



Diels–Alder and dehydration reactions of furan derivatives with ethylene catalyzed by liquid Brønsted acids and Lewis acids



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ABSTRACT

The tandem Diels–Alder and dehydration reactions of furan derivatives with ethylene represent a promising approach for the production of renewable aromatics. Herein, a series of haloacetic acids and rare-earth metal triflates are employed as liquid Brønsted and Lewis acid catalysts, respectively, in the Diels–Alder and dehydration reactions of 2,5-dimethylfuran with ethylene to get an insight of this type of acid-catalyzed reaction. With the carefully selected catalysts and solvent, a quasi-homogeneous reaction system can be formed, where accurate kinetic studies could be performed. Haloacetic acids exhibit considerable activity in the Diels–Alder and dehydration reactions with a similar apparent activity energy value of ~ 8.4 kcal/mol, and CF_2ClCOOH with a proper Brønsted acidity is optimized for the reaction. Rare-earth metal triflates also exhibit considerable activity in the Diels–Alder and dehydration reactions with a similar apparent activity energy value of ~ 13.0 kcal/mol, and $\text{Sc}(\text{OTf})_3$ with the highest Lewis acidity is optimized. On the basis of kinetic analysis results, the impacts of acidity on the performance of catalysts are discussed in detail and the reaction network is proposed. Besides, the substrate scope of furan derivatives for the Diels–Alder and dehydration reactions with ethylene is investigated using CF_2ClCOOH and $\text{Sc}(\text{OTf})_3$ as catalysts for possible extensions of the reaction.

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1. Introduction

With decreasing fossil resources and increasing demand for energy and materials, it is quite urgent to find alternative supplies for the production of fuels and chemicals [1–6]. In the past decades, great attention has been focused on the renewable fuels and chemicals derived from biomass [7,8]. Glucose and xylose are the main sugar monomers present in biomass, and a lot of platform molecules, such as 5-hydroxymethylfurfural, 2,5-dimethylfuran and levulinic acid, can be produced from these sugar monomers [9]. For example, 2,5-dimethylfuran can be produced via a combined isomerization, dehydration and hydrodeoxygenation route from glucose [10]. With these platform molecules, dozens of renewable fuels and chemicals can be further produced.

A very attractive route for the production of renewable *p*-xylene via the Diels–Alder and dehydration reactions of biomass-derived 2,5-dimethylfuran with ethylene catalyzed by acidic zeolites was

recently disclosed [11], and then triggered widespread research interests [12–22]. It was first proposed by Dauenhauer et al. that Diels–Alder reaction of ethylene and 2,5-dimethylfuran occurred without catalytic active sites, followed by the dehydration to *p*-xylene catalyzed by Brønsted acid sites. In this case, the rate of *p*-xylene formation is controlled by the initial non-catalytic cycloaddition step [11]. In contrast, Wang et al. demonstrated that acidic oxides, e.g. $\text{WO}_x\text{-ZrO}_2$, exhibited higher activity than zeolite catalysts and the formation rate of *p*-xylene showed good dependence on the density of Brønsted acid sites [13]. More recently, Vlachos et al. reported the kinetic regime change in the tandem Diels–Alder and dehydration reactions reaction on the basis of experimental results and QM/MM calculations. It was observed that the *p*-xylene production is limited by the homogeneous Diels–Alder reaction at high solid acid concentrations whereas the overall rate is limited by the heterogeneously catalyzed dehydration reaction at low acid concentrations [16].

Heterogeneous Brønsted acids, e.g. zeolites [11,12,14–16] and mixed oxides [13,17], are reported to be active in the Diels–Alder and dehydration reactions of 2,5-dimethylfuran with ethylene. Heterogeneous Lewis acids, e.g. Sn-Beta zeolite [18–20], are recently disclosed to be also active in the reaction. It appears that

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heterogeneous Brønsted acids and Lewis acids show comparable activity in the Diels-Alder and dehydration reactions and a direct comparison between them is lacking. Meanwhile, it should be mentioned that both Brønsted acid sites and Lewis acid sites exist in some catalysts, e.g. H-Beta [21], and this would further complicate the problem. In addition to the reaction of 2,5-dimethylfuran with ethylene, the reaction scope has been successfully extended to the Diels-Alder and dehydration reactions of other furan derivatives, e.g. oxidized variants of 5-hydroxymethylfurfural [18,19], with ethylene or even furan derivatives with other nucleophilic reagents, e.g. acrolein [23] and acrylic acid [24].

Despite significant achievements made so far, several key issues on the Diels-Alder and dehydration reactions of furan derivatives with ethylene are to be investigated. Since the dehydration reaction is recognized as an acid-catalyzed reaction, it is most important to know the effects of acidity, e.g. type and strength of acid sites, on the catalytic performance. To avoid the adsorption and diffusion problems in gas-liquid-solid reactions, a quasi-homogeneous reaction system is designed by using soluble acid in selected solvent. Haloacetic acids, that have been reported as efficient catalysts in biomass conversion [25], and rare-earth metal triflates [RE(OTf)₃] [26,27], are selected as Brønsted and Lewis acid catalysts, respectively. It is revealed that the Diels-Alder and dehydration reactions of biomass-derived DMF with ethylene can be performed at low temperature of 433–513 K. Besides, the problem of product selectivity during the Diels-Alder and dehydration reactions is discussed in detail and the substrate scope of furan derivatives is investigated.

2. Experimental

2.1. Chemicals

The following reagents were used in the experiments without further purification: furan (Acros, >99%), 2-methylfuran (MF; Acros, >99%), 2,5-dimethylfuran (DMF; Acros, 99%), methyl 5-methyl-2-furoate (MMF; Ark, 97%), furan-2,5-dicarboxylic acid (FDCA; Alfa, 98%), dimethyl furan-2,5-dicarboxylate (DMFDC; Ark, 99%), 1,4-dioxane (DOX; Acros, >99%), γ -valerolactone (GVL; Acros, 98%), *n*-dodecane (DOC; Acros, >99%), ethylene glycol diethyl ether (EGDE; Acros, >98%), trifluoroacetic acid (CF₃COOH; Acros, 99%), dichloroacetic acid (CHCl₂COOH; Acros, >99%), chlorodifluoroacetic acid (CF₂ClCOOH; Acros, >98%), trichloroacetic acid (CCl₃COOH; Acros, 99%), acetic acid (CH₃COOH, >99%), Sc(OTf)₃ (Acros, 99.9%), Yb(OTf)₃ (Acros, 99.9%), La(OTf)₃ (Acros, 99.9%), Ce(OTf)₃ (Acros, 99.9%) and Sm(OTf)₃ (Acros, 99.9%).

2.2. Diels-Alder and dehydration reactions

The Diels-Alder and dehydration reactions of furan derivatives with ethylene were performed in a 15 mL high-pressure autoclave reactor equipped with a magnetic stirrer (800 r/min) and electronic heater. In a typical experiment, certain amount catalyst (substrate/catalyst = 10/1 in case of haloacetic acids as catalysts, substrate/catalyst = 100/1 in case of metal triflates as catalysts or 4 mg H-beta) and 5 mL of 0.2 M furan derivatives in dioxane or other solvent were mixed in the autoclave reactor. The reactor was purged with pure nitrogen at room temperature for five times. Then, 3.5 MPa of ethylene was introduced into the reactor and the reactor was heated to desired temperature within 10 min to initiate the reaction.

2.3. Product analysis

After the reaction, the autoclave reactor was rapidly cooled down to room temperature in ice water and the high-pressure reaction gases were carefully vented. The reaction solution was

then collected for analysis by gas chromatography (Shimadzu GC-2010) and gas chromatography–mass spectrometry (Shimadzu GCMS-QP2010 SE), both with a DB-1 column (30 m, 0.25 mm i.d., stationary phase thickness 0.25 μ m). *n*-Dodecane or durene was used as an internal standard for quantification. The following temperature program was employed: isothermal heating at 313 K for 10 min, heating to 553 K with a rate of 20 K/min, and isothermal heating at 553 K for 8 min. For the reactions involving carboxylic acids, the substrates and products were analyzed by high performance liquid chromatography (Shimadzu LC-20AT) with a CarboMix H–NP column (7.8 \times 300 mm, stationary phase thickness 10 μ m) and ¹H nuclear magnetic resonance spectroscopy (Varian NMR System 400 MHz) with DMSO-*d*₆ as solvent and tetraethylsilane as an internal standard.

The substrate conversion and product yield are directly measured and the product selectivity is calculated as:

$$\text{Product selectivity (\%)} = \frac{[\text{Product}]}{[\text{Substrate}]_{\text{before}} - [\text{Substrate}]_{\text{after}}} \times 100\%$$

Here, the carbon balance is 100% and the calculated value is the true selectivity toward desired product with the consideration of all by-products and coke.

3. Results and discussion

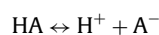
3.1. Haloacetic acids catalyzed Diels-Alder and dehydration reactions

According to literature report [16] and our experimental observations (vide infra), the reaction network for the tandem Diels-Alder and dehydration reactions of typical furan derivatives, i.e. DMF, with ethylene is shown in Fig. 1, which can be described as follows:

- Cycloaddition of DMF with ethylene to form 7-oxabicyclo [2.2.1] hept-2-ene-type adducts;
- Acid-catalyzed dehydration of cycloadducts to *p*-xylene;
- Alkylation of aromatic product *p*-xylene with ethylene to form the by-product 2-ethyl-*p*-xylene and 4-propyltoluene;
- Alkylation of *p*-xylene with *p*-xylene to produce 2,2',5,5'-tetramethylbiphenyl;
- An equilibrium between the DMF and their hydrolysis product 2,5-hexanedione;
- Condensation of 2,5-hexanedione to oligomers;
- Condensation of DMF to oligomers.

Previous reports on the Diels-Alder and dehydration reactions of DMF with ethylene are mainly based on the use of alkane solvents. However, it has been reported that polar aprotic solvents show very positive impacts on several acid-catalyzed reactions, e.g. xylose conversion into furfural [25] and cellulose dehydration to levoglucosenone [28]. Therefore, the solvent effects on the Diels-Alder and dehydration reactions of DMF with ethylene are first investigated using CF₂ClCOOH as a Brønsted acid catalyst. Here, different kinds of solvents from polar aprotic to non-polar aprotic are selected and the results are summarized in Table 1.

Water is not a good solvent because it can induce the serious hydrolysis of DMF and, accordingly, hinder the cycloaddition reaction. For nonaqueous solvents, a positive correlation between the solvent polarity and the *p*-xylene formation can be observed when using CF₂ClCOOH as catalyst. According to the Brønsted–Lowry acid–base theory, the dissociation equilibrium of acid HA is shown below.



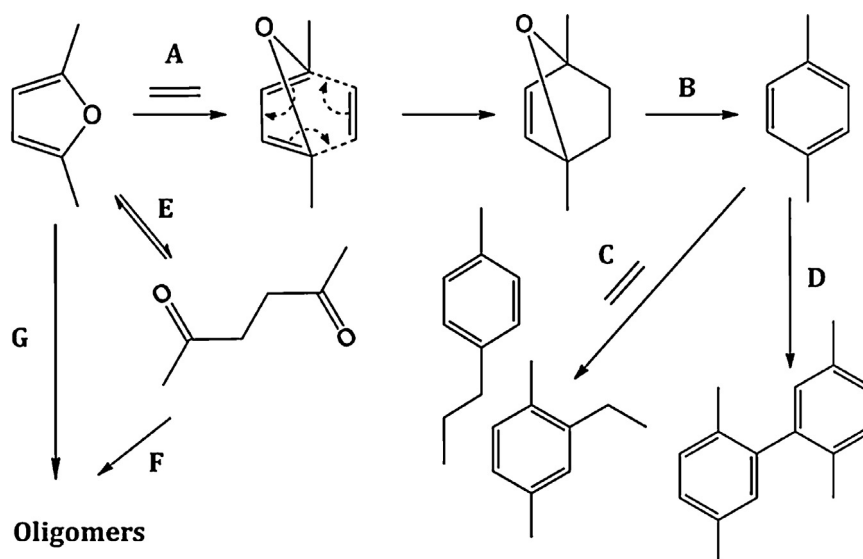


Fig. 1. Reaction network for the Diels-Alder and dehydration reactions of furan derivatives with ethylene.

Table 1
The Diels-Alder and dehydration reactions of DMF with ethylene catalyzed by CDFA in different solvents^a.

Entry	Catalyst	P_{ethylene} (MPa)	Solvent	Polarity ^b	TOF (h^{-1}) ^c	Rate ($\text{molg}^{-1} \text{h}^{-1}$) ^d
1	CF_2ClCOOH	1.0 (1.8) ^e	DOX	4.8	0.26	2.0
2	CF_2ClCOOH	2.0 (3.3)	DOX	4.8	0.38	2.9
3	CF_2ClCOOH	3.0 (4.8)	DOX	4.8	0.42	3.2
4	CF_2ClCOOH	3.5 (5.2)	DOX	4.8	0.45	3.4
5	CF_2ClCOOH	3.5 (5.0)	GVL	4.2	0.42	3.2
6	CF_2ClCOOH	3.5 (5.1)	EGDE	2.9	0.18	1.4
7	CF_2ClCOOH	3.5 (5.0)	DOC	~1.0	0.15	1.2
8	CF_2ClCOOH	3.5 (6.5)	Water	10.2	0	0
9	H-Beta ^f	3.5 (5.2)	DOX	4.8	2.7×10^3	2.0
10	H-Beta ^f	3.5 (5.0)	DOC	1.0	2.8×10^3	2.1
11	Sn-Beta ^g	3.5 (5.2)	DOX	4.8	1.9×10^4	2.9
12	Sn-Beta ^g	3.5 (5.0)	DOC	1.0	2.0×10^4	3.0

^a Reaction conditions: 5 mL 0.2 M DMF in different solvents, $T = 473 \text{ K}$, $t = 4 \text{ h}$.

^b From *Industrial Solvents Handbook*.

^c Turnover frequencies defined as the yield of *p*-xylene per mole catalyst per hour.

^d Production rate of *p*-xylene, average value within 4 h.

^e Final reaction pressures shown in the parentheses.

^f $\text{Si/Al} = 12.5$, Brønsted acid sites = 0.75 mmolg^{-1} .

^g $\text{Si/Sn} = 50$, Lewis acid sites = 0.15 mmolg^{-1} , prepared via the strategy reported in Ref. [21].

Acid can dissociate into proton (H^+) and its conjugate base (A^-), and the polarity of the medium shows significant impacts on this equilibrium. Generally, a higher degree of acid dissociation can be achieved in a solvent with higher polarity. That is to say, we will get a higher proton concentration at unit mole of monocarboxylic acid in the solvent with higher polarity. Under such circumstances, the production rate of *p*-xylene correlates well with the proton concentration, i.e. the polarity of solvent, and is consistent with literature reports on the Diels-Alder and dehydration reactions catalyzed by Brønsted acids with low concentrations [16]. DOX appears to be the optimized solvent for the reaction, which is used in the sections that follow.

In order to further confirm the effects of the proton concentration on the Diels-Alder and dehydration reactions of DMF with ethylene, a series of α -haloacetic acids spanning a wide range of pK_a values, i.e. proton concentrations, are employed as catalysts for the reaction. Generally, halogen substituents at α -C mean a strong electron-withdrawing inductive effect on carboxyl, which would make the hydrogen dissociate from the carboxyl easier and therefore a higher proton concentration could be obtained. Similarly, a stronger electron withdrawing group at α -C means a higher proton concentration. According to these considerations, the

proton concentration in haloacetic acid solution is proposed as follows: CF_3COOH ($\text{pK}_a = 0.23$) > CF_2ClCOOH ($\text{pK}_a = 0.40$) > CCl_3COOH ($\text{pK}_a = 0.66$) > CHCl_2COOH ($\text{pK}_a = 1.30$) > CH_3COOH ($\text{pK}_a = 4.76$).

CH_3COOH is completely inactive in the Diels-Alder and dehydration reactions of DMF with ethylene and no *p*-xylene could be detected even after reaction at 473 K for 24 h, probably due to its low acidity not enough to catalyze the dehydration reaction. In contrast, haloacetic acids show noticeable activity in the reaction. CF_2ClCOOH and CCl_3COOH appear to be efficient catalysts, with similar *p*-xylene production rate of $3.4 \text{ mmol h}^{-1} \text{ g}^{-1}$ ($\text{TOF} = 0.45 \text{ h}^{-1}$). These values are higher than those from H-Beta ($2.0 \text{ mmol h}^{-1} \text{ g}^{-1}$) and Sn-Beta ($2.9 \text{ mmol h}^{-1} \text{ g}^{-1}$) under the same reaction conditions (Table 1). It is interesting to note that CF_3COOH with highest proton concentration shows rather low activity in the Diels-Alder and dehydration reactions with *p*-xylene production rate of $1.1 \text{ mmol h}^{-1} \text{ g}^{-1}$ ($\text{TOF} = 0.17 \text{ h}^{-1}$). The effects of proton concentrations on the Diels-Alder and dehydration reactions of DMF with ethylene to produce *p*-xylene are summarized in Fig. 2. Obviously, a proper proton concentration can be optimized for the Diels-Alder and dehydration reactions catalyzed by haloacetic acids. Too high or too low proton concentration will result in poor

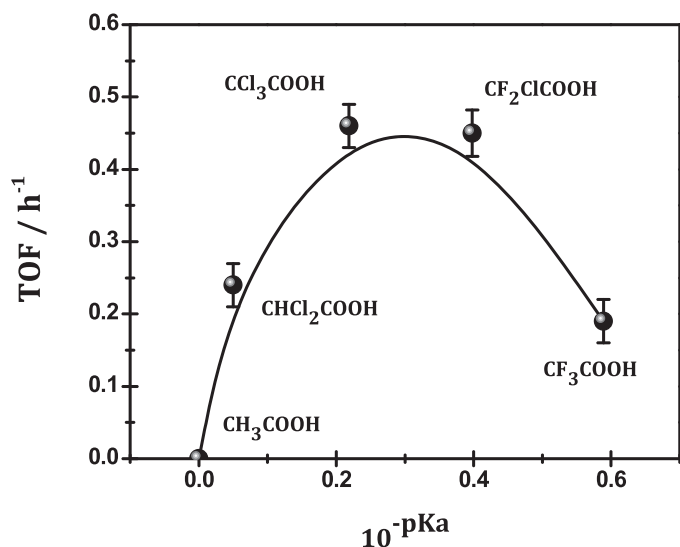


Fig. 2. Effect of proton concentrations on the Diels-Alder and dehydration reactions of DMF with ethylene to produce *p*-xylene. Reaction conditions: 5 mL 0.2 M DMF in dioxane, 0.1 mmol catalyst, $T=473$ K, $t=4$ h, $P=3.5$ MPa ethylene.

reaction activity, distinctly different from the previous reports on solid Brønsted acid catalysts [11,13,16].

Taking into account both the effects of solvents and catalysts, we come to the conclusion that a proper proton concentration should be good for the tandem Diels-Alder and dehydration reactions. A narrow range of proton concentration employed for research might be misleading. The second step of dehydration is a typical acid-catalyzed reaction and a higher concentration of protons is undoubtedly desired. In this case, the negative role of protons in

the tandem reaction should come from their impact on the first Diels-Alder step. A possible speculation is that protons will promote the transformation of DMF to 2,5-hexanedione (E, Fig. 1) and, therefore, hinder the formation of cycloadduct.

The kinetics of the Diels-Alder and dehydration reactions of DMF with ethylene over selected haloacetic acids are shown in Fig. 3. For all cases, linear increases in the *p*-xylene yield with reaction time are observed at *p*-xylene yield below 20%. Meanwhile, the *p*-xylene selectivities of ca. 65% are kept nearly unchanged during the reaction over all Brønsted catalysts investigated, indicating that the most by-products are formed in parallel with the cycloaddition reaction (Fig. 1). This is in great contrast to previous reports of the gradual increase in *p*-xylene selectivity with the progress of reaction [14], which should be explained from the different reaction conditions employed. In our quasi-homogeneous reaction system, the regional concentration difference induced by the adsorption and diffusion could be excluded and accurate kinetic studies could be performed.

Fig. 4 shows the Arrhenius plots of *p*-xylene production from the Diels-Alder and dehydration reactions of DMF with ethylene over haloacetic acid catalysts. Apparent activation energy values of 8.43, 8.35 and 8.41 kcal/mol could be calculated for CF_2ClCOOH , CHCl_2COOH and CF_3COOH , respectively. These three catalysts all belong to monocarboxylic acid and the halogen substituents only influence the proton dissociation from carboxyl, i.e. proton concentration (vide supra). Besides, they have no extra impacts on the Diels-Alder and hehydration reactions pathway. That is, the Diels-Alder and dehydration reactions of DMF with ethylene undergoes the same reaction pathway using haloacetic acid catalysts, and, therefore, shares the similar apparent activation energy of ~ 8.4 kcal/mol, which appear to be lower than the previous report using solid Brønsted acids as catalysts (10.8 ± 2.1 kcal/mol) [16].

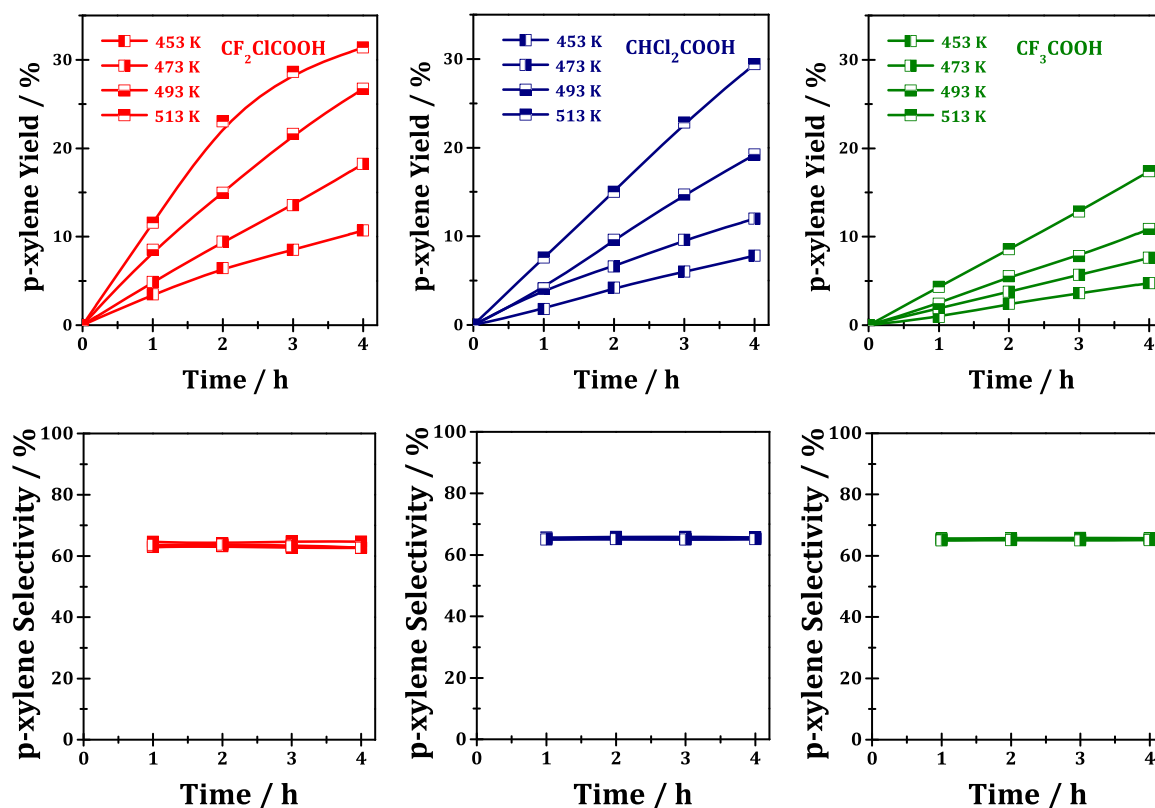


Fig. 3. Kinetics of the Diels-Alder and dehydration reactions of DMF with ethylene over haloacetic acid catalysts. Reaction conditions: 5 mL 0.2 M DMF in dioxane, 0.1 mmol catalyst, $T=453\text{K}–513$ K, $P=3.5$ MPa ethylene.

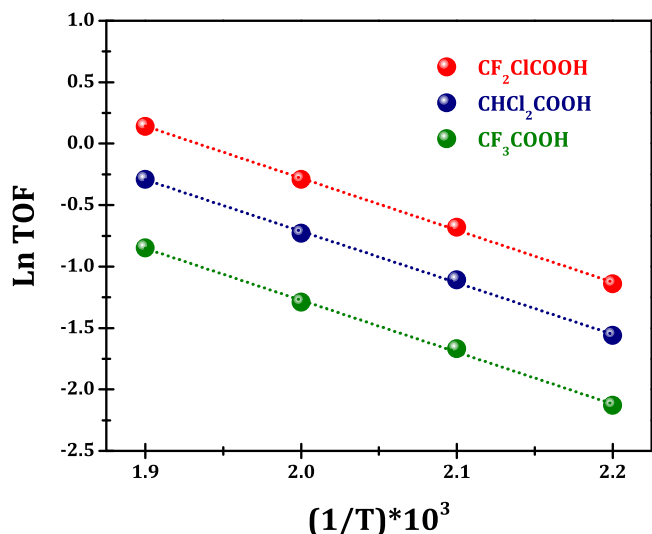


Fig. 4. Arrhenius plots of *p*-xylene production from the Diels-Alder and dehydration reactions of DMF with ethylene over haloacetic acid catalysts. Reaction conditions: 5 mL 0.2 M DMF in dioxane, 0.1 mmol catalyst, T = 453K–513 K, P = 3.5 MPa ethylene.

Table 2

The Diels-Alder and dehydration reactions of furan derivatives DMF with ethylene catalyzed by CF₂ClCOOH^a.

Entry	Substrate	Product	Conversion (%)	Yield (%)	Rate (mol·g ⁻¹ h ⁻¹) ^b
1			72.1	49.9	2.0
2			65.1	23.1	1.2
3			43.0	4.6	0.3
4			19.9	18.1	0.9
5			0	0	0
6			0	0	0

^a Reaction conditions: 5 mL 0.2 M DMF in DOX solvent, 0.1 mmol CDFA catalyst, 3.5 MPa ethylene, T = 473 K, t = 24 h.

^b Average value within 4 h.

On the basis of the above-mentioned results, CF₂ClCOOH appears to be an efficient catalyst for the Diels-Alder and dehydration reactions of DMF with ethylene in DOX solvent. We therefore investigated the Diels-Alder and dehydration reactions of several furan derivatives with ethylene catalyzed by CF₂ClCOOH and the results are summarized in Table 2. We find that the production of *p*-xylene (2.0 mmol h⁻¹ g⁻¹) is faster than toluene (1.2 mmol h⁻¹ g⁻¹) and then benzene (0.3 mmol h⁻¹ g⁻¹) under identical reaction conditions. That is to say, the reaction rate depends on the methyl substituents on the diene. Methyl substituent, as an electron donating group, on the diene will force the furan ring toward forming [4+2] cycloadduct [13,29,30]. The presence of methyl substituent on diene can also promote the dehydration of cycloadduct because the charged intermediates in the dehydration of the bicyclic adduct could be stabilized by the methyl substituents [13,31]. We also find that the selectivity of furan toward benzene (10.7%) is much lower than that of MF to toluene (35.5%) and DMF to *p*-xylene (65.3%). The lack of methyl substituent would result in the formation of more reactive dicarbonyl compounds via hydration (like E, Fig. 1; aldehyde groups are more active than ketone groups), which are easy to form dimers and oligomers (like F, Fig. 1). These results are in good agreement with literature reports [13,14], and are also supported by the darker colour of solution of furan than MF and DMF after reaction. Furan derivatives with different functional groups, MMF, FDCA and DMFDC, were further investigated as substrates for the Diels-Alder and dehydration reactions with

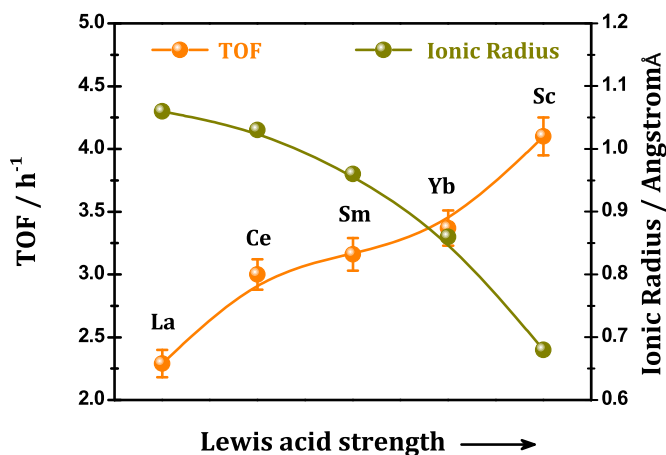


Fig. 5. Relationship between *p*-xylene production rate and the ionic diameter in rare-earth metal triflate catalysts. Reaction conditions: 5 mL 0.2 M DMF in dioxane, 0.01 mmol catalyst, T = 473 K, t = 4 h, P = 3.5 MPa ethylene.

ethylene. CF₂ClCOOH is active in the Diels-Alder and dehydration reactions of MMF with ethylene with a methyl *p*-toluate production rate of 0.9 mmol h⁻¹ g⁻¹ (Entry 4, Table 2), compared to the previous reports using Sn-Beta as catalyst [18,19]. The ~90% selectivity toward target product indicates that replacing of methyl group by carboxylate ester group efficiently inhibit the side reactions. The electron-withdrawing and steric hindrance effect of carboxylate ester substituent could make the furan ring stable and difficult to hydrolysis (In fact, no hydrolysis products could be detected). Meanwhile, this would greatly retard the desired cycloaddition, as reflected by the lower conversion of MMF (19.9%) compared to that of DMF (72.1%) under similar conditions. FDCA, the fully oxidized product of HMF, and its ester DMFDC could not reaction with ethylene under our reaction conditions and no desired products could be detected even after 24 h, in consistence with previous report with Sn-Beta as a catalyst [18]. The main reason should be the strong electron-withdrawing inductive effects of two carboxyl or carboxylic ester groups that completely suppress the formation of cycloadduct.

3.2. Metal triflates catalyzed Diels-Alder and dehydration reactions

Rare-earth metal triflates, known as versatile Lewis catalysts [32], were employed for the Diels-Alder and dehydration reactions of furan derivatives with ethylene. Here a high substrate/catalyst ratio of 100 was employed, and metal triflates were soluble in DOX solvent at elevated temperatures to form so-called quasi-homogeneous reaction system. Under our reaction conditions, all rare-earth metal triflates employed are active in the Diels-Alder and dehydration reactions of DMF with ethylene and TOF values of 2.3–4.1 h⁻¹ could be achieved for *p*-xylene production. Moreover, the ionic radii of metals in triflates show significant impacts on the TOF values. As shown in Fig. 5, a higher TOF value is obtained with a smaller ionic radius of metal in triflates. The relative Lewis acidity of rare-earth metal triflates has been evaluated based on their competitive dissociation observed by tandem mass spectrometry and a stronger Lewis acidity of triflates is obtained with smaller metal ionic radius [33]. Hence, it can be concluded that stronger Lewis acidity of rare-earth metal triflates would lead to the higher activity in the Diels-Alder and dehydration reactions of DMF with ethylene (Fig. 5). This is the first report of the effects of Lewis acidity on the tandem Diels-Alder dehydration reaction.

The kinetics of the Diels-Alder and dehydration reactions of DMF with ethylene over rare-earth metal triflates are shown in

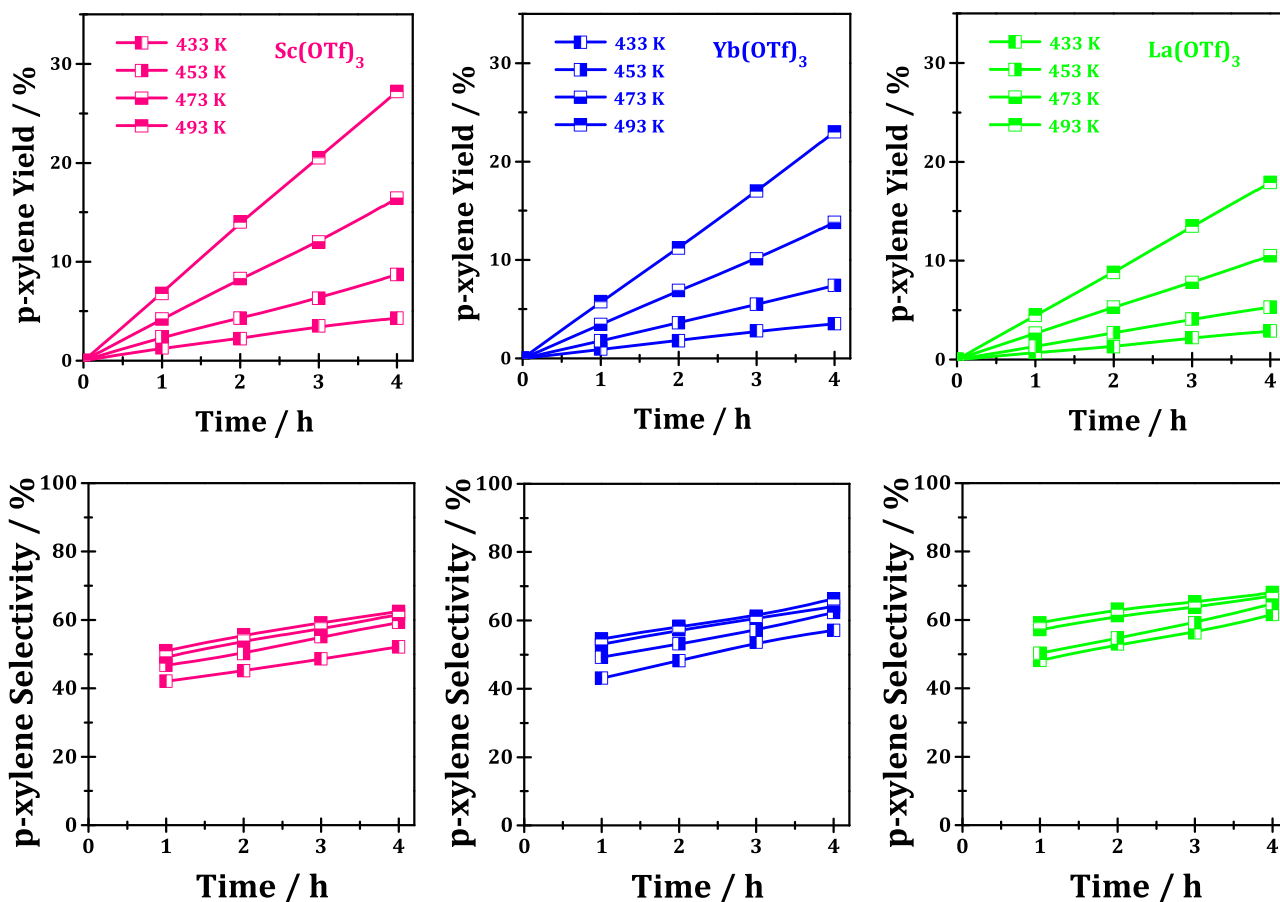


Fig. 6. Kinetics of the Diels-Alder and dehydration reactions of DMF with ethylene over rare-earth metal triflate catalysts. Reaction conditions: 5 mL 0.2 M DMF in dioxane, 0.1 mmol catalyst, $T = 433\text{K}–493\text{K}$, $P = 3.5\text{ MPa}$ ethylene.

Fig. 6. A linear increase in the *p*-xylene yield with reaction time could be observed over all catalysts employed at 433–493 K with *p*-xylene yield below 30%. In contrast to the cases of haloacetic acids catalyzed reaction processes, the *p*-xylene selectivities gradually increase with the progress of the reaction, indicating the different pathways for the formation of by-products as compared with those catalyzed by haloacetic acids.

The Arrhenius plots of *p*-xylene production from the Diels-Alder and dehydration reactions of DMF with ethylene over rare-earth metal triflates are shown in **Fig. 7**. Very similar apparent activation energy values of 13.0, 12.9 and 13.1 kcal/mol could be calculated for $\text{Sc}(\text{OTf})_3$, $\text{Yb}(\text{OTf})_3$ and $\text{La}(\text{OTf})_3$, respectively. These values are somewhat higher than that reported for the reaction catalyzed by solid Lewis acid Zr-Beta (10.5 kcal/mol) [19]. Moreover, the similar apparent activation energy values obtained indicate that the Diels-Alder and dehydration reactions of DMF with ethylene undergoes the same process over rare-earth metal triflate catalysts and the Lewis acidity does not change the reaction pathway at all.

Since $\text{Sc}(\text{OTf})_3$ is developed to be an efficient Lewis acid catalyst for the Diels-Alder and dehydration reactions of DMF with ethylene, the substrate scope of furan derivatives is further investigated. As shown in **Table 3**, the Diels-Alder and dehydration reactions of furan and MF with ethylene could be achieved with benzene and toluene production rate of 5.4 and 1.3 $\text{mmol h}^{-1} \text{g}^{-1}$, respectively. The trends in the activity and selectivity with $\text{Sc}(\text{OTf})_3$ as a Lewis catalyst is the same as those with CF_2ClCOOH as a Brønsted acid catalyst (vide supra). The Diels-Alder and dehydration reactions of MMF with ethylene could also be realized using $\text{Sc}(\text{OTf})_3$ as a Lewis catalyst, and a methyl *p*-toluate production rate of 7.7 $\text{mmol h}^{-1} \text{g}^{-1}$ with perfect selectivity of $\sim 99\%$ could be obtained

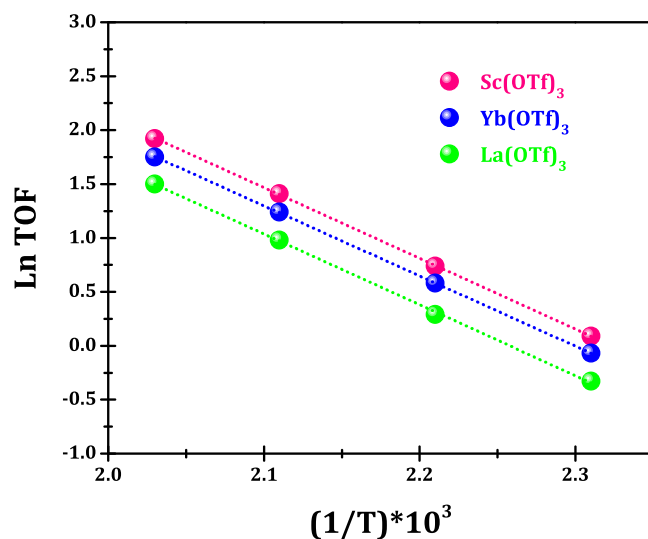














Fig. 7. Arrhenius plots of *p*-xylene production from the Diels-Alder and dehydration reactions of DMF with ethylene over rare-earth metal triflate catalysts. Reaction conditions: 5 mL 0.2 M DMF in dioxane, 0.01 mmol catalyst, $T = 433\text{K}–493\text{K}$, $P = 3.5\text{ MPa}$ ethylene.

(Entry 4, **Table 3**). Although $\text{Sc}(\text{OTf})_3$ shows very promising catalytic activity in the Diels-Alder and dehydration reactions of furan, MF, DMF and MMF with ethylene, it cannot catalyze the reaction of FDCA or DMFDC due to the strong electron-withdrawing of two carboxyl or carboxylic ester groups.

Table 3
The Diels-Alder and dehydration reactions of furan derivatives with ethylene catalyzed by $\text{Sc}(\text{OTf})_3$ ^a.

Entry	Substrate	Product	Conversion (%)	Yield (%)	Rate ($\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$) ^b
1			76.6	53.7	8.3
2			76.1	35.3	5.4
3			48.3	8.3	1.3
4			50.2	49.5	7.7
5			0	0	0
6			0	0	0

^a Reaction conditions: 5 mL 0.2 M DMF in DOX solvent, 0.01 mmol $\text{Sc}(\text{OTf})_3$ catalyst, 3.5 MPa ethylene, $T = 473 \text{ K}$, $t = 24 \text{ h}$.

^b Average value within 4 h.

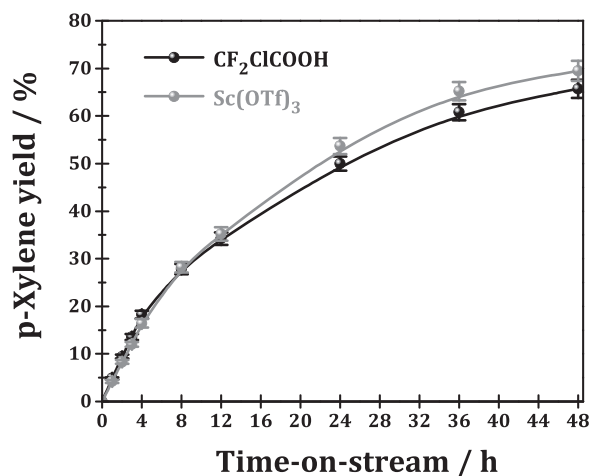


Fig. 8. Time-on-stream *p*-xylene yield from the Diels-Alder and dehydration reactions of DMF with ethylene over CF_2ClCOOH and $\text{Sc}(\text{OTf})_3$ till the complete conversion of DMF. Reaction conditions: 5 mL 0.2 M DMF in dioxane, 0.1 mmol CF_2ClCOOH or 0.01 mmol $\text{Sc}(\text{OTf})_3$, $T = 473 \text{ K}$, $P = 3.5 \text{ MPa}$ ethylene.

3.3. Brønsted acids versus Lewis acids for Diels-Alder and dehydration reactions

Solid Brønsted acids, e.g. zeolites and mixed oxides, and solid Lewis acids, e.g. Sn-Beta and Zr-beta, have been reported to be efficient heterogeneous catalysts in the tandem Diels-Alder and dehydration reactions of DMF with ethylene. In this study, we report liquid Brønsted acids, i.e. haloacetic acids, and Lewis acids, i.e. rare-earth metal triflates, to be active in the reaction. With the careful selected DOX solvent, a quasi-homogeneous reaction system could be formed, and a direct comparison between liquid Brønsted and Lewis acids catalyzed reaction could be made. As shown in Figs. 3 and 6, comparable *p*-xylene yield is obtained using optimized CF_2ClCOOH and $\text{Sc}(\text{OTf})_3$ catalysts at 473 K for 4 h. Considering that a ten times higher substrate/catalyst ratio is employed using $\text{Sc}(\text{OTf})_3$ than CF_2ClCOOH as catalyst, the TOF of *p*-xylene production catalyzed by $\text{Sc}(\text{OTf})_3$ (4.13 h^{-1}) is calculated to be ca. nine times higher than that catalyzed CF_2ClCOOH (0.45 h^{-1}). In such circumstances, $\text{Sc}(\text{OTf})_3$ is undoubtedly a more attracting catalyst than CF_2ClCOOH for the tandem Diels-Alder and dehydration reactions of DMF with ethylene although it bears a higher apparent activation energy (13.0 kcal/mol) than CF_2ClCOOH (8.4 kcal/mol). After the complete conversion of DMF, a final *p*-xylene yield of $\sim 70\%$ can be obtained over $\text{Sc}(\text{OTf})_3$, in contrast of the $\sim 65\%$ over CF_2ClCOOH (Fig. 8). Obviously, these values are determined by the final selectivity toward target product.

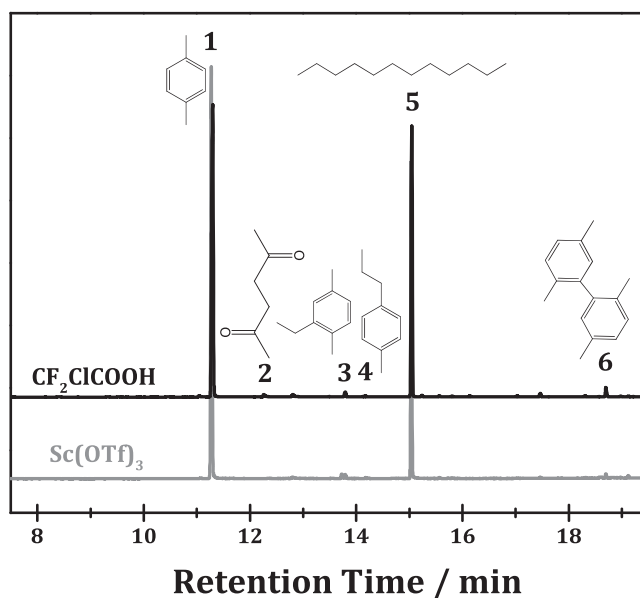


Fig. 9. GC-MS analysis of final products from the Diels-Alder and dehydration reactions of DMF with ethylene catalyzed by CF_2ClCOOH and $\text{Sc}(\text{OTf})_3$. Reaction conditions: 5 mL 0.2 M DMF in dioxane, 0.1 mmol CF_2ClCOOH or 0.01 mmol $\text{Sc}(\text{OTf})_3$, $T = 473 \text{ K}$, $t = 48 \text{ h}$, $P = 3.5 \text{ MPa}$ ethylene.

For more information on the overall reaction network in the Diels-Alder and dehydration reactions of DMF with ethylene and especial the side reaction, the final reaction products were analyzed by GC-MS. As shown in Fig. 9, the final products appear to be very clean and the target product *p*-xylene (1) of $>95\%$ among all detectable products can be achieved by using both CF_2ClCOOH and $\text{Sc}(\text{OTf})_3$ as catalysts. For the reaction catalyzed by CF_2ClCOOH , traces of 2,5-hexanedione (2) from the ring-opening hydrolysis of DMF, 2-ethyl-*p*-xylene (3) and 4-propyltoluene (4) from the alkylation of *p*-xylene product with ethylene and 2,2',5,5'-tetramethylbiphenyl (5) from the self-alkylation of *p*-xylene could be observed. In zeolite-catalyzed reaction system, the concentration of 2,5-hexanedione increases first and then decreases with increasing the conversion of DMF [14–16]. While the concentration of 2,5-hexanedione is very low and kept constant during the reaction. Clearly, the hydrolysis of DMF to 2,5-hexanedione can be efficiently suppressed by liquid monocarboxylic acids as catalysts. For the reaction catalyzed by $\text{Sc}(\text{OTf})_3$, only traces of 2-ethyl-*p*-xylene and 2,2',5,5'-tetramethylbiphenyl could be observed as by-products by GC-MS analysis. However, the *p*-xylene selectivity calculated from the internal standard *n*-dodecane only gives a value of $\sim 70\%$, indicating the formation of a fair amount of bulky products that could not be analyzed by GC-MS. These bulky products should come from the condensation of DMF or its hydrolysis product 2,5-hexanedione. On the basis of these results and the former kinetic data, a simplified reaction network can be established, as shown in Fig. 1.

It should be noted that more bulky by-products would be formed when solid acids were used as catalysts and a low carbon balance value was reported if these bulky by-products were not calculated as the by-products [13]. Under our reaction conditions, the final selectivities toward *p*-xylene in the Diels-Alder and dehydration reactions of DMF with ethylene were determined to be ~ 40 and ~ 50 using H-Beta and Sn-Beta as solid acid catalysts, respectively. These values are distinctly lower than those using liquid acid catalysts in a quasi-homogeneous reaction system.

4. Conclusion

In this study, a series of liquid Brønsted acids, i.e. haloacetic acids, and Lewis acids, i.e. rare-earth metal triflates are employed as catalysts for the tandem Diels-Alder and dehydration reactions of DMF with ethylene in a quasi-homogeneous reaction system. For haloacetic acids catalyzed Diels-Alder and dehydration reactions, a similar apparent energy value of ~ 8.4 kcal/mol is obtained for all catalysts investigated and a proper Brønsted acidity, i.e. proton concentration, is found to be good for the reaction. For metal triflates catalyzed Diels-Alder and dehydration reactions, a similar apparent energy value of ~ 13.0 kcal/mol is obtained and higher Lewis acidity is found to be good for the reaction.

Rare-earth metal triflates appear to be better catalysts than haloacetic acids in the tandem Diels-Alder and dehydration reactions of DMF with ethylene with a distinct higher TOF value of 4.13 h^{-1} than 0.45 h^{-1} under similar reaction conditions. Using the optimized catalysts CF_2ClCOOH and $\text{Sc}(\text{OTf})_3$, the reaction can be completed after 48 h at 473 K, giving final *p*-xylene yields of ~ 65 and $\sim 70\%$, respectively. The major by-products should be bulky oligomers from the condensation of DMF or its hydrolysis product 2,5-hexanedione, which could not be analyzed by GC or GC-MS. The substrate scope in the Diels-Alder and dehydration reactions reaction catalyzed by CF_2ClCOOH and $\text{Sc}(\text{OTf})_3$ can be successfully extended other furan derivatives, i.e. furan, MF and MMF, with ethylene, while the reaction of FDCA and DMFDC with ethylene could not proceed due to the strong electron-withdrawing inductive effects of functional groups.

Acknowledgements

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