Catalysis Communications 72 (2015) 11–15

Contents lists available at ScienceDirect

Catalysis Communications

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

Short communication

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

Xiaojun Chan [a], Wei Nan [a], Devinder Mahajan [a,b], Taejin Kim [a,b,*]

[a] *Materials Science and Engineering Department, Stony Brook University, Stony Brook, NY 11794, USA*
[b] *Chemical and Molecular Engineering Department, Stony Brook University, Stony Brook, NY 11794, USA*

ARTICLE INFO

Article history:
Received 27 May 2015
Received in revised form 27 August 2015
Accepted 30 August 2015
Available online 3 September 2015

Keywords:
Heterogeneous catalysis
Furfuryl alcohol oligomers
Tungsten oxide
Analytical method
Infrared and Raman spectroscopy

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

---

[*] Corresponding author at: Materials Science and Engineering Department, Stony Brook University, Stony Brook, NY 11794, USA.
E-mail address: taejin.kim@stonybrook.edu (T. Kim).

http://dx.doi.org/10.1016/j.catcom.2015.08.027
1566-7367/

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].

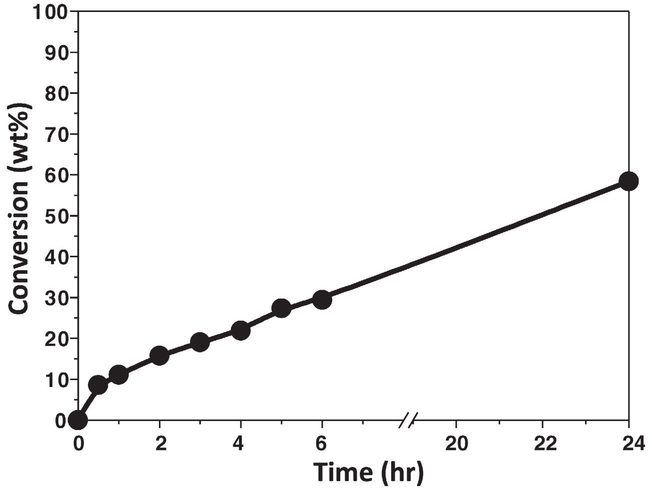


Fig. 1. FA conversion in the presence of WO_3 catalysts. Reaction conditions: Temp = 100 °C, pressure = atmosphere, time = 0–24 h.

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.

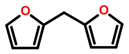
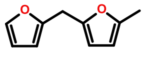
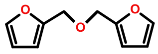
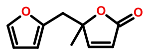
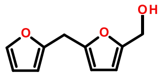
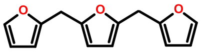
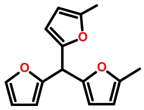
In Fig. S2, we compared the catalytic performance of WO_3 with other two acid catalysts (sulfuric acid and **γ**-Al_2O_3). In general, WO_3 showed highest conversion, as well as the highest C_9–C_{15} selectivity compare to H_2SO_4 and γ-Al_2O_3. These results provide that WO_3 is a strong candidate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

Table 1
Products (dimers and trimers) identified by GC/MS for the furfuryl alcohol oligomerization reaction over WO_3 catalyst.

	Oligomer	Name	Formula	M.W.
	D1	2,2′–Difurylmethane	$C_9H_8O_2$	148
	D2	2–(2–Furylmethyl)–5–methylfuran	$C_{10}H_{10}O_2$	162
	D3	Difurfuryl ether	$C_{10}H_{10}O_3$	178
	D4	4–Furfuryl–2–pentenoic acid γ–lactone	$C_{10}H_{10}O_3$	178
	D5	5–Furfuryl–furfuryl alcohol	$C_{10}H_{10}O_3$	178
	T1	2,5–Difurfurylfuran	$C_{14}H_{12}O_3$	228
	T2	2,2′–(Furylmethylene) bis(5–methylfuran)	$C_{15}H_{14}O_3$	242

1715 cm^{-1} peak intensity was keep increased with time, we can avoid that 1715 cm^{-1} carbonyl band is related to the PAL. We can conclude that observed 1715 cm^{-1} peak might be assigned to C═O stretching mode, while molecular information is unsure.

The degree of FA oligomerization can be estimated by plotting the intensity of the 1715 cm^{-1} peak against the 1504 cm^{-1} as a function of reaction time, as shown in Fig. S3. The peak intensity ratio ($I_{1715\ cm^{-1}}/I_{1504\ cm^{-1}}$) increases linearly with increasing reaction times, which is similar to conversion results. Contrary to C═O peak intensity changes, hydroxyl group (—OH) IR peak intensity decrease with increasing reaction time and OH stretching band position was shifted to higher wavenumber, as shown in Fig. S4. Similar results were obtained by sulfuric acid catalyst and it was claimed that larger molecules which connect to hydroxyl group affect OH stretching band wavenumbers [23]. M. Choura et al. synthesized FA polymer over $TiCl_4$ and found OH stretching band at 3447 cm^{-1} which is ~82 cm^{-1} higher than our 24 h sample's OH band position (~3365 cm^{-1}) [19]. This is certainly due to the higher concentration of FA polymer or heavy FA oligomers. This comparison confirms that OH band position can be also used to estimate a relative degree of FA oligomerization reaction. Recently, N. Guido et al. reported that cured FA polymer's OH band intensity is much lower than FA monomer which matches to our results, although authors didn't explain the shift of OH band positions in detail [6]. The decrease of OH band must be inferred from the FA condensation reaction which leads the decrease of number of methylene-OH group during the oligomerization reaction.

3.2.2. Raman spectroscopy studies of the FA monomer molecular structure evolution

The Raman spectra during the FA oligomerization reaction are presented along with the FA monomer alone in Fig. 4. The FA monomer Raman spectrum contains strong and weak/broad bands at 1509 and 1604 cm^{-1} (shoulder at 1618 cm^{-1}) which are assigned to symmetric C═C stretching bands of the aromatic furan group, [9,24,25] while

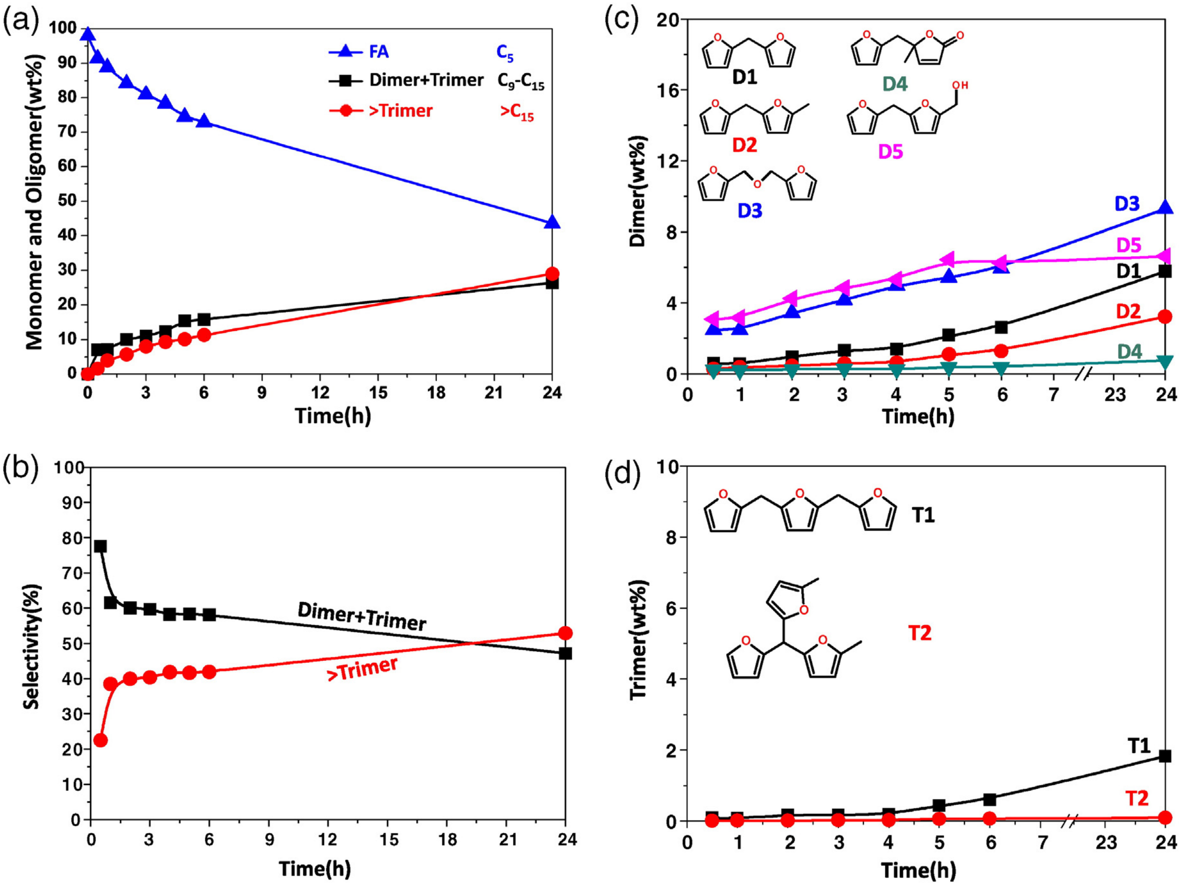


Fig. 2. The effect of reaction time on the (a) wt.% of monomer and oligomers (dimer + trimer and >trimer) (b) selectivity of oligomers (dimer + trimer and >trimer) (c) wt.% of D1–D5 FA dimers, and (d) wt.% of T1–T2 FA trimers. Reaction conditions: Temp = 100 °C, pressure = atmosphere, time = 0–24 h.

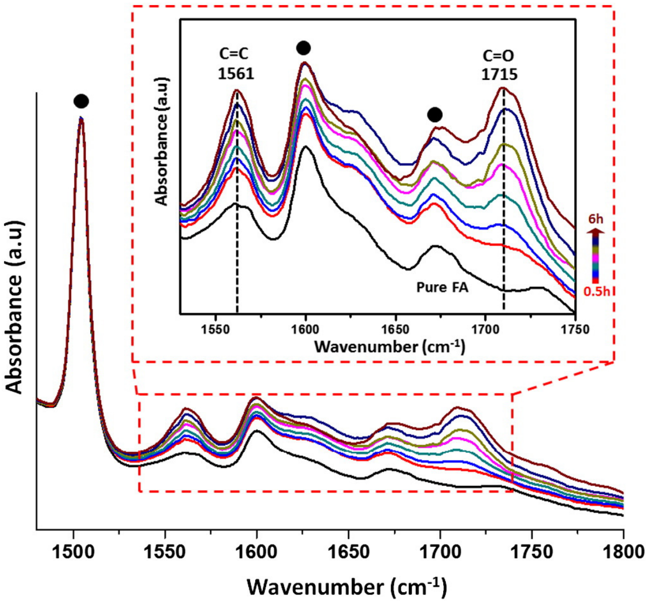


Fig. 3. FTIR spectra of the furfuryl alcohol (3.00 g) and WO_3 catalysts (0.30 g) in the 1450–1800 cm^{-1} region. Reaction conditions: Temp = 100 °C, pressure = atmosphere, time = 0.5–6 h. For a comparison pure furfuryl alcohol spectrum is provided (black line). Closed circle: Typical FA IR bands (1504 cm^{-1}, 1600 cm^{-1} and 1675 cm^{-1}).

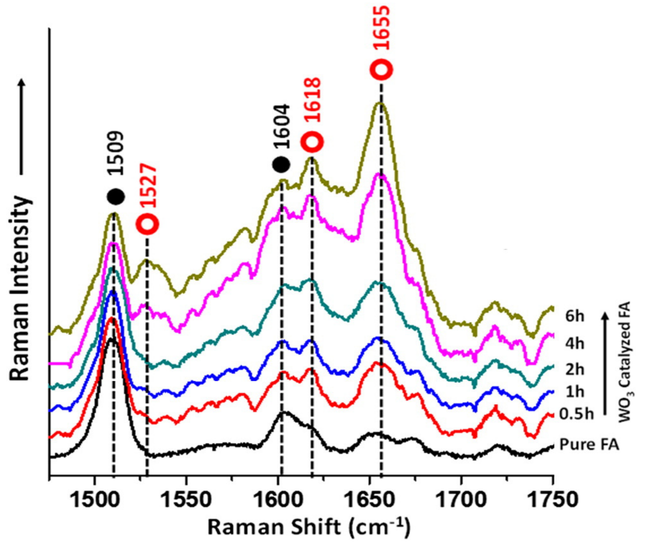


Fig. 4. Raman spectra of the furfuryl alcohol (3.00 g) and metal oxide catalysts (0.30 g) in the 1450–1800 cm^{-1} regions using UV (325 nm) excitation. Reaction conditions: Temp = 100 °C, pressure = atmosphere, time = 0.5–6 h. For a comparison pure furfuryl alcohol Raman spectrum is provided (black line). Closed black circle: Typical FA Raman bands (1509 cm^{-1} and 1604 cm^{-1}).

unidentified very weak peaks (or background noise) were also observed. Compared with the FA monomer Raman spectrum, WO_3 catalyzed FA Raman spectra shows new bands at 1527 (weak) and 1655 (strong) cm^{-1}. Under homogeneous catalysis environment using H_2SO_4, previous paper reported that 1529 and 1654 cm^{-1} can be attributed to endocyclic and exocyclic C═C bond, respectively, which are well match to the WO_3 catalyzed FA oligomers' Raman bands positions [9]. These similar positions provide that both homogeneous (H_2SO_4) and heterogeneous (WO_3) catalyzed FA oligomers contain relatively similar molecular structure.

Recently, theoretically calculated Raman spectra with optimized difurfuryl furan, diketone, and conjugated molecular structure proved that measured 1655 cm^{-1} Raman band was only shown in the conjugated diene structure [9]. During the reaction, it was also observed that broad and weak FA monomer peaks between 1580 and 1630 cm^{-1} were split into two peaks, 1604 and 1618 cm^{-1}. Although we could not clearly assign the 1618 cm^{-1} peak, based on the previously reported homogeneous catalyzed FA Raman spectra, we expect that it relates to a C═C stretching band in the FA oligomer structure. It should be emphasized that 1655 cm^{-1} Raman band was not observed in the IR spectra, while Raman spectra doesn't contain a strong 1715 cm^{-1} IR band (C═O stretching mode). These combined Raman and IR results provide the coexistence of both conjugated diene and diketone molecular species in the WO_3 catalyzed FA oligomers.

3.3. Catalysts recyclability analysis

The reusability of catalyst is an important factor as a heterogeneous catalyst. Both fresh and regenerated WO_3 visible Raman spectra contain similar characteristic vibration at 807, 715, and 273 cm^{-1}, as shown in Fig. S5. Although visible Raman is very sensitive to the bulk WO_3, the peak intensity ratio between the ν(O–W–O) at 807 and 715 cm^{-1} with the δ(W–O–W) at 273 cm^{-1} showed close value [26]. The curve in XRD pattern (Fig. S6) revealed that the crystal phase of fresh and regenerated WO_3 was **γ**-phase with the major diffraction peaks at about 22.9°, 23.4°, 24.2°, 33.2°, and 34.0°, which could be perfectly indexed to the (002), (020), (200), (022), and (202/220) crystal faces (JCPDS 43-1035) [27], respectively. These results provide that the used WO_3 can be regenerated without structure modification. In addition to the WO_3 recyclability, both regenerated and fresh WO_3 catalyzed FA conversion (~29 wt.%) and C_9–C_{15} selectivity (54–58%) values were very similar (inset figure in Fig. S5).

4. Conclusions

In this paper, comprehensive studies using different analytical (GC and GC/MS) and spectroscopic (FTIR and Raman) methods on the FA oligomerization over the WO_3 catalysts have been carried out and investigated to prove the feasibility of using WO_3 catalyst under liquid phase reaction conditions. The results provide that difurfuryl ether (D3) and 5-Furfuryl-furfuryl alcohol (D5) dimers are the dominant products among the observed five dimers which are very similar to homogeneous catalysis results. Using IR and Raman spectroscopic techniques, we assert that both conjugated diene and diketone structures can be co-existed in the WO_3 catalyzed FA oligomers. Based on the current catalyst recycle test, we can suggest that WO_3 catalyst is an alternative to current homogeneous catalysts (sulfuric acid) for the FA oligomerization reaction.

Acknowledgments

We gratefully acknowledge the financial support for this study from the Department of Materials Science & Engineering and the Program in Chemical and Molecular Engineering at Stony Brook University through startup research funding. Prof. I.E. Wachs, Dr. C.J. Keturakis (Lehigh University), and Prof. J. Moon (Stony Brook University) are also thanked for their help in conducting UV-Raman spectroscopy and XRD experiments.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2015.08.027.

References

[1] J.J. Bozell, G.R. Petersen, Green Chem. 12 (2010) 539–554.
[2] C. Moreau, M.N. Belgacem, A. Gandini, Top. Catal. 27 (2004) 11–30.
[3] G.M.G. Maldonado, R.S. Assary, J. Dumesic, L.A. Curtiss, Energy Environ. Sci. 5 (2012) 6981–6989.

[4] B. Yi, R. Rajagopalan, H.C. Foley, U.J. Kim, X. Liu, P.C. Eklund, J. Am. Chem. Soc. 128 (2006) 11307–11313.

[5] H. Wang, L. Zhang, G.R. Gavalas, J. Membr, Science 177 (2000) 25–31.

[6] N. Guigo, A. Mija, L. Vincent, N. Sbirrazzuoli, PCCP 9 (2007) 5359–5366.

[7] Y.R. Dong, N. Nishiyama, Y. Egashira, K. Ueyama, Ind. Eng. Chem. Res. 46 (2007) 4040–4044.

[8] S. Bertarione, F. Bonino, F. Cesano, S. Jain, M. Zanetti, D. Scarano, A. Zecchina, J. Phys. Chem. B 113 (2009) 10571–10574.

[9] T. Kim, R.S. Assary, C.L. Marshall, D.J. Gosztola, L.A. Curtiss, P.C. Stair, ChemCatChem 3 (2011) 1451–1458.

[10] S. Bertarione, F. Bonino, F. Cesano, A. Damin, D. Scarano, A. Zecchina, J. Phys. Chem. B 112 (2008) 2580–2589.

[11] G.E. Maciel, I.S. Chuang, G.E. Myers, Macromolecules 15 (1982) 1218–1220.

[12] C.R. Mendonça, P.S. Batista, M.F. Souza, S.C. Zilio, Chem. Phys. Lett. 343 (2001) 499–506.

[13] E.M. Wewerka, E.D. Loughran, K.L. Walters, J. Appl. Polym. Sci. 15 (1971) 1437–1451.

[14] J.T. Scanlon, D.E. Willis, J. Chromatogr. Sci. 23 (1985) 333–340.

[15] T. Kim, R.S. Assary, R.E. Pauls, C.L. Marshall, L.A. Curtiss, P.C. Stair, Catal. Commun. 46 (2014) 66–70.

[16] A.J.G. Zarbin, R. Bertholdo, M.A.F.C. Oliveira, Carbon 40 (2002) 2413–2422.

[17] R.T. Conley, I. Metil, J. Appl. Polym. Sci. 7 (1963) 37–52.

[18] T. Kim, J. Jeong, M. Rahman, E. Zhu, E. Mahajan, D. Korean, J. Chem. Eng. 31 (2014) 2124–2129.

[19] M. Choura, N.M. Belgaem, A. Gandini, Macromolecules 29 (1996) 3839–3850.

[20] M. Pérez-Mendoza, M. Domingo-Garcıa, F.J. López-Garzón, Carbon 37 (1999) 1463–1474.

[21] I.S. Chuang, G.E. Maciel, G.E. Myers, Macromolecules 17 (1984) 1087–1090.

[22] W. Hoareau, W.G. Trindade, B. Siegmund, A. Castellan, E. Frollini, Polym. Degrad. Stab. 86 (2004) 567–576.

[23] T. Kim, R.S. Assary, L.A. Curtiss, C.L. Marshall, P.C. Stair, J. Raman Spectrosc. 42 (2011) 2069–2076.

[24] T. Kim, R.S. Assary, H. Kim, C.L. Marshall, D.J. Gosztola, L.A. Curtiss, P.C. Stair, Catal. Today 205 (2013) 60–66.

[25] M.F. Daniel, B. Desbat, J.C. Lassegues, B. Gerand, M. Figlarz, J. Solid State Chem. 67 (1987) 235–247.

[26] C.D. Baertsch, K.T. Komala, Y.H. Chua, E. Iglesia, J. Catal. 205 (2002) 44–57.

[27] S.H. Lee, R. Deshpande, P.A. Parilla, K.M. Jones, B. To, A.H. Mahan, A.C. Dillon, Adv. Mater. 18 (2006) 763–766.