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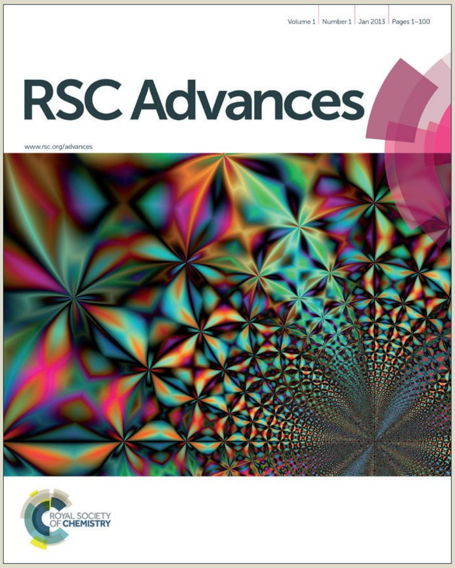

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ARTICLE

Efficient conversion of furfuryl alcohol to ethyl levulinate with sulfonic acid-functionalized MIL-101(Cr)

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Catalytic ethanolysis of furfuryl alcohol (FA) to ethyl levulinate (EL) with MIL-101(Cr)-SO_3H, prepared by simple one-pot hydrothermal treatment, is presented for the first time. The as-prepared catalyst with high surface area, hydrothermal and chemical stability, good dispersion, and feasible accessibility of -SO_3H Brønsted acid sites was found to show superior performance to others sulfonic acid-functionalized solid catalysts. Besides the special textural properties, the obtained good catalytic activity of 79.2% EL yield and 100% FA conversion was also depended on the density and strength of Brønsted acid, and the reaction parameters. A slight loss of catalytic activity in five consecutive recycles and hot filtration experiment confirmed the good stability of MIL-101(Cr)-SO_3H. Two coexisting reaction paths for the ethanolysis of FA to EL catalyzed by MIL-101(Cr)-SO_3H were proposed, wherein 2-ethoxymethylfuran (2-EMF) was observed to be the dominant intermediate.

1. Introduction

With the gradual depletion of fossil resources and environmental degradation, utilizing the abundant and renewable biomass resources *via* catalytic processes for the production of sustainable biofuels and biochemical has been stimulated as an alternative tendency.[1] The exploration of synthesizing alkyl levulinates (ALs) from green and biomass-derived molecules such as levulinic acid[2] and furfuryl alcohol (FA) via esterification or alcoholysis has been becoming the meaningful and popular research subjects. However, levulinic acid (LA) has a high cost as raw material for the industrial-scale production, the byproduct water formed during esterification may decelerate the reaction process and be energy-intensive for water evaporation. As a result, the alternate route involving alcoholysis of the inexpensive feedstock FA to prepare ALs has been expected.

ALs including methyl, ethyl, and *n*-butyl levulinates have been extensively used as solvents, plasticizing agents, odorous substances, and fuel additives,[3] and as precursors to produce chemicals (e.g., γ-valerolactone (GVL)) that can be further transfered into liquid fuels.[4,5] Conventional catalysts for the preparation of ALs are homogeneous acids (e.g., sulphuric acid, hydrofluoric acid, and *p*-toluenesulfonic acid), which are efficient for the target reaction, but suffer from serious environmental pollution, equipment corrosion, and difficulty in separation and purification. Therefore, the eco-friendly, sustainable, recyclable and low-cost heterogeneous acid catalysts can cater for the requirement of the application.

A great number of the conventional heterogeneous acid catalysts, such as macroporous ion-exchange resins (e.g., Amberlyst-15),[6] mesoporous aluminosilicates (e.g., Al-TUD-1),[7] sulfated metal oxides (e.g., SO_4^{2-}/TiO_2 and SO_4^{2-}/ZrO_2),[8] sulfonic acid grafted silica (e.g., SO_3H-SBA-15),[9] arylsulfonic acid functionalized hollow mesoporous carbon spheres (e.g., $ArSO_3H$-HMCSs)[10] and organosulfonic acid functionalized organosilica nanohybrids (e.g., $ArSO_3HSi(Et)Si$-Ph-NTs, Si(Et)Si-Pr/$ArSO_3H$ and Pr/$ArSO_3H$-Et/Ph-HNS)[11-13] have been explored for the production of ALs in the past five years. Good to excellent catalytic activity of the aforementioned catalysts in FA alcoholysis and LA esterification, the catalysts were urgently demanded in terms of the perfect morphology, high density and accessibility of the Brønsted acid sites, inexpensive raw materials and brief preparation protocols.

Owing to the diversity and large surface area and pore size, numerous unsaturated metal sites, and high hydrothermal and chemical stability,[14] metal-organic frameworks (MOFs) have obtained tremendous attention. Among more than 20,000 well-known MOFs, MIL-101, consisting of rigid terephthalate organic linkers and trimeric octahedral metal-oxo clusters, possesses two kinds of quasi-spherical mesoporous cages of 29 and 34 Å, with 12 and 16 Å windows and large surface areas (3100-5900 m^2/g).[15] Upon intentional functionalization during preparation, MIL-101(Cr) contains multiple functional sites (e.g., -NH_2, -SO_3H and HPW) that provide basicity and acidity, and is demonstrated to be efficient for the Knoevenagel condensation and Heck reaction, acetalization and ring opening reaction of styrene oxide. [16-18] A sulfonic acid functionalized MIL-101(Cr) [MIL-101(Cr)-SO_3H] emerged as an inert catalyst for cellulose hydrolysis, giving only 5.3% yield of total

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mono- and disaccharides at 120 ºC for 3 h in water.[19] MOF-SO_3H prepared by post-synthetic modification (PSM) were investigated for the fructose-to-HMF conversion in DMSO, showing 90% HMF yield with a full conversion of fructose at 120 ºC in 60 min.[20] Considering the bifunctional Lewis acid and Brønsted acid sites, MIL-101(Cr)-SO_3H was further explored for the transformation of glucose in GVL with 10 wt% water, achieving a high HMF yield of 44.9% and selectivity of 45.8%.[21] As the heterogeneous catalyst, MIL-53(Al), without any functionalization, was also discussed for the synthesis of HMF from carboxymethyl cellulose (CMC) in water, and a moderate HMF yield of 40.3% could be obtained at 200 ºC for 4 h.[22] Naturally plant-derived building blocks, phytic acid (PhyA), coordinated with Nb^{5+} forming the niobium phytate showed very high catalytic activities for both cyanosilylation of carbonyl compounds with TMSCN and dehydration of carbohydrates to produce HMF.[23] The new organic-inorganic mesoporous catalyst Zr-PhyA and Zr-CA with both Lewis acidic and basic sites could achieve excellent catalytic performance for the conversion of LA and its esters to produce GVL.[24,25] Similarly, a new Zr-HBA was prepared from the coprecipitation of 4-hydroxybenzoic acid dipotassium salt and $ZrOCl_2$, which was very active for the catalytic transfer hydrogenation (CTH) of EL to GVL, giving a high GVL yield of 94.4%.[26] Due to the heterogeneous nature, the intrinsic structure-activity is still subjected to debate.

Herein, for the first time, the simple one-pot hydrothermal prepared catalyst MIL-101(Cr)-SO_3H was investigated in the alcoholysis of FA. For comparison, the catalytic properties of other classic SO_3H-functionalized solid acid catalysts were also explored. The mechanism of the alcoholysis of FA catalysed by MIL-101(Cr)-SO_3H was finally discussed.

2. Experimental

2.1 Material

2-Sulfoterephthalic acid monosodium salt (>98%) was purchased from J&K Chemical Ltd (shanghai, China); protonated Nafion NR50 was purchased from Alfa Aesar (Tianjin, China); and FA (98%) was purchased from Maya reagent Co. Ltd. Terephthalic acid (99%), Amberlyst-15, EL and angelica lactone in analytical grade were purchased from Shanghai Aladdin Industrial Inc; 2-ethoxymethylfuran (2-EMF) (>98%) was purchased from Shanghai Bide Pharmatech Ltd; CrO_3, concentrated hydrochloric acid and EtOH (AR grade) were purchased from Chongqing Chuandong Chemical Reagent Company and used without further purification. Deionized water was obtained from Milli-Q Advantage A10 (USA) ultrapure water purification system.

2.2 Catalysts preparation

The preparation of MIL-101(Cr)-SO_3H by hydrothermal method was carried out, according to a recent literature[19] with slight modifications. In a general procedure, 2-sulfoterephthalic acid monosodium salt (2-$NaSO_3$-H_2BDC) (3.35 g, 12.5 mmol), CrO_3 (1.25 g, 12.5 mmol), and concentrated hydrochloric acid (0.91 g (12 M), 25 mmol) were dissolved into 50 mL of deionized water and stirred for a few minutes at room temperature. The resulting mixture was then transferred to a Teflon-lined stainless steel autoclave maintained in an oven at 180 ºC for 6 d. The produced solid was filtered and washed with deionized water and then with methanol for three times. The resulting sulfonic acid-functionalized MIL-101(Cr) was denoted as MIL-101(Cr)-SO_3H.

For comparison, UiO-66(Zr)-SO_3H and Fe_3O_4@SiO_2-SO_3H catalysts were also prepared by following previously described methods.[27-29]

2.3 Catalysts characterization

The crystalline structures were analyzed by X-ray diffraction (XRD) with a Shimadzu XRD-6000 diffractometer using Cu Kα radiation (λ= 0.1541 nm) in a scanning range of 2-10° at 0.5°/min. The textural properties of the prepared samples were measured by N_2 adsorption at -196 ºC in a Micromeritics ASAP 2020 instrument. The sample was outgassed in vacuum at 150 ºC for 10 h prior to the adsorption measurement. FT-IR spectra were recorded on a Nicolet 360 FT-IR instrument (KBr disks). The amount of sulfonic acid groups of MIL-101(Cr)-SO_3H was determined by acid-base titration using saturated NaCl solution as an ion-exchange agent. In a typical procedure, 0.5 g of MIL-101(Cr)-SO_3H was suspended in 20 g of aqueous NaCl saturated solution. The resulting suspension was stirred at room temperature for at least 24 h until the equilibrium reached, followed by filtration and washing with 30 mL of deionized water. Finally, the filtrate was titrated with 0.1 M NaOH solution. For comparison, elemental analysis by Vario EL *III* was used to determine the contents of sulphur in the MIL-101(Cr)-SO_3H catalysts. The morphology of the catalysts was investigated using a field-emission scanning electron microscopy (FE-SEM) Zeiss SUPRA 55 with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were recorded with Philips Tecnai 20 and JEOL JEM-2010 HR-TEM. The accelerating voltage was 200 kV in each case. The actual total amount of chromium leaching was determined by ICP-MS on a Vista Axial instrument (Varian of USA).

2.4 Typical procedure for catalytic conversion of furfuryl alcohol into ethyl levulinate

In a typical procedure, FA (0.1 mL, 1.15 mmol), MIL-101(Cr)-SO_3H (100 mg), and ethanol (4 mL, 69.00 mmol) were added into a 25 mL stainless steel vessel with a Teflon lining and sealed by a screw cap. The reactor was placed into a preheated oil bath maintained at 140 ºC under autogeneous pressure for 2 h with magnetically stirring. Zero time was recorded when the reactor was immersed into the preheated oil bath. After the desired reaction time, the reactor was quickly removed from the oil bath and the reaction was quenched by tap-water. Samples were withdrawn, diluted with ethanol, and centrifuged at 12000 rpm for 5 min. The clear liquid was filtered with a 0.45 μm syringe filter prior to analysis by gas chromatography (GC) on an Agilent 7890 B.

2.5 Analytical methods

Quantitative analysis of FA, 2-EMF and EL was implemented by gas chromatography (GC) on an Agilent 7890 B instrument with a HP-5 column (30 m × 0.32 mm ID × 0.25 μm) equipped with a flame ionization detector (FID). Operating conditions were as follows: the flow rate of the N_2 carrier gas was 1 mL/min, the injection port temperature was 250 ºC, the initial temperature of oven was 100 ºC

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(held for 2 min) and then increased to 245 ºC (keeping for 5 min), and the detector temperature was 245 ºC. Naphthalene was applied as an internal standard. The qualitative analysis of the liquid products of the reaction was performed by GC/MS (Agilent 6890-5973) with DB-17 capillary column (60 m×0.25 mm×0.25 μm).

FA conversion = [1- (mole of FA) / (mole of initial FA)] ×100%

2-EMF yield = [mole of 2-EMF/mole of starting FA] ×100%

EL yield = [mole of EL/mole of starting FA] ×100%

3. Results and discussion

3.1 Synthesis of EL from FA catalyzed by various acidic catalysts

Initially, the one-pot conversion of FA to EL was investigated with various sulfonic acid-based solid catalysts, their physical properties and catalytic performance results are shown in Table 1. The controlled trial without any catalyst (Table 1, Entry 1) showed <2% yield of EL with only 3.2% that of intermediate 2-EMF, demonstrating the need of external catalysts for the catalytic ethanolysis of FA. The use of MIL-101(Cr) as catalyst was also carried out, but no reaction for converting FA to EL, which could be ascribed to the adsorption of trace intermediate and target product into pores of MIL-101(Cr).

Among the examined multiple sulfonic acid-functionalized solid catalysts, almost complete conversion was obtained with MIL-101(Cr)-SO_3H, Nafion NR50, Fe_3O_4@SiO_2-SO_3H and Amberlyst-15 but the selectivity to EL showed significant difference (Table 1, Entries 4-7). The lower catalytic activity (3.1% EL yield; Table 1, Entry 3) of UiO-66(Zr)-SO_3H with the high 20.8% yield of 2-EMF confirmed that the first step of FA ethanolysis can be easily reacted and the modicum of active sites can satisfy the reaction demand. MIL-101(Cr)-SO_3H (79.2% EL yield; Table 1, Entry 4) possessed similar textural properties to UiO-66(Zr)-SO_3H; however, the Brønsted acid site density of the aforementioned UiO-66(Zr)-SO_3H (0.03 mmol (H^+)/g) was clearly lower than that of MIL-101(Cr)-SO_3H (1.01 mmol (H^+)/g). The results showed that protonation of the hydroxyl groups of FA molecules by -SO_3H groups was the first step of the ethanolysis of FA, wherein the Brønsted acid site density significantly influenced the catalytic activity. The MIL-101(Cr)-SO_3H catalyst (79.2% EL yield; Table 1, Entry 4) possesses unique textural properties, including 3D periodic mesocages (~29 and 34 Å)[30] and high specific surface area of 1492 m^2/g, assuring that the plentiful -SO_3H sites well disperse throughout the hybrid catalysts, which can improve the accessibility of FA molecules to -SO_3H sites, thus facilitating the mass transfer of FA-to-EL molecules. Accordingly, the fact partially explained the lower yield of EL catalyzed by Fe_3O_4@SiO_2-SO_3H (61.6%; Table 1, Entry 6) and Amberlyst-15 (51.7%; Table 1, Entry 7), which separately provided a little higher (1.2 mmol/g) and more higher -SO_3H density (4.7 mmol/g), yet the poor textural properties with small S_{BET} and pore volumn go against the mass transport and the formation of EL. The low yield also ascribed to the much higher unit space acidic sites resulted from the disadvantaged textural properties, which was in favour of the side reaction to yield oligomeric condensation products of FA such us 2,2-methylenebisfuran[31] and trace angelica lactone.[10,11] It can be concluded that the heterogeneous acid catalytic activity is determined remarkably by their morphological characteristics and textural properties. Additional, catalyst Nafion NR50 with low Brønsted acid site density and poor textural property showed moderate EL yield (60.1%; Table 1, Entry 5). It is proposed that the F group can provide stronger electron-withdrawing microenvironments, which leads to stronger Brønsted acid strength and stronger prnton-releasing ability.[12]

Table 1 Conversion of FA into EL catalyzed by various catalysts[a]

Entry	Catalyst	S_{BET} [m^2/g]	Pore volumn [cm^3/g]	$A_{titration}$ [mmol(H^+)/g]	FA conv. (%)	EL yield (%)	2-EMF yield (%)
1	No catalyst	—	—	—	14.9	1.6	3.2
2	MIL-101(Cr)	2603	1.30	—	—	—	—
3	UiO-66(Zr)-SO_3H	975[19]	0.44[19]	0.03	23.4	3.1	20.8
4	MIL-101(Cr)-SO_3H	1492	0.86	1.01	100	79.2	0
5	Nafion NR50[b]	<1	—	0.45	100	60.1	0
6	Fe_3O_4@SiO_2-SO_3H[c]	37.6[21]	0.08[21]	1.20	>99.5	61.6	14.5
7	Amberlyst-15[d]	~50	—	4.70	100	51.7	0

a Reaction conditions: molar ratio of FA to EtOH =1:60, MIL-101(Cr)-SO_3H (100 mg), 140 ºC, and 2 h.

b Adding 0.2222 g Nafion NR50, corresponding to 0.1 mmol H^+.

c Adding 0.0833 g Fe_3O_4@SiO_2-SO_3H, corresponding to 0.1 mmol H^+.

d Adding 0.0213 g Amberlyst-15, corresponding to 0.1 mmol H^+.

Hence, the Brønsted acid density and strength ensured the target ethanolysis reaction to proceed at a fast rate, while the textural properties dominated the catalytic activity to a great extent.

3.2 Effect of reaction temperature on FA-to-EL conversion

The influence of temperature on the ethanolysis of FA was studied at 120, 140 and 160 ºC and the results are shown in Fig. 1a and 1b. It was revealed that temperature had a significant effect on EL formation. With a fixed reaction temperature at 120 ºC, the yield of EL increased rapidly with the prolonged reaction time, which grew from 18% (30 min) to 70.2% (120 min) (Fig. 1a). Meanwhile, the 2-EMF yield dropped to 3.1% (180 min) from 36.1% (30 min) (Fig. 1b),

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which implied that the 2-EMF as an intermediate was further transferred to EL, in accordance with the previous reports.[10,11,13,32,33]At a higher temperature of 140 ºC, a sharp increase in the EL yield (up to 79.2%) was obtained with MIL-101(Cr)-SO_3H at 140 ºC in 2 h, while further extending the reaction time didn't increase the yield of EL. Furthermore, 2-EMF cannot be detected at 140 ºC, suggesting that the conversion of 2-EMF was a fast response and by-products or intermediates may produce in the reaction system, accompanying with the formation of EL. Fig. 2 further demonstrated that the conversion of 2-EMF for the EL affected mostly by temperature, and 2-EMF was the main intermediate according to the supposed path 1 in 3.7. As expected, some oligomeric condensation products derived from furfuryl alcohol were identified by GC-MS. Formation of the hydrophilic compounds might be adsorbed on the surface of the catalyst MIL-101(Cr)-SO_3H, which inhibited the accessibility of the active sites and effective mass transfer, decreased the catalytic performance of MIL-101(Cr)-SO_3H. When the reaction was performed at 160 ºC, the rate of EL formation was rather slow in Fig. 1a. Even with an increased reaction time, a quite stable EL yield of around 77% was observed. At a higher temperature of 160 ºC, the conversion of intermediates to EL was facilitated, indicating that the reaction pathway mainly involved the etherification of FA followed by translation of the 2-EMF to EL.

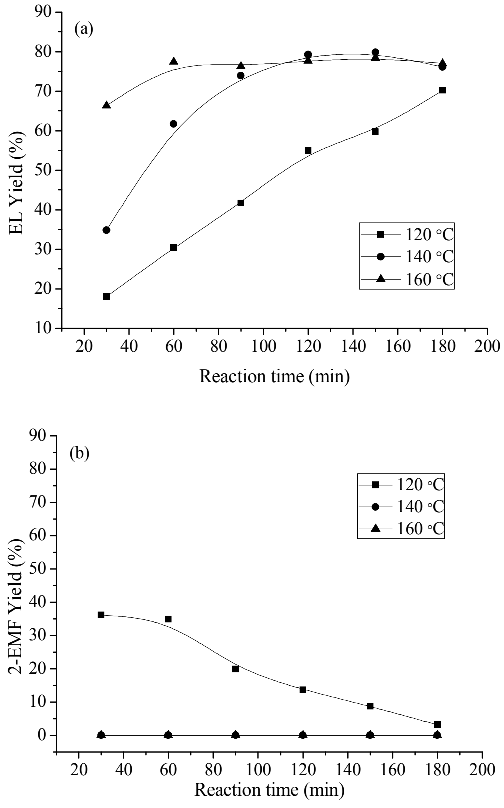

Fig. 1 Effects of reaction temperature on catalytic conversion of FA to EL over MIL-101-SO_3H. a) Yield of EL, b) yield of 2-EMF. Reaction conditions: molar ratio of FA to EtOH=1:60, and MIL-101(Cr)-SO_3H (100 mg).

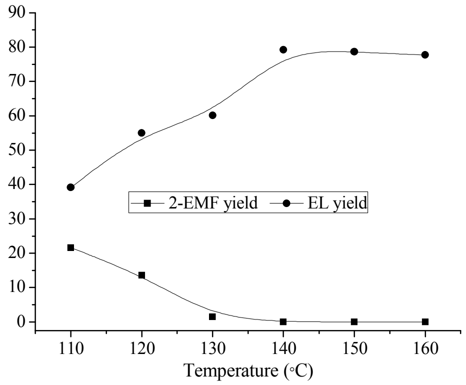

Fig. 2 Yield of EL converted from 2-EMF with temperature react for 2 h. Reaction conditions: molar ratio of FA to EtOH=1:60, and MIL-101(Cr)-SO_3H (100 mg).

3.3 Influence of FA-to-EtOH molar ratio on the conversion of FA to EL

One of the important process parameters was the FA-to-EtOH molar ratio, for which the concentration of FA determined by the concentration of EtOH with the crucial factor for the FA polymerization degree.[10,32,34] The effect of molar ratio on conversion and selectivity pattern was studied by varying the ratio from 1:30 to 1:75 and the results are shown in Fig. 3. With an increase in molar ratio from 1:30 to 1:60, the EL selectivity increased significantly due to the inhibition of the partial FA polymerization to some extent. The used minimum volume of EtOH also determined the relatively higher density of acidic sites, which resulted in a similar lower EL yield in line with Fe_3O_4@SiO_2-SO_3H (Table 1, Entry 6). At a higher FA-to-EtOH molar ratio such us 1:75, the substrate was diluted and the accumulation of higher concentration of the intermediate 2-EMF on the active sites retarded further rehydration to EL. The molar ratio of 1:60 was optimum to obtain complete conversion of FA and accelerate the intermediate 2-EMF for the further acidification.

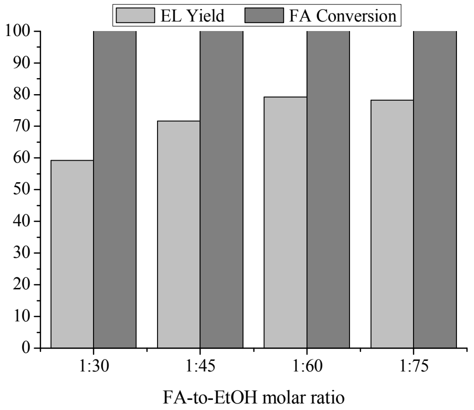

Fig. 3 Influence of FA-to-EtOH molar ratio on the catalytic activity of MIL-101-SO_3H in ethanolysis of FA to EL. Reaction conditions: MIL-101(Cr)-SO_3H (100 mg), 140 ºC, and 2 h.

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3.4 The results of the conversion of FA into EL with different catalyst amounts

The study on the effect of catalyst amounts on the ethanolysis of FA showed that the yield of EL increased from 47.4 to 79.2% with a gradually increase of catalyst dosage from 25 to 100 mg (Fig. 4). Moreover, the intermediate 2-EMF was completely converted, with a sharp decrease in the yield of which from 36.1% (25 mg) to 0, the conversion induced the increase of the EL yield by 1.7 times (~80%). The lowest EL yield with relatively high yield of 2-EMF indicated that the second step of rehydration of 2-EMF to EL needed enough acidic sites and the formation of 2-EMF from FA was easy, which is in accordance with that of UiO-66(Zr)-SO_3H (Table 1, Entry 3). The higher catalyst loading with equivalent Brønsted acid concentration resulted in the more availability of Brønsted acid sites, thus facilitating a faster consumption of FA and rehydration of the intermediates to EL. When the amount of MIL-101(Cr)-SO_3H further increased to 125 and 150 mg which is the augment of unit space acidic sites, the complete conversion of FA remain unchanged, but the EL yield dropped to 67.2% and 67.3%, respectively. Accelerated accumulation of some oligomers derived from the FA polymerization may cover and block the Brønsted acid sites of the MIL-101(Cr)-SO_3H, which eventually lead to the reduction of EL formation. The obtained experimental results were very consistent with the former data, which achieved a lower EL yield over Amberlyst-15 with higher unit space acidic sites (Table 1, Entry 6).

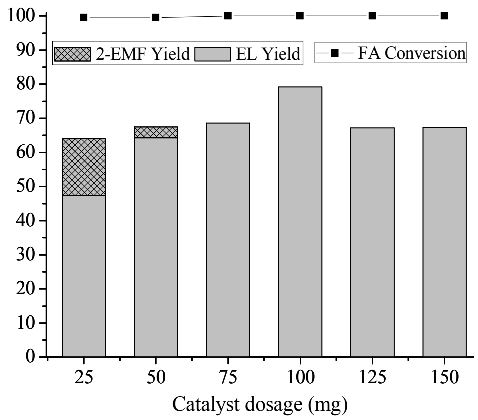

Fig. 4 The results of the conversion of FA into EL with different catalyst amounts. Reaction conditions: molar ratio of FA to EtOH =1:60, 140 ºC, 2 h.

3.5 Reaction of FA with different alcohols to form alkyl levulinates

Furthermore, a variety of alkyl alcohols were chosen to implement the alcoholysis of FA to study the scope of the reaction (Fig. 5). All of the reactions were carried out at 140 ºC in a FA-to-Alcohol molar ratio of 1:60 for 2 h. When methanol was used, methyl levulinate was only obtained in a yield of 31.3%. The minimum molar mass of the methanol among the alcohols decided the highest Brønsted acid sites concentration for the minimum volume. It accorded that more catalyst amounts led to the accumulation of oligomers even the reduction of methyl levulinate formation. In contrast to the methyl levulinate formation, treatment of FA with *n*-propanol or isopropanol, the yields of *n*-propyl levulinate and isopropyl levulinate increased significantly to 79.5% and 61.8% within 2 h, respectively. The crucial difference between the formation of *n*-propyl levulinate and isopropyl levulinate was significantly depended on the steric effects, the same effect of which was much more obvious when using *n*-butanol and *i*-butanol. With improving carbon chain length of the alcohol, the reactions of FA with the *n*-butanol and *i*-butanol being converted to the corresponding intermediate 2-butoxymethylfuran, 2-(*i*-butoxy)methylfuran, the followed translation of the intermediates into the BL became much more difficult, only a low yield of BL (55.9% and 50.8%, respectively) was obtained. When the carbon chain of alcohol increased, a space hindrance occured on the hydroxyl of the alcohol,[35] which probably reduced the efficient nucleophilic attack of them to the protonized hydroxyl groups of FA by -SO_3H sites.

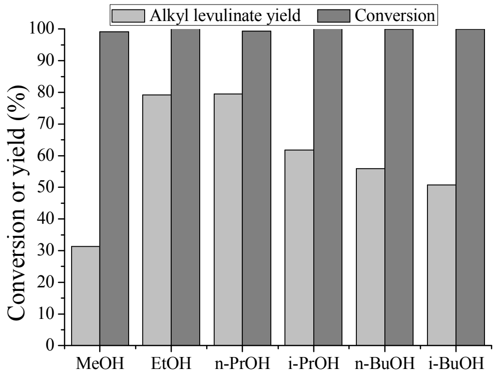

Fig. 5 Reaction of FA with different alcohols to form alkyl levulinates. Reaction conditions: molar ratio of FA to EtOH =1:60, MIL-101(Cr)-SO_3H (100 mg), 140 ºC, 2 h.

3.6 Catalyst recycling

Apart from good catalytic activity, long-term stability is an important issue needed to concern for solid catalysts. In order to demonstrate the reusability of MIL-101(Cr)-SO_3H, a five-cycle experiment was carried out, the catalyst was separated by centrifugation and then washed successively with water and ethanol three times followed by drying at 80 ºC in a vacuum oven for the next cycle. As shown in Fig. 6, the measured yields of the desired product EL decreased from 79.2% to 71.9%, indicating that the catalyst was almost stable at the optimum reaction condition during the recycling process. Furthermore, the FT-IR spectran and XRD patterns (Figures 7 & 8) of the fresh and recovered catalysts maintained almost no change, verifying the stability of the structure and the active sites. Unfortunatedly, the slight loss of catalytic activity of EL yield (71.9%) in fifth run could be attributed to the adsorption of some oligomeric products (detected by GC-MS in Fig. S2) derived from the FA polymerization on the solid catalyst and even blocked the active sites.

To further verify whether the catalytic process was heterogeneous or homogeneous, the MIL-101(Cr)-SO_3H catalyst was removed from the reaction solution by filtration after reacting for 30 min at 140 ºC. The filtrate without solid catalyst was continued to react at 140 ºC for another 150 min. As shown in Fig. S1, stable yields of EL (around 38%) were observed after removal of the MIL-101(Cr)-SO_3H

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catalyst, while a sharp increase in EL yield was detected in the presence of the catalyst for the rest of time. These results demonstrated that MIL-101(Cr)-SO_3H was heterogeneous in the production of EL from FA. ICP-MS analysis confirmed that less than 0.3 wt% of total Cr was leached from MIL-101(Cr)-SO_3H to EtOH during the reaction, which indicated the high stability of the catalyst under the optimal conditions.

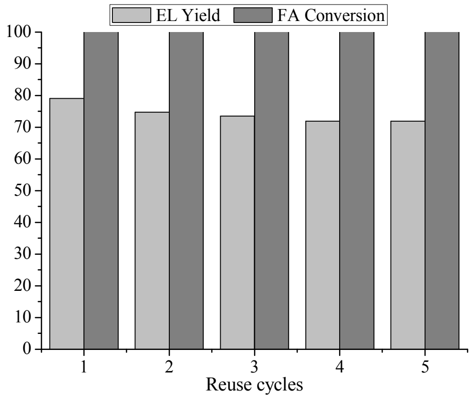

Fig. 6 Catalyst recycling experiments of MIL-101-SO3H. Reaction conditions: molar ratio of FA to EtOH =1:60, MIL-101(Cr)-SO_3H (100 mg), 140 ºC, 2 h.

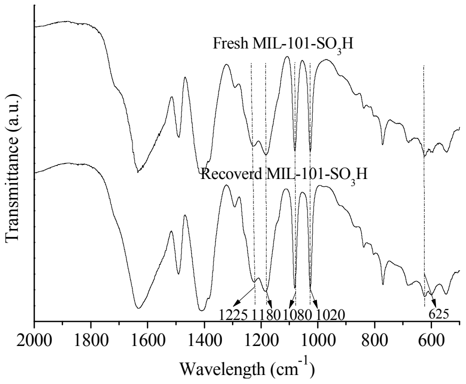

Fig. 7 FT-IR spectra of the fresh and recovered MIL-101(Cr)-SO_3H catalysts.

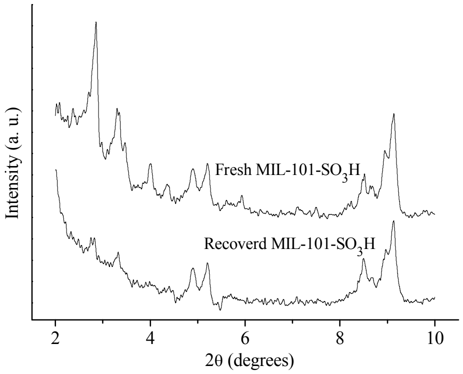

Fig. 8 XRD patterns of the fresh and recovered MIL-101(Cr)-SO_3H catalysts.

3.7 Possible mechanism

According to the literature[11,13,36] and the identified intermediates and byproducts (Fig. S2, Table S1) in the work, two possible reaction paths for the ethanolysis of FA to prepare EL are proposed (Scheme S1). Observations from the sulfonic acid-functionalized catalysts, a possible mechanism of FA transformation to EL always involves the formation of intermediate 2-EMF derived from the ethanolysis of FA and the followed acidification of the 2-EMF to EL, as show in the path 1 (Scheme S1). The process includes the first step of the protonation of the hydroxyl group to form intermediates 4,5-diethoxy-5-hydroxypentan-2-one (DHP) and 4,5,5-triethoxy-pentan-2-one (TEP), the former of which can be further attacked by EtOH to turn to the latter with the release of water. 2-EMF, DHP and TEP were all detected by GC-MS in our explored catalytic reaction, which implied the possible of the co-existence of the two paths. Table S1 indicates that the relative amount of the intermediate 2-EMF is much higher than that of TEP. To further verify the primary reaction in our studied system, the intermittent sampling reaction was carried out and detected by GC-MS. As shown in Fig. S3, the relative content of EL increased with the prolonged time, meanwhile, the intermediate EMF decreased inversely with the TEP raised, which indicates that the reaction is mostly to proceed via the path 1, and the transformation by path 2 for EL is negligible and slow. Diethyl ether (DEE) was the product of the TEP isomerization for EL. The results in Fig. S3 show the negligible formation of DEE, ulteriorly indicating that the conversion of FA to EL is conducted mainly through 2-EMF while by TEP hardly no transformation for the formation of EL. Furthermore, we speculated that the negligible formation of DEE catalyzed by MIL-101(Cr)-SO_3H is partly related to the mesoporosity of the catalyst.[7]

4. Conclusions

The unique textural properties catalyst MIL-101(Cr)-SO_3H was investigated for the alcoholysis of FA, the catalytic properties comparing with other classic sulfonic acid-functionalized solid acid catalysts. It was demonstrated that Brønsted acid density and strength of MIL-101(Cr)-SO_3H mainly accelerated the ethanolysis reaction, while the textural properties dominated the catalytic activity to a great extent. Under the optimum reaction conditions (FA:EtOH=1:60, MIL-101(Cr)-SO_3H (100 mg), 140 ºC, and 2 h), up to 79.2% yield of EL and 100% FA conversion were obtained. Finally, the reusability and hot filtration experiments were discussed, confirming the stability and heterogeneous of MIL-101(Cr)-SO_3H. The transformation of the ethoxylysis of FA catalysed by MIL-101(Cr)-SO_3H proceeded mainly in path 2 with 2-EMF acted as the intermediate.

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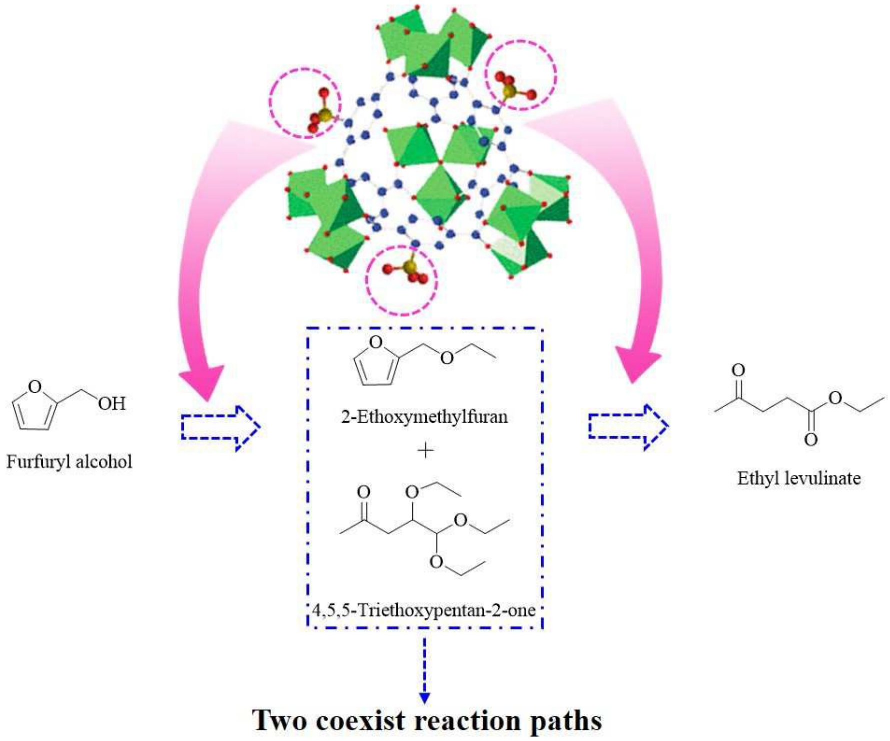
Graphic Abstract:



MIL-101(Cr)-SO_3H with highly dispersed Brønsted acid sites was efficient and robust for ethanolysis of furfural alcohol to ethyl levulinate