst for the liquid-phase etherification of 1-dodecanol. Investigations of the mechanism and kinetics of this reaction suggest that cooperation between Brønsted- and Lewis-acid sites on tungstated zirconia enhances the selectivity to ether by increasing the surface concentration of adsorbed alcohol, thereby promoting bi-molecular ether formation relative to unimolecular alcohol dehydration. The suggested rate limiting step for etherification is the formation of a C–O bond between two adsorbed alcohol molecules, and the suggested rate-limiting step for dehydration is the cleavage of the C–H bond of the  $\beta$ -carbon atom in an adsorbed alcohol. Measurements of the kinetic isotope effects for etherification and dehydration support the proposed mechanism. A microkinetic model based on the proposed mechanism for dodecanol etherification and dehydration over tungstated zirconia accurately describes the observed effects of alcohol concentration and product inhibition.

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## 1. Introduction

Continued use of fossil energy resources to produce fuels contributes to an increase in atmospheric CO<sub>2</sub> and in turn to changes in the global climate [1]. This concern has motivated the exploration of biomass as a possible source of renewable carbon for the production of fuels and lubricants [2]. A central question is how to convert biomass into synthons that could be used to produce fuels and lubricants. One of the appealing approaches is to ferment the sugars derived by hydrolysis of cellulose and hemicellulose into alcohols such as ethanol and butanol. The condensation of furfural with acetone under hydrogen can also produce 1-octanol [3]. Other longer-chain alcohols such as 1-dodecanol can be produced by hydrolysis of triglycerides and fatty acids. These linear alcohols can also be converted to higher carbon-number alcohols with branched carbon chains via the Guerbet reaction, and the corresponding Guerbet alcohols can be converted to ethers [4].

Ethers are attractive products because they can be used as diesel additives and automotive lubricant base oils. Diesel-range linear ethers produced from biomass are of interest because they have high cetane numbers as well as high energy density [5–8]. Shorter chain branched ethers have high octane numbers and can be added to gasoline [9]. Ethers are also of interest as lubricants. For example, alkylated di-phenyl ether and glyceryl ethers have excellent properties [10,11], and branching in the alkyl portions of ethers lowers the pour points and raises the viscosity of the ether [12,13]. Therefore, ether-based lubricants sourced from biomass provide a stable, tunable, and renewable alternative to poly-alpha-olefins produced from petroleum [14,15].

Ethers can be prepared either by direct, acid-catalyzed etherification of alcohols, or by reductive etherification of an alcohol and an aldehyde or ketone. Direct etherification of alcohols is advantageous because it does not require the use of hydrogen and precious metal catalysts for reduction [16]. The competing reaction in the presence of an acid catalyst is alcohol dehydration to produce the corresponding alkene, a process that is favored thermodynamically at temperatures above approximately 350 K. Since higher temperatures are desirable for increasing reaction rates, this raises

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the question of how one can favor etherification over alkene formation.

Selective etherification has been reported for the liquid-phase reactions of 1-octanol, 1-hexanol, and 1-pentanol over acid catalysts such as Amberlyst 70 [17,18], Nafion NR-50 [18,19], and H-BEA zeolite [20]. While polymeric resins are selective to ether, they are not as thermally stable as metal oxides [18,21]. Zeolites, on the other hand, are thermally stable, but catalyze unwanted side products and deactivate due to coking [22].

In this study, we screened a series of solid-acid catalysts for the direct etherification of 1-dodecanol and identified tungstated zirconia as a highly active and selective catalyst. Tungstated zirconia has been employed previously for acid-catalyzed reactions including gas-phase isomerization of n-butane [23], gas-phase dehydration of alcohols to alkenes [24], and liquid-phase reactions, such as esterification, transesterification, and alkylation [24–26]. Investigations of the gas-phase kinetics for the dehydration of short-chain, linear alcohols over tungstated zirconia indicate that dehydration occurs via a unimolecular mechanism but that these alcohols are not converted to ethers [27,28]. By contrast, we found that the etherification of dodecanol in the liquid phase is highly selective over tungstated zirconia. Motivated by this finding, we undertook an investigation of the mechanism and kinetics of the etherification and dehydration of 1-dodecanol over tungstated zirconia with the objective of developing an explanation for the high selectivity of this catalyst for etherification in the liquid phase.

## 2. Materials and methods

### 2.1. Materials

All chemicals obtained commercially were used without further purification. The following compounds were obtained from Sigma-Aldrich: 1-hexanol (>98%), 1-dodecanol (>98%), decane (>95%), dodecane (>99%), hexane (>99%), 1-hexene (>99%), and pyridine (99.8%). N-tetradecane was obtained from Spectrum Chemical (>99%), and was used as an internal standard for analytical purposes. Di-dodecyl ether (>95%) and 1-dodecene (>95%) were obtained from TCI. Di-n-hexyl ether (>98%), and 2,6-di-tert-butylpyridine (97%) were obtained from Alpha Aesar. Hexan-1,1-d<sub>2</sub>-1-ol (>99%) was obtained from CDN Isotopes Inc. Hexan-2,2-d<sub>2</sub>-1-ol was synthesized and purified to >98% according to Ref. [29]. Amberlyst 15 (hydrogen form, dry), and Amberlyst 36 were obtained from Sigma-Aldrich. Amberlyst 70 was obtained from Dow Chemical, and was dried at 368 K and stored in a desiccator before use. Zeolite BEA was obtained from Alpha Aesar, and was calcined at 873 K for 6 h before use. Gamma-alumina was obtained from Strem Chemicals. Mesostructured silica (MCM-41 hexagonal type), Nafion NR-50, and mesostructured aluminosilicate (MCM-41, hexagonal) were obtained from Sigma-Aldrich. Para-toluene sulfonic acid was obtained from Spectrum Chemical.

### 2.2. Synthesis of zirconia and tungstated zirconia

Porous amorphous zirconia, monoclinic zirconia, and tungstated zirconia were synthesized using previously reported methods [23,30,31]. Amorphous zirconium oxyhydroxide (ZrO<sub>x</sub>(OH)<sub>4-2x</sub>) was formed by adding ammonium hydroxide (Spectrum, 28–30%) dropwise to a stirred solution of 0.5 M zirconyl chloride octahydrate (Sigma Aldrich, 98%) at 298 K. The precipitate was filtered and rinsed with 10% ammonium hydroxide and dried at 383 K for 24 h. Tungstated zirconia (4.1, 7.7, 10.2, 12.6, 15.4, 22.3 wt% W) was prepared via incipient wetness impregnation of amorphous zirconium oxyhydroxide with aqueous ammonium metatungstate hydrate (Spectrum). After impregnation, all

catalysts were heated at 10 K/min and treated in air at 1073 K for 3 h, then cooled to room temperature. To prepare pure zirconia, amorphous zirconium oxyhydroxide was calcined at 1073 K under the same incipient wetness impregnation conditions but without the addition of ammonium metatungstate. Each catalyst was then crushed to <250 μm mesh using a mortar and pestle.

### 2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns for WO<sub>x</sub>/ZrO<sub>2</sub> (0–22 wt % W) were taken with a Bruker D8 GADDS diffractometer equipped with a Cu-Kα source (40 kV, 40 mA). Raman spectra were obtained with a LabRAM HR Horiba Scientific Raman spectrometer equipped with a 633 nm<sup>-1</sup> laser. BET surface area measurements were performed with a Micrometrics TriStar BET and pretreated with a Micrometrics FlowPrep 060. Brønsted- and Lewis-acid sites were identified and the ratio of these sites was determined from IR spectra of adsorbed pyridine. Spectra were acquired using a Thermo Scientific Nicolet 6700 Fourier Transform Infrared Spectrometer (FT-IR) equipped with a Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) cell. A mixture of catalyst (50 mg) diluted with KBr (250 mg) was added to the DRIFTS cell and pretreated at 573 K for 2 h under helium. Background scans of the catalyst were taken at 393 K, 423 K, 473 K, 523 K, and 573 K. Pyridine was introduced into the He flow at 393 K, and spectral data was taken after stabilization of adsorbed pyridine at 393 K. The temperature was then raised to measure the amount of pyridine that remained adsorbed at 423 K, 473 K, 523 K, and 573 K. Spectral intensities were calculated using the Kubelka-Munk function. The concentration of Brønsted-acid sites was determined by titration with NH<sub>4</sub>OH. The protons on the catalysts were first exchanged for Na<sup>+</sup> cations by placing the catalyst in a 1 M NaCl solution overnight, and then the solution was titrated with NH<sub>4</sub>OH until the pH was neutral, using phenolphthalein as an indicator. The moles of base added was used as a metric for the number of H<sup>+</sup> ions in solution [32]. ICP Elemental analysis was performed by Galbraith Laboratories, Inc. in order to determine tungsten weight loadings.

### 2.4. Isotopic labeling and NMR

Isotopic labeling of the alpha and beta hydrogen atoms in 1-hexanol was used to support the proposed mechanisms of etherification and dehydration. Hexan-2,2-d<sub>2</sub>-1-ol was prepared according to literature and the structure was confirmed using <sup>1</sup>H NMR [29]. Kinetic isotope effects (k<sub>H</sub>/k<sub>D</sub>) were determined by measuring the initial rates of alkene and ether formation for 1-hexanol, hexan-1,1-d<sub>2</sub>-1-ol, and hexan-2,2-d<sub>2</sub>-1-ol. NMR spectra of the reaction products were recorded with a Bruker AVQ-400 spectrometer.

### 2.5. Batch reactions

All reactions were carried out in sealed 12 mL Q-Tube batch reaction vessels with magnetic stirring at 600 RPM using an IKA C-MAG HS 10 digital hot plate with temperature control accurate to within ±1 K. For determination of the reaction kinetics, a separate batch reaction was carried out for each time point to ensure consistency of volume and concentration of each sample. All reactions over tungstated zirconia were carried out either in the absence of solvent or in decane with 100 mg of catalyst and 250 μL of dodecanol (unless otherwise noted). N-tetradecane (100 μL) was added post-reaction as a standard for analysis. The reactants and catalyst were added to the Q-Tube in the pre-heated hot plate with an aluminum heating block, and after the specified reaction time, the vials were removed from the hot plate and placed in an ice bath to stop the reaction. Products were diluted with 5 mL of acetone, and centrifuged at 4000 RPM for

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