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Short communication

Comprehensive investigation of the biomass derived furfuryl alcohol oligomer formation over tungsten oxide catalysts

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ABSTRACT

The feasibility of using tungsten oxide catalysts for furfuryl alcohol (FA) oligomerization reaction was investigated in the liquid phase at 100 °C and ambient pressure. Five dimers (2,2′-difurylmethane, 2-(2-furylmethyl)-5-methylfuran, difurfuryl ether, 4-furfuryl-2-pentenoic acid γ-lactone, 5-fufuryl-furfuryl alcohol) and two trimers (2,5-difurfurylfuran and 2,2′-(furylmethylene)bis(5-methylfuran)) were observed in GC and GC/MS, while Infrared (IR) and Raman spectroscopy provided the co-existence of conjugated diene and diketone molecular structures, respectively. It was observed that C_9–C_{15} oligomers' selectivity decreased as the reaction time increased. Ether bridge and terminal alcohol are dominant FA dimers which are very similar to sulfuric acid (homogeneous catalysis) catalyzed dehydration/condensation reaction of FA.

1. Introduction

Over the last several decades, there is an extensive growing need to develop and investigate renewable energy resources, such as lignocellulosic biomass, due to the depleting petroleum sources and increasing greenhouse gas emissions [1]. One of the attractive chemical products during the biomass conversion reaction is furfuryl alcohol (FA), which is the product obtained by a selective hydrogenation process from furfural [2]. FA is considered as an important template chemical [3]. FA monomer conversion into oligomer (Oligomerized FA, OFA) and polymer (Polymerized FA, PFA) has been explored because of a wide range of applications, such as nanocomposite carbon, carbon nanotubes, graphitic compositions, resin, membrane, and fuel blending components [4,5]. Homogeneous catalysts (H_2SO_4, HCl and H_3PO_4) have been used in OFA and PFA production from FA monomer through the pyrolysis, vapor deposition and carbonization methods [6,7]. Homogeneous catalysts, however, should be replaced by heterogeneous catalysts because of difficulties associated with recycling and separating the catalyst from products. Several OFA and PFA molecular structures have been proposed by means of spectroscopic and analytic techniques [8,9]. 2,2′-Difurylmethane (DFM, $C_9H_8O_2$), 2,2′-difurfuryl ether (DFE, $C_{10}H_{10}O_3$), 2,2′-difuryl-ethylene (DFEt, $C_{10}H_8O_2$), 2-hydroxymethyl-5(5-furfuryl)furan (HFF, $C_{10}H_{10}O_3$) and hydroxyl-carbon bridge dimer were proposed as dimer products [10–12]. In addition to aforementioned dimers, E.M. Wewerka et al. reported that 4-furfuryl-2-pentenoic acid γ-lactone ($C_{10}H_{11}O_3$, PAL) can be produced over γ-alumina during FA polymerization, while HFF is present only in the maleic anhydride FA polymerized products [13]. Based on GC, IR, NMR, and MS data, authors claimed that HFF and PAL can't be coexisted in either acid-polymerized or γ-alumina-polymerized FA although analytical results were not enough to support the evidence of PAL existence [13]. To the best of our knowledge, very little information is available for the quantitative analysis of oligomer products during the FA oligomerization reaction over heterogeneous catalysts. This paper describes the feasibility of using tungsten oxide catalysts for the FA oligomerization reaction. FA oligomers, C_9–C_{14}, were identified by combined spectroscopic technique and analytical methods, i.e., UV/Visible Raman and Infrared spectroscopy, gas chromatography and mass spectrometer.

2. Experimental sections

2.1. Catalytic FA oligomerization reaction

Tungsten oxide (99.9%) and furfuryl alcohol (98%) were obtained from Sigma-Aldrich and used without further purification. In a typical FA oligomer sample preparation, 3.00 g FA and 0.30 g WO_3 mixtures in clean vials were stirred at 100 °C and ambient pressure in an aluminum block which covered by heating tape (HTS/Amptek, 1.30A, 156 W) for 0.5–24 h. After target reaction time was reached, the glass vials were immediately transported to an ice water to stop further reaction. For the catalyst recyclable test, after 6 h FA oligomerization reaction, WO_3 catalysts were separated from the products, and thoroughly

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washed with methanol and water 3 times. The separated WO_3 catalysts were initially dried overnight at ambient temperature, and then calcined in air (Praxair, Extra dry) at 400 °C for 4 h with a ramping rate of 4 °C/min. The calcined WO_3 catalysts were investigated by visible Raman spectroscopy and X-ray diffraction and oligomerization reaction was also performed with regenerated WO_3 catalysts under the same experiment condition (100 °C and 6 h). Compositions of OFA were identified by a PerkinElmer Clarus 680 GC equipped with a PerkinElmer SQ8T mass detector. Quantitative analyses were carried out using a PerkinElmer Clarus 680 GC equipped with a flame ionization detector and a split/splitless injector. The split ratio was maintained at 30:1. PerkinElmer Elite-5MS (30 m × 0.25 mm × 1.0 μm) capillary column was used in both GC and GC/MS. Response factor for lower molecular weight oligomers (dimer and trimer) were estimated using a computational approach where FA was used as the internal standard [14]. Due to the limitation of column temperatures, we mainly investigated and analyzed FA dimer and trimers in detail. Undetected and smaller GC peaks were added together and reported as heavy oligomers, >trimer.

2.2. Characterization of WO_3 catalyzed FA samples

UV Raman (325 nm) spectra were recorded on a Horiba-Jobin Yvon LabRam HR Raman spectrometer equipped with a confocal microscope. The spectral acquisition time was 30 s/scan for a total of ~9 min/spectrum (20 scans). The visible excitation was generated by a diode-pumped solid state continuous wave laser (532 nm, BaySpec Nomadic™ Raman Microscope, 50 mW). For the visible Raman spectra, the spectral acquisition time was 1 scan for a total of 3 s/spectrum (3 scans). Infrared spectra were obtained with a PerkinElmer Frontier Fourier transform infrared spectroscopy (FTIR), which is equipped with an attenuated total reflectance (ATR) accessory, with a 0.4 cm^{-1} resolution and 4 scans. The X-ray diffraction (XRD) spectra were collected using a Rigaku MiniFlex600, where a Cu target Kα ray was used as the X-ray source. The 2θ scans were measured at room temperature in the angle range of 10–60°.

3. Results and discussion

3.1. Composition analysis

Catalytic activity and product distributions in the FA oligomerization reaction over WO_3 catalysts were analyzed by GC and GC/MS. Quantitative data was plotted in a range of 0.5–24 h while the trend between 6 and 24 h was deduced from 6 h and 24 h data. It was observed that WO_3 catalyzed FA conversion gradually increased with time on stream and reach 60% in 24 h (Fig. 1). Fig. S1 (GC/MS, Supporting information) and Table 1 provide that five dimers (C_9–C_{10}) and two trimers (C_{14}–C_{15}) were produced over WO_3 catalysts, which are similar to previously reported FA oligomers catalyzed by homogeneous catalysts [9,13, 15–17]. Although conjugated diene and diketone structure were proposed in the previous paper [7,9,10], we could not identify these oligomers within our experimental and equipment conditions. Based on the carbon balance calculation (0.5–6 h: 100–91%, 24 h: 75%), we confirm the possible presence of long chain-length oligomer (e.g. tetramer, pentamer, or even hexamer) and hypothesize that undetected conjugated diene and diketone structure might exist in these large oligomers or polymers. Another possibility is unidentified peaks at longer retention times (up to 78 min) in GC/MS might contain these two proposed structure oligomers. In the 5 different dimers, we were able to identify both 4-furfuryl-2-pentenoic acid γ-lactone (PAL, D4) and 5-furfuryl-furfuryl alcohol (HFF, D5) although E.M. Wewerka et al. claimed that both HFF and PAL can't be coexisted at the same catalyzed FA oligomers [13].

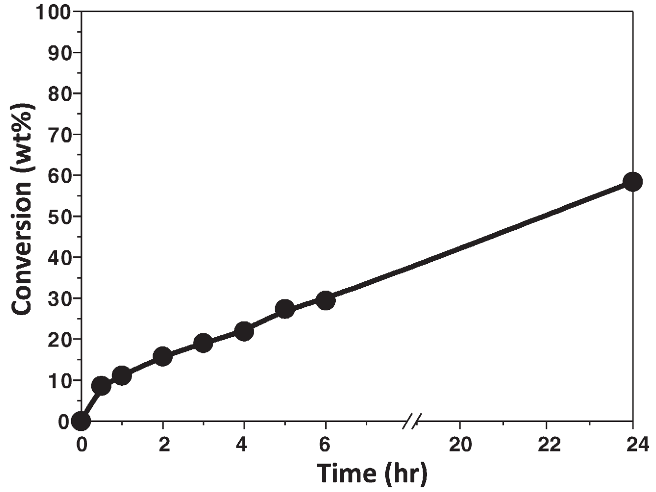

Fig. 1. FA conversion in the presence of WO_3 catalysts. Reaction conditions: Temp = 100 °C, pressure = atmosphere, time = 0–24 h.

Fig. 2(a) shows that both low (C_9–C_{15}) and heavy ($>C_{15}$) oligomers' formations increase as a function of time. Up to 6 h, C_9–C_{15} wt.% in products is higher than $>C_{15}$. After 6 h, however, $>C_{15}$ oligomers gradually exceed C_9–C_{15} oligomers. At 24 h, the concentration of $>C_{15}$ oligomers and C_9–C_{15} oligomers are ~29 wt.% and ~26 wt.%, respectively. As expected, heavy oligomer (>trimer) selectivity increased as a function of time, while the selectivity of dimer + trimer decreased with reaction time, as shown in Fig. 2(b). Especially dimer + trimer selectivity decreased sharply <1.5 h and then slightly decreased up to 24 h. In order to acquire a higher selectivity of short chain-length oligomers, short reaction times, typically <1.5 h, are required. Fig. 2(c) and (d) show detailed dimers' and trimers' wt.% for 24 h reaction. Ether bridged (D3), terminal alcohol (D5), and linear-shape trimer (T1) are dominant dimers and trimer products. It was, however, observed that D5 dimer's wt.% wasn't changed after 5 h, while D1, D2, and D4 formation were increased up to 24 h. Possibly, D5 dimer converts into T1 via dehydration and condensation reaction. The calculated enthalpy of dimers' formation from FA monomer with one proton showed that D5 formation is thermodynamically more favorable than D3 by ~12 kcal/mol [15]. D5 (terminal OH dimer) was the dominant dimer with sulfuric acid [15] which is similar to the current experimental results with WO_3 up to 5 h.

In Fig. S2, we compared the catalytic performance of WO_3 with other two acid catalysts (sulfuric acid and **γ**-Al_2O_3). In general, WO_3 showed highest conversion, as well as the highest C_9–C_{15} selectivity compare to H_2SO_4 and γ-Al_2O_3. These results provide that WO_3 is a strong candidate as a heterogeneous catalyst to replace H_2SO_4, which has been frequently used in FA oligomerization.

3.2. Vibrational spectroscopy analysis

3.2.1. FT-IR spectroscopy studies of the FA monomer molecular structure evolution

In order to obtain more information of the FA oligomer molecular structure changing over WO_3, IR spectroscopy was applied during the reaction at different reaction times, as shown in Fig. 3. With increasing the reaction time, peak intensity of both 1561 cm^{-1} and 1715 cm^{-1} are increased. According to previous studies, 1561 cm^{-1} peak is assigned to C═C stretching vibration inside furan ring structure [18]. R. Zavaglia et al. reported that observed 1565 cm^{-1} peak is C═C bond of a furan-methylene-furan group [16]. Several papers reported that the band at 1715 cm^{-1} is attributed to C═O stretching mode in the diketone structure which was not obtained in our GC/MS results [6,19, 20–22]. It has been claimed that open-ring structure (γ-diketone) forms during the acid catalyzed FA polymerization reaction via protonic species react with oxygen in furan ring [17,20–22]. However, experiment evidence of diketone structure was not reported. In addition to diketone structure, we can't avoid the possibility of PAL. However, because concentration of PAL was very low (see Fig. 2(d)), while