

Dehydration of Carbohydrates to 5-Hydroxymethyl-furfural over Lignosulfonate-Based Acidic Resin

Hao Tang^{†,‡}, Ning Li,^{,†,§} Guangyi Li[†], Wentao Wang[†], Aiqin Wang^{†,§}, Yu Cong[†],
Xiaodong Wang[†]*

[†]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, No. 457 Zhongshan Road, Dalian 116023, China.

[‡]University of Chinese Academy of Sciences, Beijing 100049, China.

[§]*iChEM* (Collaborative Innovation Centre of Chemistry for Energy Materials), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, No. 457 Zhongshan Road, Dalian 116023, China.

The number of pages: 13

The number of figures: 6

The number of tables: 3

E-mail address of the corresponding author: lining@dicp.ac.cn (N. Li).

Seperation of HMF. DMSO has high boil point (462 K). Therefore, it is hard to separate HMF from it by distillation. As a solution to this problem, we developed a new method for the separation of DMSO and HMF. Typically, 8.8 g dehydration product (DMSO/HMF mass ratio = 11.5), 20 mL water and 20 mL organic solvent (ethyl ether, methyl isobutyl ketone (MIBK) or dichloromethane) were added into a flask. The mixture was stirred at room temperature for 5 mins and became two phases after we stopped stirring. According to analysis of HPLC (see Table S3), the DMSO/HMF mass ratios in organic phases are lower than that in the dehydration product. In contrast, the DMSO/HMF mass ratios in aqueous phase are higher than that in the dehydration product. This result indicates that the DMSO was extracted into water and HMF was extracted into organic phase at the same time. Compared with ethyl ether and MIBK, dichloromethane has better extracting effect for HMF. In future application, we can separate the DMSO and HMF by repeatedly extraction with water and dichloromethane.

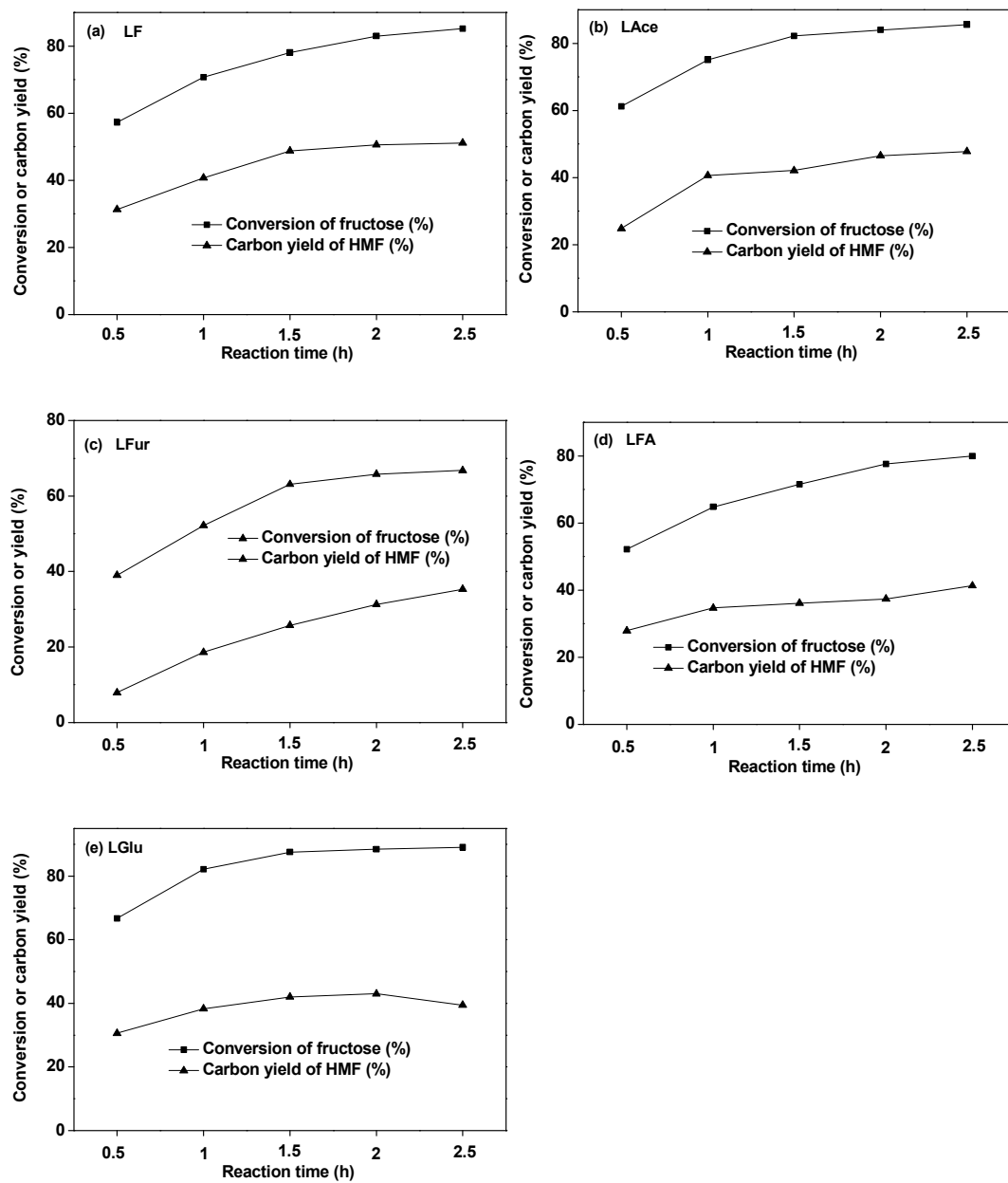


Figure S1. Conversions of fructose and the carbon yields of HMF over the lignosulfonate-based acidic resins as the functions of reaction time. Reaction conditions: 1 g fructose, 7 g DMSO, 0.1 g catalyst; 353 K.

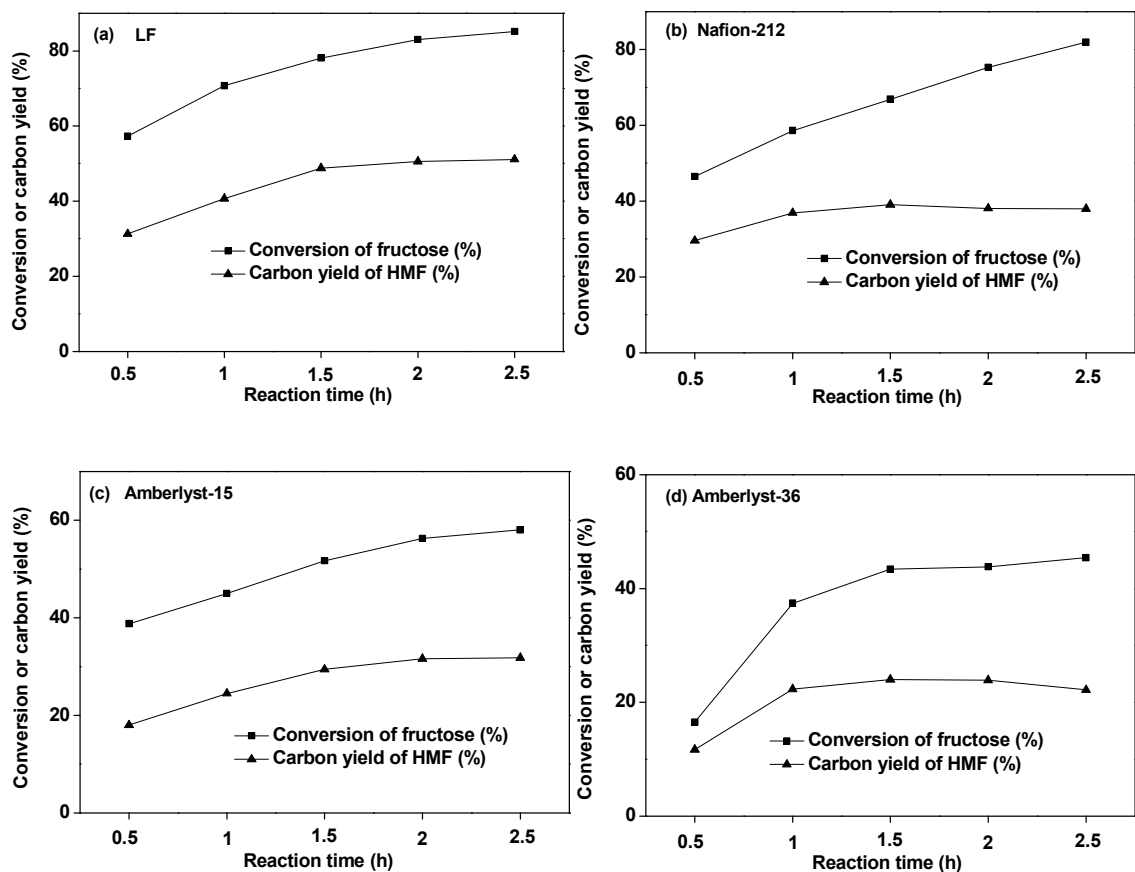


Figure S2. Conversions of fructose and the carbon yields of HMF over the LF and commercial acidic resins as the functions of reaction time. Reaction conditions: 1 g fructose, 7 g DMSO, 0.1 g catalyst; 353 K.

From Figures S1 and S2, we can see that the carbon yield over the LF resin reached the maximum at 1.5 h. No decrease of HMF carbon yield over other catalysts was observed at this time. Due to this reason, we selected 1.5 h as the reaction time for the activity comparison of different catalysts.

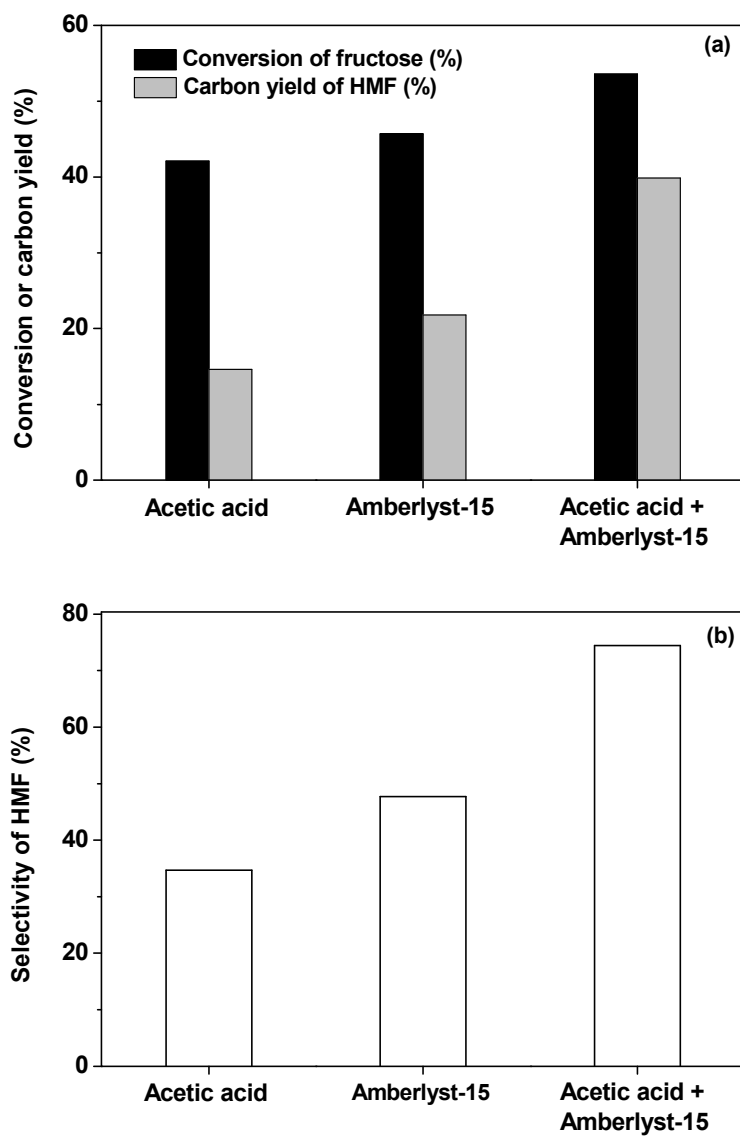


Figure S3. Conversions of fructose, the carbon yields and selectivity of HMF over acetic acid, Amberlyst-15 or a mixture of acid and Amberlyst-15. Reaction conditions: 1 g fructose, 7 g DMSO, 0.06 (or 0) g acetic acid, 0.06 (or 0) g Amberlyst-15, 353 K, 1.5 h.

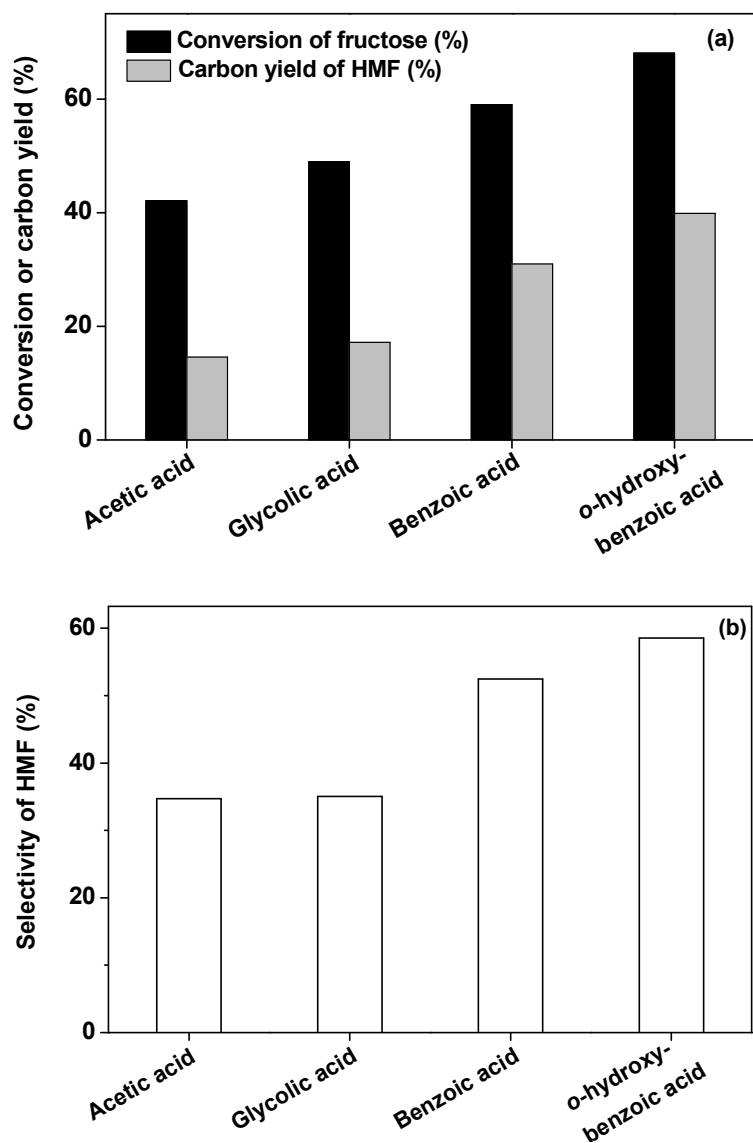


Figure S4. Fructose conversions and the molar yields of HMF over different carboxylic acid catalysts. Reaction conditions: 1 g fructose, 7 g DMSO, 1 mmol catalyst; 353 K, 1.5 h.

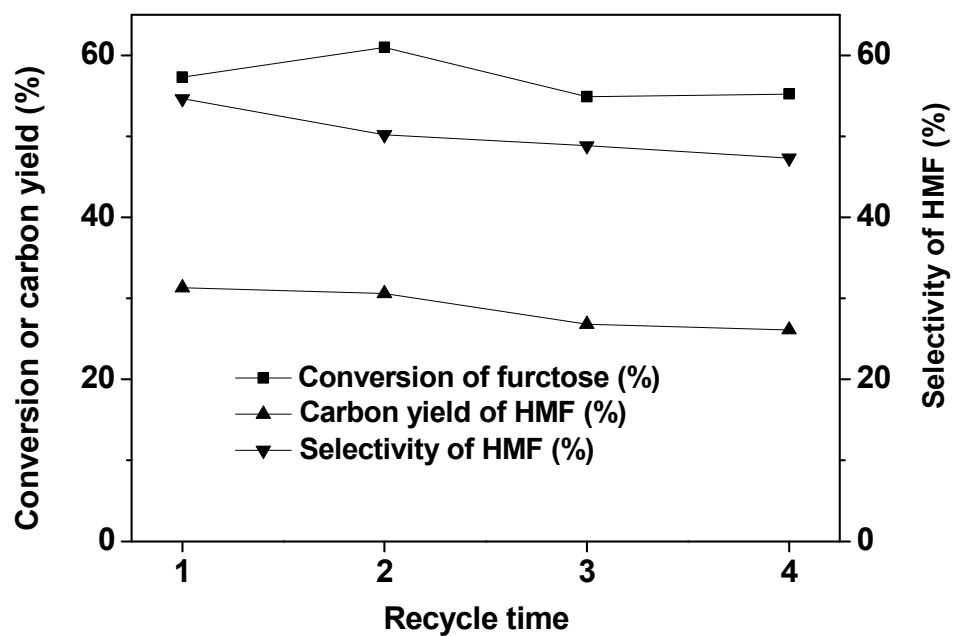


Figure S5. Conversions of fructose, the carbon yields and selectivity of HMF over the LF resin as the function of recycle time. Reaction conditions: 1 g fructose, 7 g DMSO, 0.1 g catalyst; 353 K, 0.5 h.

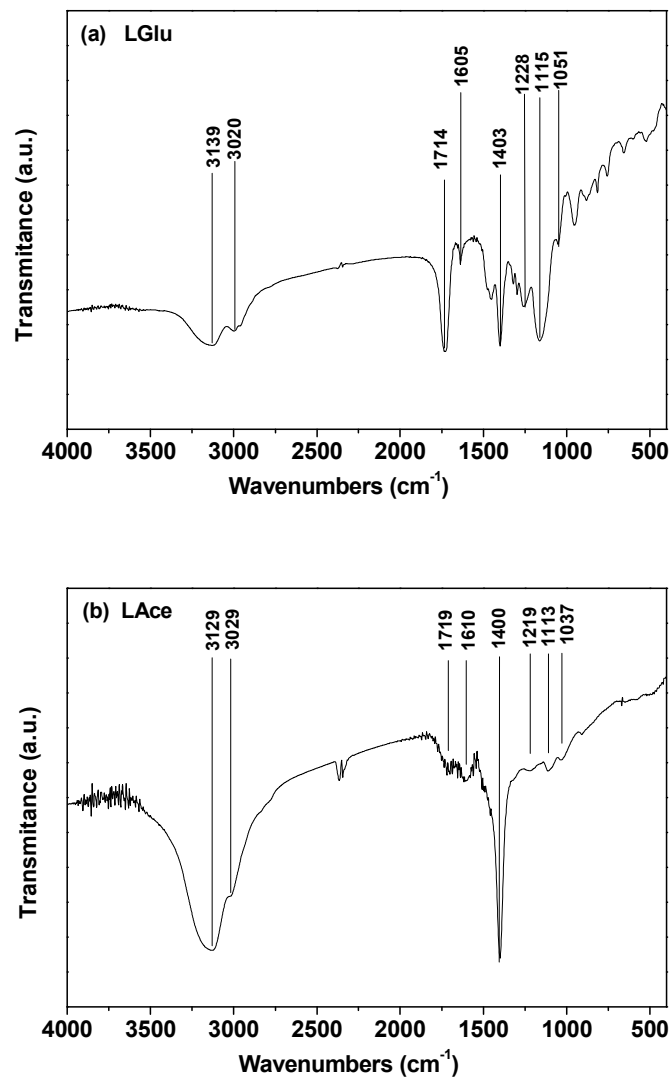


Figure S6. FT-IR spectrum of the LGlu and LAce resins which were prepared by the protonation of the condensation product of sodium lignosulfonate and glucose (or acetaldehyde).

According to literature,¹ the shoulder peaks at $\sim 3020 \text{ cm}^{-1}$ can be attributed to stretching vibration of $-\text{CH}_2-$ which was formed during the phenol-aldehyde condensation of sodium lignosulfonate and formaldehyde. The bands at $\sim 1228 \text{ cm}^{-1}$ and $\sim 1034 \text{ cm}^{-1}$ can be assigned to the sym-stretching of $\text{O}=\text{S}=\text{O}$ and $\text{SO}_3\text{-H}$ stretching in

$\text{-SO}_3\text{H}$ groups,^{2,4} respectively. The peaks at $\sim 1115\text{ cm}^{-1}$ represent the in-plane bending vibration of aromatic C-H.⁵ The peaks at $\sim 1403\text{ cm}^{-1}$ and $\sim 1605\text{ cm}^{-1}$ can be attributed to the characteristic vibrations of benzene ring.^{1, 5, 7} The wavenumbers at $\sim 1714\text{ cm}^{-1}$ indicated the existence of -COOH group on the surfaces of LGlu and LAce resins.^{4, 8} The broad peaks at $\sim 3139\text{ cm}^{-1}$ can be attributed to the phenolic -OH groups which are linked with the neighbor oxygen atom or $\text{-SO}_3\text{H}$ group by hydrogen-bond.¹

Table S1. Specific BET Surface Areas (S_{BET}) and the Amounts of Acid Sites on the Surfaces of Fresh and Used LF Resin Catalysts.

Catalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$) ^b	Amount of acid sites (mmol g^{-1})	
		Chemical titration ^c	NH_3 chemisorption ^d
Fresh LF	2	2.37	0.83
Used LF ^a	0.24	1.88	0.67

^aThe LF resin which has been used for four times under the reaction conditions of Figure S5. ^bMeasured by N_2 -physisorption. ^cMeasured by chemical titration. ^dMeasured by NH_3 chemisorption.

Table S2. Specific BET Surface Areas (S_{BET}) and the Amounts of Acid Sites on the Surfaces of Catalysts.

Catalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$) ^a	Amount of acid sites (mmol g^{-1})	
		Chemical titration ^b	NH_3 chemisorption ^c
LF	2	2.37	0.83
LGlu	0.17	2.01	0.70
LAce	1.42	1.92	0.68

^aMeasured by N_2 -physisorption. ^bMeasured by chemical titration. ^cMeasured by NH_3 chemisorption.

Table S3. Separation Effects of Different Bi-phase Solvent Systems on the Dehydration Product.

Bi-phase solvent system	DMSO/HMF mass ratio			$C_{\text{HMF in organic phase}} / C_{\text{HMF in aqueous phase}}^c$
	Dehydration product	Aqueous phase ^a	Organic phase ^b	
Ethyl ether/H ₂ O	11.5	11.6	7.5	0.27
MIBK/H ₂ O	11.5	14.6	3.1	0.55
Dichloromethane/ H ₂ O	11.5	14.7	2.9	0.55

^a The DMSO/HMF mass ratio in aqueous phase. ^b The DMSO/HMF mass ratio in organic phase. ^c The ratio of HMF concentration in organic phase to HMF concentration in aqueous phase.

References

- (1) Zhang, X.; Zhang, Z.; Wang, F.; Wang, Y.; Song, Q.; Xu, J., Lignosulfonate-based heterogeneous sulfonic acid catalyst for hydrolyzing glycosidic bonds of polysaccharides. *J. Mol. Catal. A: Chem.* **2013**, 377, 102-107.
- (2) Suganuma, S.; Nakajima, K.; Kitano, M.; Yamaguchi, D.; Kato, H.; Hayashi, S.; Hara, M., Hydrolysis of Cellulose by Amorphous Carbon Bearing SO₃H, COOH, and OH Groups. *J. Am. Chem. Soc.* **2008**, 130, 12787-12793.
- (3) Li, X.; Jiang, Y.; Shuai, L.; Wang, L.; Meng, L.; Mu, X., Sulfonated copolymers with SO₃H and COOH groups for the hydrolysis of polysaccharides. *J. Mater. Chem.* **2012**, 22, 1283-1289.
- (4) Lee, D., Preparation of a sulfonated carbonaceous material from lignosulfonate and its usefulness as an esterification catalyst. *Molecules* **2013**, 18, 8168-8180.
- (5) Bai, W.; Wang, Y.; Song, X.; Jin, X.; Guo, X., Modification of urea-formaldehyde microcapsules with lignosulfonate-Ca as co-polymer for encapsulation of acetochlor. *J. Macromol. Sci. Part A* **2014**, 51, 737-742.
- (6) Ge, Y.; Li, Z.; Pang, Y.; Qiu, X., Influence of molecular mass of lignosulfonates on the resulting surface charges of solid particles. *Int. J. Biol. Macromol.* **2013**, 52, 300-304.
- (7) Ouyang, X. P.; Ke, L. X.; Qiu, X. Q.; Guo, Y. X.; Pang, Y. X., Sulfonation of alkali lignin and its potential use in dispersant for cement. *J. Dispersion Sci. Technol.* **2009**, 30, 1-6.
- (8) Demir-Cakan, R.; Baccile, N.; Antonietti, M.; Titirici, M.-M., Carboxylate-rich carbonaceous materials via one-step hydrothermal carbonization of glucose in the presence of acrylic acid. *Chem. Mater.* **2009**, 21, 484-490.