



## Short Communication

## Solid acid-catalyzed conversion of furfuryl alcohol to alkyl tetrahydrofurfuryl ether

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## ABSTRACT

The acidic zeolite HZSM-5 (Si/Al = 25) achieved 58.9% selectivity of methyl furfuryl ether (MFE) and 44.8% selectivity of ethyl furfuryl ether (EFE) from etherification of furfuryl alcohol with methanol and ethanol. MFE and EFE were quantitatively hydrogenated into methyl tetrahydrofurfuryl ether (MTE) and ethyl tetrahydrofurfuryl ether (ETE) using a Raney Ni catalyst.

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## 1. Introduction

With depleting reserves of fossil fuels, tremendous efforts have been dedicated to seeking effective chemical conversion of renewable biomass into fuels [1]. Furfural, an important platform chemical and often obtained by hydrolysis and dehydration of hemicellulose, has been commercialized for decades [2]. It can be further converted into furfuryl alcohol (FA) and 2-methylfuran (MF) by hydrogenation. These compounds are often used as intermediates to synthesize fuels and many other high value-added products [2]. Extensive investigations have been conducted on the conversion of furfural, FA and MF into fuels or fuel additives [3–5].

Producing diesel-range compounds from furfural and its derivatives FA and MF has been reported in recent studies. Alkanes and alkyl tetrahydrofurfuryl ether (ATE), derived from MF and FA respectively, are regarded as promising candidates for producing bio-diesel, as shown in Scheme 1 [4,6]. MF was first catalyzed by acids and underwent hydroxyalkylation with the carbonyl-containing compounds. The products generated were then hydrogenated. In this way, MF was converted to an alkane [4,5]. The high cetane number enables those alkanes to be used as diesel [3]. Ed de Jong and his co-workers investigated the combustion of diesel–ethyl tetrahydrofurfuryl ether (ETE) mixture using a PACCAR diesel engine [6] and concluded that the mixture substantially mitigated the emission of particulate matters and smoke. With the cetane number reported to be 80–90, ETE presents to be a potential diesel

additive [6]. It is notable that 6 mol of hydrogen was consumed to synthesize alkanes when furfural was adopted as the primary substrate and went through the complete hydrodeoxygenation of furans. Besides, all the oxygen atoms of the reactants are removed, against the atom economy [4]. Converting FA to ATE is, thus, significant for just 3 mol of hydrogen consumed with only one oxygen atom being removed. However, only few studies on its synthetic method have been conducted.

In the present study, a method to synthesize alkyl tetrahydrofurfuryl ether (ATE) is reported. Furfuryl alcohol was first catalyzed by solid acids and then reacted with methanol and ethanol via etherification to produce corresponding alkyl furfuryl ether (AFE). AFE is further hydrogenated to yield ATE. Solid acids such as supported protic acid, resin, zeolite and heteropoly acid are less corrosive and have been used in various organic syntheses such as etherification, acetal and esterification [7]. Methanol and ethanol are selected, for they present to be potential feedstock for fuels and chemicals [8,9].

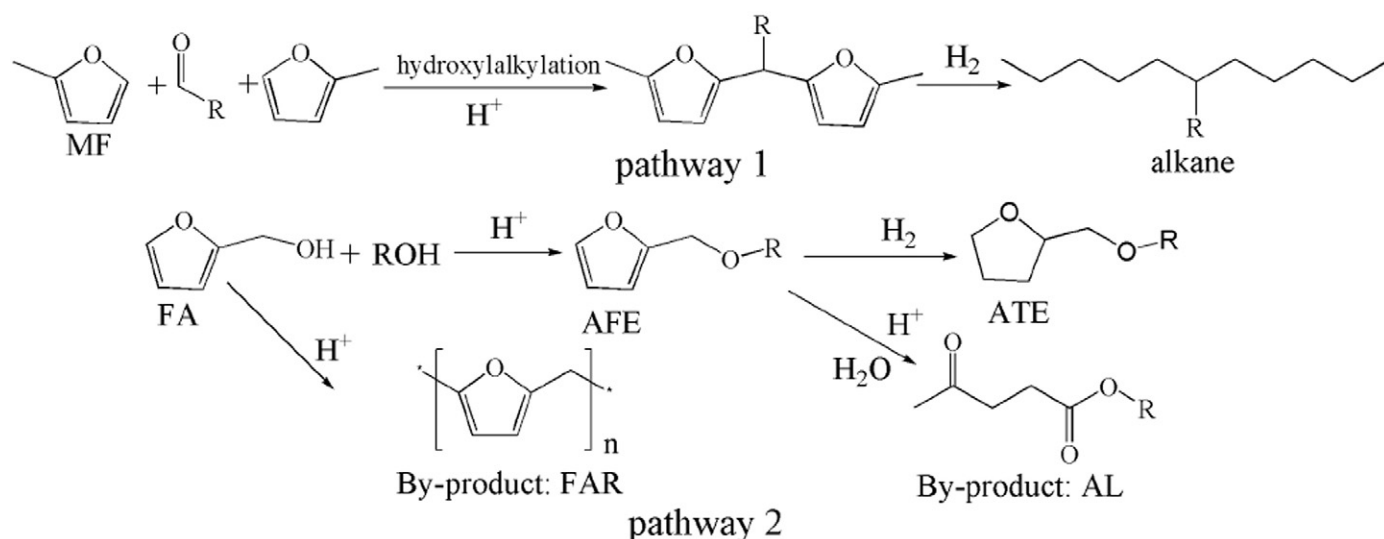
## 2. Experimental

## 2.1. Typical experimental procedures

4 g HZSM-5 (Si/Al = 25), 50 mL methanol and 5 g furfuryl alcohol were charged into a 100 mL vessel one by one. It was then put in an oil bath preset at 25 °C with magnetic stirring (600 rpm) for 24 h. The reaction was repeated for two times with negligible errors.

The catalyst in Table 1 Entry 1 was filtered, washed with 100 mL methanol for three times, dried at 100 °C for 3 h and then used for the

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**Scheme 1.** Reaction pathways for the conversion of FA and MF into biodiesel candidate alkane (pathway 1) and alkyl tetrahydrofurfuryl ether (ATE, pathway 2).

second run. Then it was calcinated at 500 °C for 3 h and used for the third run.

After the catalyst was filtered, the sample in Table 4 Entry 3 and 1 g humid Raney Ni after being washed by 100 mL ethanol were charged into a 250 mL autoclave. The autoclave was filled with H<sub>2</sub> of 4 MPa after being purged three times. Zero time and mechanical stirring started after the autoclave was heated to 100 °C. The reaction lasted for 2 h. The liquid product of 0.1 mL was diluted with 80 mL ethanol and analyzed by gas chromatography–mass spectrometry (GC–MS) to confirm the formation of ETE.

The materials used, detailed experimental procedures and analytical methods are described in Supplemental information.

### 3. Results and discussion

#### 3.1. Etherification of furfuryl alcohol with methanol

Methyl tetrahydrofurfuryl ether (MTE) can be theoretically synthesized by direct etherification of tetrahydrofurfuryl alcohol (TFA) with methanol. Although HZSM-5 (Si/Al = 25) was reported to synthesize dimethyl ether from methanol via etherification at 150 °C [10], the GC–MS analysis indicated that no MTE was produced except the expected dimethyl ether even after four-hour reaction at 160 °C. This can be explained by the steric effect caused by the tetrahydrofuran ring. It leads to the relatively low reactivity of the hydroxyl group in TFA. Therefore, an alternative pathway was suggested in Scheme 1, where MTE was generated through first making furfuryl alcohol (FA) react with methanol to produce methyl furfuryl ether (MFE) and then conducting hydrogenation. The route is believed to be feasible because the hydroxyl group in FA shows higher reactivity than that in TFA and FA is able to

form a stable oxonium ion [11]. Alkyl furfuryl ether (AFE) was reported as an intermediate product in synthesizing alkyllevulinate (AL) from FA (Scheme 1) [12–17]. Such minor by-product as furfuralcohol resin (FAR) formed by polymerization of FA molecules was also observed in this process [18,19] (Scheme 1). It was found that the system turned yellow during the reaction and some viscous yellow liquid remained in the reactor after the volatile components such as methanol, MFE and ML were evaporated. The liquid was believed to be FAR [18,19]. AL can be used as a flavor agent or gasoline additive [13,20,21] and FAR is an indispensable polymer in paints [18], but it is preferable to carry out the reaction without generating these undesirable by-products in the synthesis of MFE.

The three solid acid catalysts of HZSM-5 (Si/Al = 25), HZSM-5 (Si/Al = 80), and Amberlyst-15 were compared in their ability to convert furfuryl alcohol to MFE in methanol in the initial screening. Figs. 1 and S1 demonstrate the changes of the MFE yield as time goes by. It was found that HZSM-5 (Si/Al = 25) achieved a higher MFE selectivity than HZSM-5 (Si/Al = 80) and Amberlyst-15. Lange et al. used different solid acids to investigate the synthesis of ethyl levulinate (EL) through FA reacting with ethanol and found that over 80% EL yield was achieved using Amberlyst-15 at a temperature as high as 125 °C [13]. However, the present study revealed that the overall yield of MFE and methyl levulinate (ML) in the presence of Amberlyst-15 was less than 45% at 25 °C. FA turned to produce FAR due to its self-polymerization at a low temperature. The influence of Si/Al ratio on the MFE and ML yields was further studied and it was found that the decreasing Si/Al ratio from

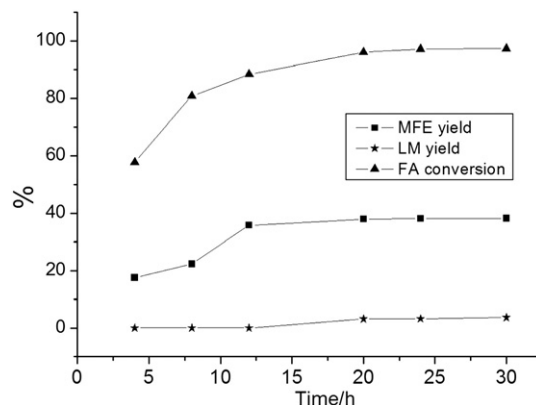
**Table 1**  
Conversion of FA in methanol with HZSM-5.<sup>a</sup>

Entry	HZSM-5 (Si/Al)	FA conversion (%)	MFE yield (%)	ML yield (%)	MFE selectivity (%)
1	25	94.2	55.4	16.9	58.9
2 <sup>b</sup>	25	51.2	27.2	7.1	53.2
3 <sup>c</sup>	25	78.8	43.1	12.0	54.7
4	38	82.1	42.3	15.8	51.5
5	50	75.4	39.7	14.9	52.7
6	80	64.8	33.4	8.4	51.5

<sup>a</sup> Reaction conditions: FA 5 g; methanol 50 mL; HZSM-5 4 g; 25 °C; 24 h reaction time.

<sup>b</sup> HZSM-5 (Si/Al = 25) was recycled for the second run after Entry 1.

<sup>c</sup> HZSM-5 (Si/Al = 25) was recycled for the third run after calcination.



**Fig. 1.** MFE yield, LM yield and FA conversion versus reaction time. Reaction conditions: Amberlyst-15 1 g; FA 5 g; methanol 50 mL; 25 °C.

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