Dipolar Modification in Heterogeneous Catalysts under Electron Beam Irradiation for the Conversion of Biomass-Derived Platform Molecules

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KEYWORDS: biomass-derived platform molecules, electron beam irradiation, irradiation, dipolar catalyst, biomass

ABSTRACT: Herein, an efficient and practical approach for dipolar modification of commercially available solid catalysts is reported. The solid catalysts HMS (hexagonal mesoporous silica)-DMSO decorated with organic dipolar layers are designed and synthesized by radiation technology under simple and accessible conditions. The dipolar catalysts can serve as platforms to introduce various active sites, benefiting from the flexibility and diversity of the dipolar layer, which in turn allow them to achieve catalytic performance in relatively friendly systems. Specifically, the upgraded dipolar catalyst HMS-DMSO-SO_3H exhibits good performance in converting the oxidized lignin model compound of α-hydroxyacetophenone to 1,3-dioxolane derivatives and dehydrating isomaltulose to glycosyloxymethyl-furfural (GMF).

With the world energy crisis and total global energy consumption increasing dramatically, it is essential to develop methods for the efficient use of renewable resources.[1-3] Biomass, as an attractive carbon-based source, has been widely used to produce value-added fine chemicals and fuels.[4-8] The catalytic activation/cleavage of ubiquitous C–C/C–O bonds in biomass is crucial through various methods, including oxygen removal processes and increasing the molecular weight *via* C–C coupling reactions.[9-11] Efficient regulation of the state of reaction intermediates derived from C-C/C-O bond activation/cleavage to maximize the selectivity and yield of bio-based products is a key challenge. In this context, a valid strategy for this goal in heterogeneous catalysis is to enrich the dipolarity of the solid catalyst surface, allowing the reactants to participate in specific non-covalent interactions to stabilize or destabilize the reaction intermediates, thereby enabling the transformations to proceed smoothly.[12-18] However, there is still a lack of universal methods to prepare dipolar catalysts.

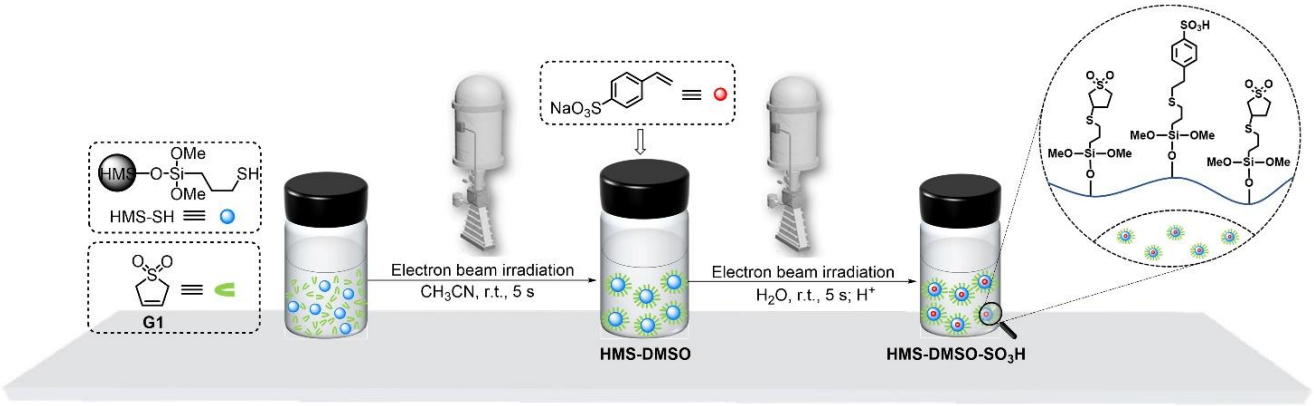
Despite these encountered challenges, with great efforts and contributions from many pioneers, various dipolar catalysts have been designed and synthesized successfully for the conversion of biomass.[12, 19] For example, the organic–inorganic nanocomposite catalysts with dipolar microenvironments were prepared, which exhibited excellent catalytic performance for the selective conversion of fructose to HMF in a mixed solvent of water and tetrahydrofuran.[20] Xiao and co-workers developed the heterogeneous catalyst with strong dipolar moieties through constructing microenvironment to tune the performance of active sites.[21] The catalysts exhibit high yields of fructose to 5-hydroxymethylfurfural in THF. Parallelly, a dipolar and flexible linear polymer polyvinylpyrrolidone (PVP) was incorporated into the pores of the acidic COF material to facilitate the fructose dehydration reaction.[22] Recently, the HCP materials with a dipolar moiety have been developed as alternatives to DMF in the conversion of NaN_3 to benzylic azides and triazoles.[23] Although these strategies have been developed, complex designs, long synthesis periods and lack of clean processes lead to high costs of catalyst synthesis, which are the important factors that limiting their application in industry.[24] From a catalyst

design perspective, it is generally recommended to optimize the already existing catalyst for a specific process, which mainly depends on the needs of the user, rather than to develop an entirely new catalyst material.[25] Obviously, the development of general and eco-efficient methods for dipolar modification of readily available catalysts or supports is one of the important issues that chemists need to address urgently at present.

Currently, electron beam irradiation (EBI) technology has been used as a green replacement method for traditional chemical processing, especially surface modification processes.[26-30] The EBI process is a flow of energetic electrons generated by an accelerator that directly injects energy to the materials, and then initiates a series of chemical reactions through free radicals to improve product quality by changing its chemical and physical properties. Compared with other conventional methods, the EBI technology is an efficient method of chemical modification because no catalysts or additives are required to initiate the reaction, and the chemical reaction can be easily adjusted by varying the radiation conditions under simple operation, thus enabling large-scale production. The EBI technology thus offers a great opportunity for the production of dipolar catalysts that are not easily accessible by chemical methods.

Out of all these considerations, in this work, without changing the specific preparation process of the original catalysts, an efficient and versatile method is reported for dipolar modification of commercially available solid catalysts by EBI technology. The high-density dipolar moieties were anchored on the surface of catalyst *via* rapid thiol-ene reaction, which endows the catalyst with polar properties. Notably, the upgrade catalyst exhibits outstanding performance in the conversion of lignin model compound to valuable 1,3-dioxolane derivatives and the dehydration of isomaltulose to glycosyloxymethyl-furfural (GMF). The successful implementation of this protocol not only brings innovation to the catalysts synthesis industry, but also significantly relieves the dependence on unfriendly polar aprotic solvents in the conversion process of biomass-derived platform molecules.

Scheme 1. Schematic illustration of the preparation process of dipolar silica-based catalysts by electron beam irradiation[a]



[a]Reaction conditions: Step 1: HMS-SH (0.20 g, 0.43 mmol), 10.0 mmol of G1, 5.0 mL of CH_3CN, N_2 atmosphere, 2100 kGy, 5 s. Step 2: HMS-DMSO (0.50 g, 1.55 mmol), 4-vinylbenzenesulfonic acid sodium salt (1.03 g, 5.0 mmol), 2.0 mL of H_2O, N_2 atmosphere, 1800 kGy, 5 s, treat with HCl (1 mol/L, 40 mL).

In order to confirm the structures of the grafted moieties, the prepared catalysts including HMS-DMSO and HMS-DMSO-SO_3H were characterized by various spectroscopic methods. The FTIR spectroscopy showed that the profiles of fresh and irradiated silica-based catalysts were quite similar, as shown in **Figure 1a**, indicating that the chemical structure of catalysts was not significantly changed through electron beam irradiation. The silica-based HMS-SH catalysts showed weak characteristic peak appearing at about 2527 cm^{-1}, which was assigned to the vibration of the HS group.[31-32] Meanwhile, the bands at 2985 cm^{-1} and 2934 cm^{-1} corresponded to the symmetric stretching vibrations and asymmetric stretching vibrations of the $-CH_2$ group.[33] The disappearance of the S-H stretching band, while the peaks of catalysts with DMSO moieties, including HMS-DMSO and HMS-DMSO-SO_3H, were significantly enhanced at these locations, indicating that the grafting of sulfolane onto the surface of silica-base was successful. Despite the fact that the broad area at 1250-1000 cm^{-1} may include many characteristic peaks, the emerging peaks at 1188 cm^{-1} and 1132 cm^{-1} in HMS-DMSO-SO_3H were related to stretching vibration of the S=O bonds of aromatic sulfonic acid.[34-35] These results implied that the grafting of double bond-containing species onto the silica-based surface *via* electron beam irradiation was successful. Besides, the characterization with ^{13}C MAS NMR spectra also suggested dipolar moieties and acid sites were successfully introduced, as demonstrated in **Figure 1b**. It was clearly observed that the chemical shifts of three catalysts varied with the grafted species. Compared with the starting material of HMS-SH, the carbon peaks in HMS-DMSO around 55.8, 51.9, 39.8 and 33.9 ppm were ascribed to sulfolane species. After treatment of acidification, the emerging peaks at 149.0, 147.1, 140.4, 126.7 ppm in HMS-DMSO-SO_3H were related to the aromatic sulfonic acid.[36-37] In addition, with the increase of the strong electron-withdraw groups, the resonance-absorption peaks move to lower

field, resulting in larger chemical shifts of HMS-DMSO-SO_3H.

As representative samples, X-ray photoelectron spectroscopy (XPS) of HMS-DMSO-SO_3H was shown in **Figure 1**, while the detailed characterization results of other samples are provided in the **ESI** (**Figures S6-S7**). As expected, all the essential elements were observed (**Figure S8**), and the conspicuous signal of C 1s appeared at 284.79 eV was assigned to the C-C bond (**Figure 1d**).[38] The two peaks were located at 285.80 and 286.45 eV, which were assigned to the C-S and C-O bands, respectively.[39] The O 1s clearly evidenced the presence of three chemical environments for the oxygen atoms (**Figure 1e**). The predominant peak at 532.71 eV was characteristic of the HMS backbone, while the peak at 533.68 corresponds to the C–O groups.[40] Notably, in the O 1s XPS spectra of HMS-DMSO-SO_3H, the existence of S–O band was evidenced by the peak appearing at 531.80 eV. Indeed, the S–O bands were also found in the O 1s XPS spectrum of HMS-DMSO, and the content of surface elements increased significantly after sulfonation. Correspondingly, it was clearly showed that in the S 2p region (**Figure 1f**), the characteristic peaks at 168.12 eV and the peaks area ratio were about 2:1, which can be attributed to the S-O bond.[41-42] The pattern of the S 2p region showed peaks located at around 163.47 eV, which is attributed to the presence of C–S groups on the surface of HMS-DMSO-SO_3H (**Tables S2-S3**). These results indicated that the grafting of dipolar moieties and –SO_3H groups onto the surface was successful.

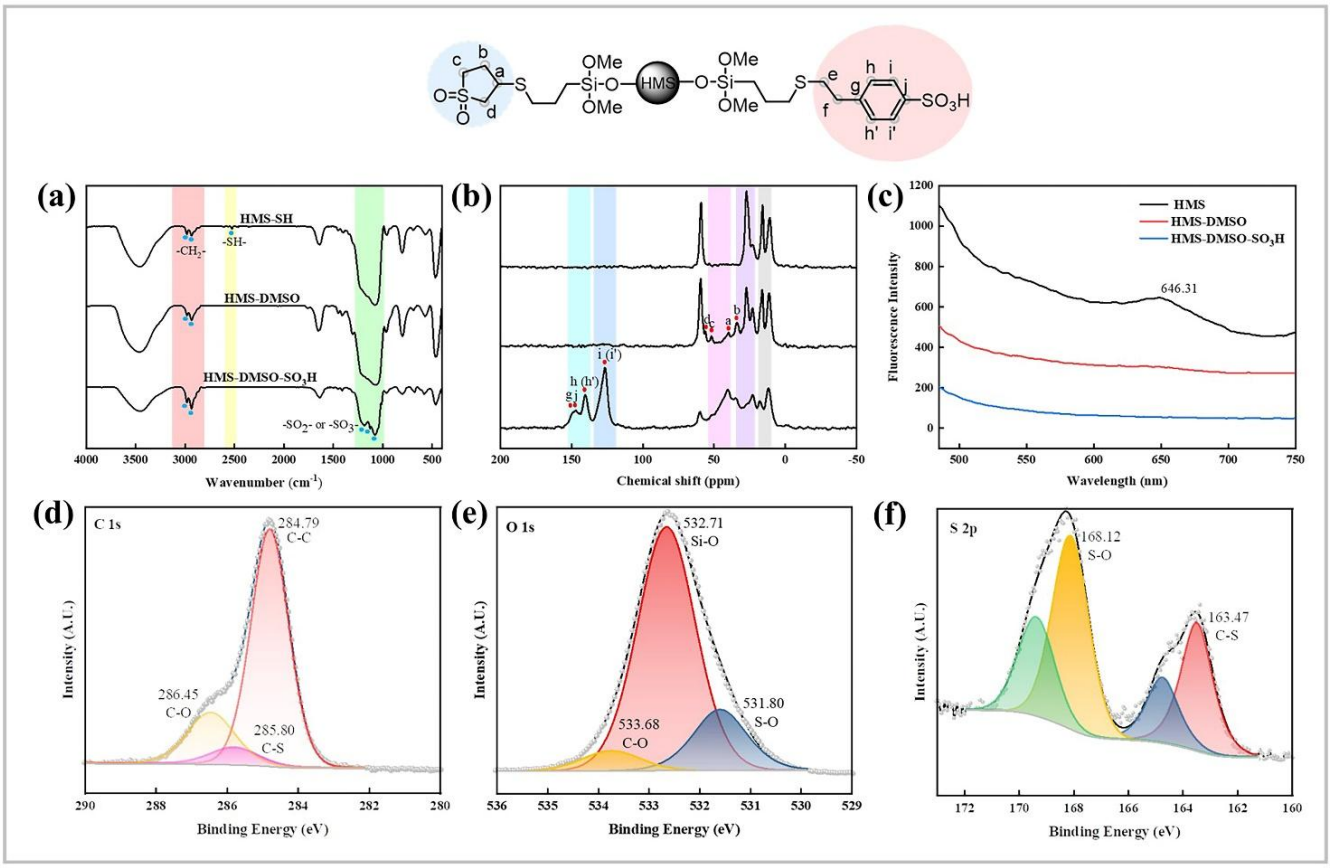


Figure 1. a) The FT-IR spectra of HMS-SH, HMS-DMSO, and HMS-DMSO-HSO_3H; b) solid-state ^{13}C NMR spectra of different dipolar catalysts; c) fluorescence emission spectra of Nile red adsorbed in three catalysts; XPS spectra of HMS-DMSO-SO_3H, including magnifications of the C 1s (d), O 1s (e), S 2p region (f), the data of HMS-SH and HMS-DMSO are shown in figure S6-S7.

The morphologies of the obtained catalysts were investigated by emission scanning electron microscopy (FE-SEM), and the changes of the three catalysts were shown in **Figure 2**. With the increase of monomer **G1**, a large number of particles are generated on the surface of the smooth massive solid (**Figure 2a)**, forming unique spatial structures (**Figure 2b**). After treatment of sulfonic modification, the structures were more compact (**Figure 2c**), which was consistent with the above description. The energy-dispersive spectroscopy (EDX) analysis indicated that all the expected elements were present and uniformly distributed in the HMS-DMSO-SO_3H (**Figure 2d-2f**) catalyst as well as HMS-DMSO (**Figure S9**). Furthermore, the effect of electron beam energy on the catalyst preparation process is evaluated by means of the Monte Carlo code FLUKA. Electron beam energy is one of the most vital parameters in the process of electron irradiation, which affects the absorbed dose distribution in catalysts and determines the quality of the product.[43-44] The results show that the EBI technology is amenable for the role of surface modification due to its strong penetrating ability and uniform distribution (**Figures S12-S15**). In addition, the prepared materials including HMS-SH, HMS-DMSO and HMS-DMSO-SO_3H were also submitted to elemental analysis to confirm the amount of grafted DMSO or –SO_3H fragment on silica-based composite. Compared with the raw material of HMS-SH,

the sulfur content of HMS-DMSO increased significantly after treating HMS-SH with 3-sulfolene, indicating the occurrence of grafting. By attributing the increase in sulfur content to the anchoring of monomer **G1** onto HMS-SH, the amount of grafted DMSO moieties was approximately 1.1 The concentration of the grafted -SO_3H fragment on the HMS-DMSO is approximately 0.88 mmol/g (**Table S1**).

The N_2 sorption isotherms were collected and the N_2 isotherms corresponded to type-IV isotherm, which was typical for mesoporous materials (**Figures S10**). Analysis of pore-size distribution evaluated shows that pore-sizes were predominantly distributed at 4.0 nm. The Brunauer–Emmett–Teller (BET) surface areas of all the obtained materials were also calculated. The S_{BET} of the dipolar catalysts decreased from 1351 $m^2\ g^{-1}$ of HMS-SH to 979 $m^2\ g^{-1}$ of HMS-DMSO, mainly contributed by the increase of **G1** content. After treatment of sulfonation, the catalysts still exhibited high surface areas (768 $m^2\ g^{-1}$) and no significant change in surface area was observed. The thermal stability of the obtained catalysts was inspected by thermogravimetric analysis (TGA) (**Figure S11**). Although the organic components in HMS-DMSO or HMS-DMSO-SO_3H were significantly higher than that in HMS-SH, it was observed from the TGA curves that all the catalysts were quite stable below 240 °C. When the temperature was elevated to around 270 °C, the weight loss was clearly observed in HMS-DMSO-SO_3H. The TGA results implied that the obtained catalysts have an excellent thermostability, it is feasible to use them in harsh conditions.

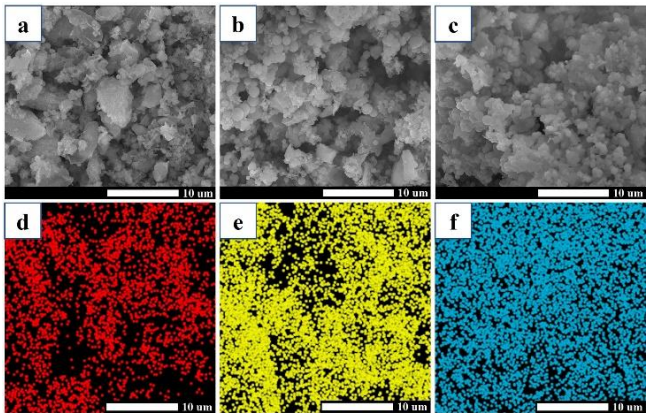


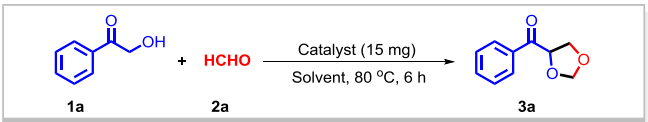
Figure 2. FSEM image characterizations of different dipolar catalysts, a) HMS-SH; b) HMS-DMSO; c) HMS-DMSO-SO_3H; d-f) elemental mapping of HMS-DMSO-SO_3H for C (d), O (e) and S (f), the data of HMS-SH and HMS-DMSO are shown in figure S8.

The fluorescence emission spectra were also analyzed, as shown in **Figure 1c**. To the best of our knowledge, Nile red was a sensitive probe, which was considered the best choice to determine the local polarity of some media in a variety of heterogeneous systems because the photophysical properties of Nile red vary with the polarity of the solvent.[46-48] Upon photo- excitation at 400 nm, the fluorescence intensity of Nile red adsorbed in HMS-DMSO and HMS-DMSO-SO_3H almost disappeared with the increase content of sulfone group, while the obvious peak at 649 nm was maintained after treatment with HMS-SH (see **ESI** for details). Significant decrease or even disappearance in intensity has been attributed to a formation of the twisted intramolecular charge transfer (TICT) state.[49] The results demonstrated that the polarity of HMS-DMSO and HMS-DMSO-SO_3H significantly enhanced by decoration of polar moieties.

mmol/g. Indeed, HMS-SH exhibits a better ability to graft monomer **G1** due to its high loading of thiol groups (2.21 mmol/g).[45] To facilitate the subsequent introduction of active sites to maximize the catalytic ability, an excess amount of aromatic sulfonic acid was used.

To verify the applicability of dipolar catalysts as reaction medium, lignin model compound[50] (**1a**) and formaldehyde (**2a**) were employed as reaction substrates to synthesize 1,3-dioxolane derivative **3a**, which is useful intermediates in the synthesis of pharmaceuticals and fine chemicals.[51-53] In the presence of HMS-DMSO-SO_3H, various solvents were screened (**Table 1**, entries 1-4). EtOH and 2-methyltetrahydrofuran (2-Me-THF) were not suitable for this reaction (entries 1 and 2). Although **1a** didn't completely converted (entry 3), the result indicated that the dipolar catalyst is promising for achieving a good result. A moderate yield of **3a** was obtained in cyclopentyl methyl ether (CPME, entry 3). When the reaction was performed in isopropyl acetate (^{i}PrOAc), **3a** was obtained in 95% of yield (entry 4). Under the identical conditions, the reactions over *p*-toluenesulfonic, Amberlyst-15 and HMS-SO_3H gave only moderate yields (entries 5–7). HMS-DMSO has no acidic site, but contains **G1** fragment in the solid surface, has no catalytic acitivity for the synthesis of **3a** (entry 8). When HMS-DMSO was used along with TsOH, **3a** can be isolated with 56% yield (entry 9). To evaluate the effect of acid content, the catalysts with different ratios were prepared and the results were described in **Table S4**. Furthermore, the reference catalyst PSS-DMSO-SO_3H[21] with dipolar moieties also exhibits good catalytic performance, affording the desired product in 62% yield (entry 10). These results demonstrate that the presence of dipolar components is indeed effective in enhancing the activity of the catalyst. The reactions over the analogous dipolar catalysts that were prepared through the conventional chemical grafting with free radical initiators proceeded sluggishly (entries 11 and 12). These results implied that the use of EBI is a key for ensuring the dipolar catalyst to have a good catalytic performance. It should be noted that the catalyst is also recyclable (**Figure S23**) and still maintains good catalytic activity after 5 cycles. Finally, a possible mechanism is illustrated, as depicted in **Figure S16- S21**.

Table 1. Condition optimization of the reaction lignin model compound and 2a.



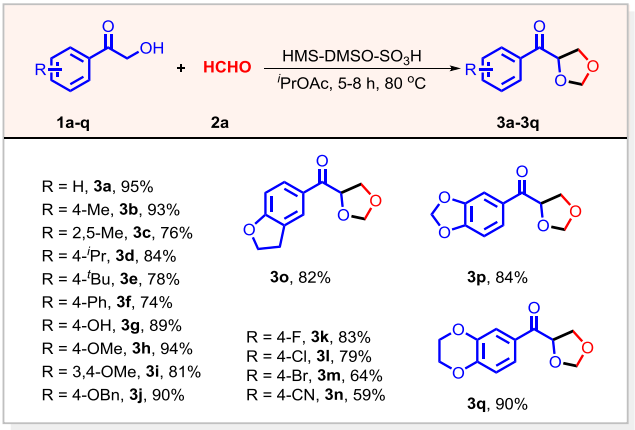
1a 2a 3a

Entry[a]	Catalyst	Solvent	Conv. (%)[e]	Select. (%)[e]	Yield (%)[e]
1	HMS-DMSO-SO_3H	EtOH	43	63	27
2	HMS-DMSO-SO_3H	2-Me-THF	28	36	10
3	HMS-DMSO-SO_3H	CPME	67	82	55
4	HMS-DMSO-SO_3H	^{i}PrOAc	>99	95	95
5	TsOH	^{i}PrOAc	66	50	33
6	Amberlyst-15	^{i}PrOAc	60	82	49
7	HMS-SO_3H	^{i}PrOAc	65	74	48
8	HMS-DMSO	^{i}PrOAc	24	0	0
9[b]	HMS-DMSO	^{i}PrOAc	72	78	56
10	PSS-DMSO-SO_3H	^{i}PrOAc	85	73	62
11[c]	HMS-DMSO-SO_3H	^{i}PrOAc	45	51	23
12[d]	HMS-DMSO-SO_3H	^{i}PrOAc	49	55	27

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (30% solution 0.9 mmol), catalyst (15 mg), solvent (1.0 mL), 80 °C, 6 h; [b]: addition of TsOH (20 mol%) [c]: AIBN (azodiisobutyronitrile); [d]: TBHP (^{t}butyl hydroperoxide); [e]: the selectivity and yield of product were determined by the combination of liquid chromatography and gas chromatography.

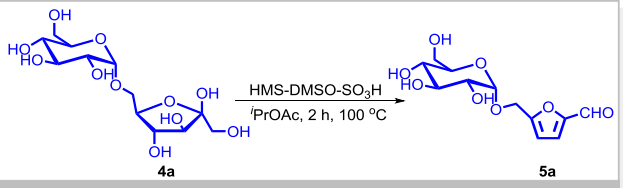
Various substituents patterns and diverse functional groups in the aryl ring were used as viable substrates to react with **2a** (**Scheme 2**). A series of compounds bearing electron-donating groups (**3b**, **3g**, **3h**) can also be successfully converted to the desired products with excellent yields. Di-substituted electron-rich α-hydroxyacetophenones (**3c**, **3i**) can react smoothly with **2a**, affording the desired products in good yields. Various electron-withdraw groups, varying from halogen to cyano group (**3k-3n**), were also able to efficiently offer the corresponding products with the yields ranging from 83% to 59%. Lignin model compounds contained large steric hindrance groups (**3d-3e**, **3j**) was also well-tolerated in this reaction. Notably, the substituent bearing phenyl group reacted smoothly in the presence of HMS-DMSO-SO_3H, and the desired product **3f** was obtained in 74%, which has been reported by using HCl as a catalyst in HOAc at 110 °C for 24 h.[54] Interestingly, the heteroaromatic substrates could also be easily delivered uneventfully into the target product in moderate to good yields (**3o-3q**). These results indicated that the dipolar solid acids prepared with the aid of EBI were indeed efficient catalysts for the transformations of lignin model compounds to 1,3-dioxolane derivatives.

Scheme 2. The substrate scope of lignin model compounds to 1,3-dioxolane derivatives.



The conversion of isomaltulose to glucosyloxymethylfurfural (GMF) was also evaluated. GMF is an interesting analog of 5-hydroxymethylfurfural (HMF) with a glucosyl moiety that has several applications and is highly sensitive to the dipolar environment.[55-57] As shown in **Table 2**, the reaction proceeded smoothly in γ-valerolactone (GVL), but hardly proceeded in THF and CPME (entries 1-3). Gratifyingly, when HMS-DMSO-SO_3H was used as the catalyst, the conversion of isomaltulose proceed smoothly in ^{i}PrOAc, providing the desired product **5a** in 63% yield (entry 4). Given that **5a** can be effectively separated in a low boiling solvent, the results are acceptable (see the NMR spectra of the product in **ESI**), despite the fact that the yields obtained are not as good as those already reported for the method performed in DMSO. When TsOH and Amberlyst-15 were used as catalysts, the yield obtained is inferior to the former catalysts of HMS-DMSO-SO_3H (entries 5 and 6). In addition, HMS-DMSO and HMS-SO_3H proved to be unsuitable for this reaction (entries 7 and 8). When TsOH was introduced into the reaction system of HMS-DMSO, only 17% of the desired product was obtained (entry 9). Besides, when the grafting rate of sulfolene was decreased, the yield of the product also decreased significantly (entry 12). Furthermore, the desired product can be obtained in 25%, when the reference catalyst PSS-DMSO-SO_3H was used (entry 10). These observations imply the cooperative effect between the dipolar moieties and the acid groups are important factors in promoting chemical reactions (the mechanism see **Figure S22** for details). The catalyst of HMS-DMSO-SO_3H prepared by free radical initiators did not display the expected catalytic performance (entry 11). These results further demonstrate that the dipolar catalysts modified by EBI techniques are indeed necessary to enhance the catalytic capacity in the process of transformation, especially the transformation of biomass-derived platform molecules.

Table 2. Catalytic reaction in the dehydration of isomaltulose to GMF.



Entry[a]	Catalyst	Solvent	Conv. (%)[e]	Select. (%)[e]	Yield (%)[e]
1	HMS-DMSO-SO_3H	THF	31	48	15
2	HMS-DMSO-SO_3H	CPME	10	0	0
3	HMS-DMSO-SO_3H	GVL	80	68	54
4	HMS-DMSO-SO_3H	^{i}PrOAc	89	71	63
5	TsOH	^{i}PrOAc	81	22	18
6	Amberlyst-15	^{i}PrOAc	68	32	22
7	HMS-SO_3H	^{i}PrOAc	62	11	7
8	HMS-DMSO	^{i}PrOAc	0	0	0
9[b]	HMS-DMSO	^{i}PrOAc	32	53	17
10	PSS-DMSO-SO_3H	^{i}PrOAc	58	43	25
11[c]	HMS-DMSO-SO_3H	^{i}PrOAc	8	0	0
12[d]	HMS-DMSO-SO_3H	^{i}PrOAc	25	48	12

[a]Reaction conditions: **4a** (50.0 mg, 0.15 mmol), catalyst (based on the amount of sulfonic acid 2.0 mol%), solvent (3.0 mL), 100 °C, 2 h; [b]: addition of TsOH (20 mol%) [c]: AIBN (azodiisobutyronitrile); [d]: the amount of grafted DMSO moieties was approximately 0.6 mmol/g; [e]: the selectivity and yield of GMF were determined by the combination of liquid chromatography and gas chromatography.

In summary, the EBI technology provides an efficient and general method for dipolarization based on existing catalysts. Compared with traditional chemical methods, it has the advantages of simple steps, high efficiency, no initiator and easy engineering production. The use of the dipolar catalysts, not only enables successfully conversion of the biomass platform molecules, but also facilitated the separation of products in low boiling point solvent. Considering the economy and high efficiency of this method, this work opens up an avenue for the design, synthesis, and application of catalysts.

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

The synthetic procedures, optimization data, chemical computations, experimental procedures, and characterization data (PDF)

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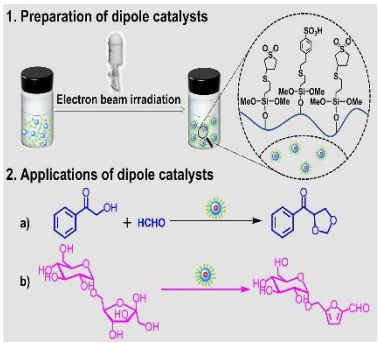

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