

## Supporting Information

# Bifunctional Brønsted-Lewis solid acid as recyclable catalyst for conversion of glucose to 5-hydroxymethylfurfural and its hydrophobicity effect

### 1. Cr(III) XRF analysis

CrCl<sub>3</sub>·6H<sub>2</sub>O and KBr were mixed at constant total mass of 0.8 g, but various ratio. After grinding, pellet technique was performed for test. The ratios and experimental results are listed in Table. S1, and the calibration curve is in Fig. S1.

Table. S1. Components ratios of pellet and XRF peak areas of Cr(III)

No.	1	2	3	4	5
Mass of CrCl <sub>3</sub> (g)	0.0103	0.0503	0.0998	0.2005	0.2999
Mass of KBr (g)	0.7898	0.7500	0.7003	0.6000	0.4996
Cr(III) content (mg/g)	2.512	12.27	24.34	48.88	73.21
Cr(III) peak area	387.5	1256	2010	3623	5475

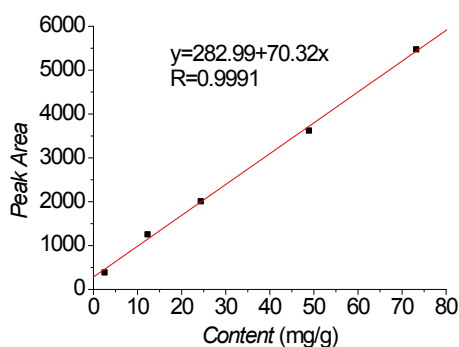


Fig. S1 XRF Calibration curve of Cr(III)

### 2. EDX analysis of Cr(III)-PDVB-0.3-SSFBI

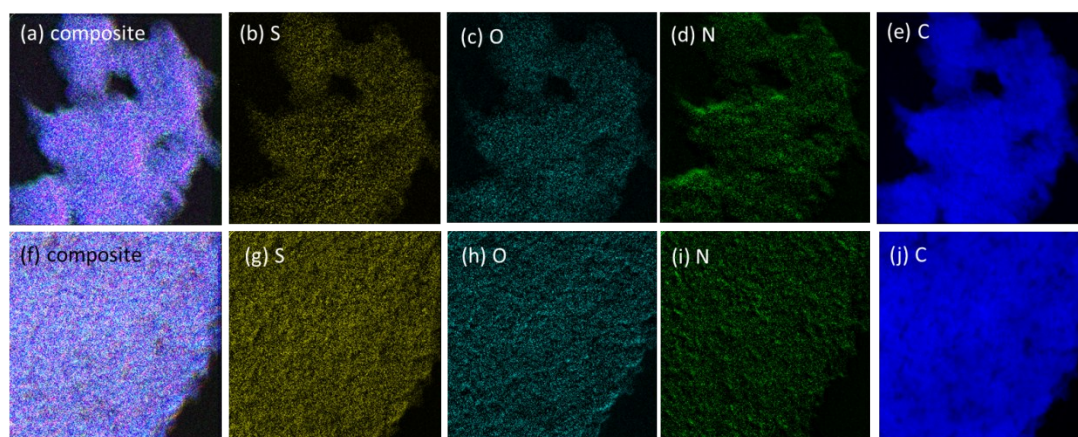


Fig. S 2 Elemental maps of fresh(a-e) and spent (f-j) Cr(III)-PDVB-0.3-SSFBI.

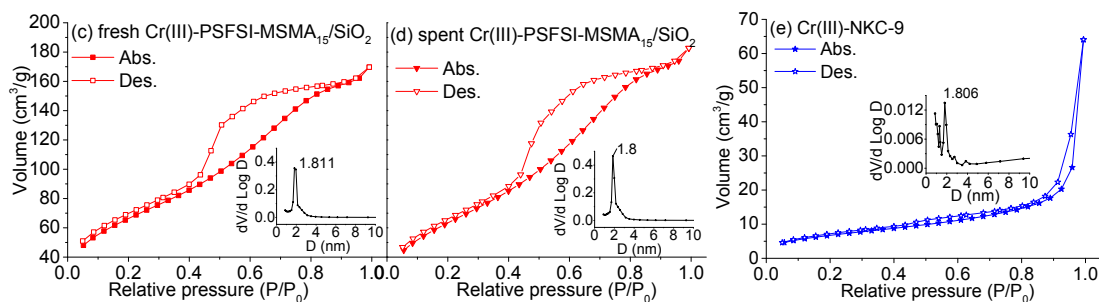


Fig. S3 N<sub>2</sub> adsorption-desorption isotherms and BJH mesopore size distribution from desorption branch (inset). (c) fresh Cr(III)-PSFSI-MSMA<sub>15</sub>/SiO<sub>2</sub>; (d) spent Cr(III)-PSFSI-MSMA<sub>15</sub>/SiO<sub>2</sub>; (e) Cr(III)-NKC-9.

Table. S2 Textural parameters of various solid acid samples

No.	samples	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>total</sub> (cm <sup>3</sup> /g)	Pore size (nm)
1	fresh (III)-PSFSI-MSMA <sub>15</sub> /SiO <sub>2</sub>	239.0	0.248	1.97
2	spent (III)-PSFSI-MSMA <sub>15</sub> /SiO <sub>2</sub>	234.3	0.266	1.94
3	fresh (III)-PDVB-0.3-SSFBI	302.1	0.265	1.81
4	spent (III)-PDVB-0.3-SSFBI	236.0	0.242	1.85
5	fresh NKC-9	25.0	0.032	-

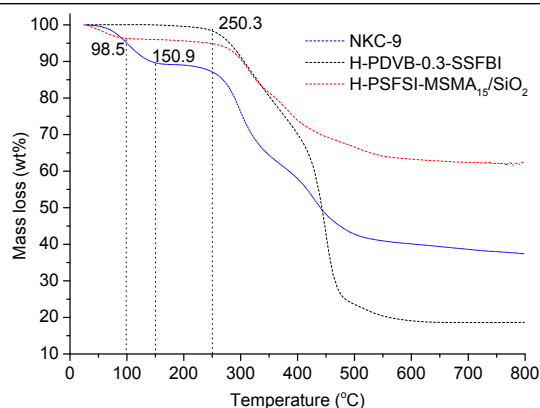


Fig. S4 TG analysis of various solid Brønsted acids

## 2. Experimental results of glucose conversion catalysed by bifunctional solid acids

Table. S3 HMF yield catalyzed by Cr(III)-NKC-9

Reaction time (h)	Run1	Run2	Run3	average	Standard deviation
1	49.3	47.2	48.1	48.2	1.05
1.5	55.5	56.8	53.1	55.1	1.88
2	59.8	58.7	58.6	59.0	0.67
2.5	63.8	61.2	62.9	62.6	1.32
3	62.3	63.9	67.2	64.5	2.50
3.5	67.9	68.2	65.8	67.3	1.31
4	67.5	68.3	65.5	67.1	1.44

Table. S4 Glucose conversion catalyzed by Cr(III)-NKC-9

Reaction time (h)	Run1	Run2	Run3	average	Standard deviation
1	66.9	67.1	71.5	68.5	2.60

1.5	81.3	78.8	77.3	79.1	2.02
2	84.9	86.2	89.6	86.9	2.43
2.5	95.8	95.2	93.4	94.8	1.25
3	93.4	93.1	95.7	94.1	1.42
3.5	92.9	94.2	97.3	94.8	2.26
4	100	98.2	95.8	98.0	2.11

Table. S5 HMF yield catalyzed by Cr(III)-PSFSI-MSMA<sub>15</sub>/SiO<sub>2</sub>

Reaction time (h)	Run1	Run2	Run3	average	Standard deviation
1	45.3	47.2	45.8	46.1	0.98
2	57.3	59.5	59.6	58.8	1.30
3	60.8	61.5	63.7	62.0	1.51
4	63.4	60.1	64.0	62.5	2.10
5	60.5	62.5	60.3	61.1	1.22
6	63.8	63.1	60.1	62.3	1.97

Table. S6 Glucose conversion catalyzed by Cr(III)-PSFSI-MSMA<sub>15</sub>/SiO<sub>2</sub>

Reaction time (h)	Run1	Run2	Run3	average	Standard deviation
1	65.4	66.8	70.9	67.7	2.86
2	88.5	86.7	83.1	86.1	2.75
3	91.2	93.5	85.3	90.0	4.23
4	100	100	100	100.0	0.00
5	100	100	100	100.0	0.00
6	100	100	100	100.0	0.00

Table. S 7 HMF yield catalyzed by Cr(III)-PDVB-0.3-SSFBI

Reaction time (h)	Run1	Run2	Run3	average	Standard deviation
3	45.2	49.5	49.6	48.1	2.51
4	49.7	48.3	51.5	49.8	1.60
5	53.6	53.1	52.1	52.9	0.76
6	57.6	58.2	54.8	56.9	1.81
7	59.5	60.8	57.3	59.2	1.77
8	55.3	57.2	57.9	56.8	1.35
9	54.5	56.3	51.8	54.2	2.26

Table. S 8 Glucose conversion catalyzed by Cr(III)-PDVB-0.3-SSFBI

Reaction time (h)	Run1	Run2	Run3	average	Standard deviation
3	78.9	77.3	73.5	76.6	2.77
4	79.2	79.9	81.2	80.1	1.01
5	86.1	85.3	81	84.1	2.74
6	89.8	91.3	95.3	92.1	2.84
7	94.7	91.2	93.9	93.3	1.83
8	95.3	92.4	96.2	94.6	1.99

3. Experimental results of cycle experiments of Cr(III)-PDVB-0.3-SSFBI

Table. S 9 HMF yields of cycle experiments catalyzed by Cr(III)-PDVB-0.3-SSFBI

Cycle	1	2	average
1	60.5	57.8	59.2
2	56.6	57.9	57.3
3	55.9	59.8	57.9
4	57.3	55.8	56.6
5	55.2	59.9	57.6
6	59.3	57.1	58.2
7	59.5	58.1	58.8
8	57.3	59.9	58.6
9	58.5	59.8	59.2
10	56.9	56.3	56.6
11	58.7	56.5	57.6
12	58.3	59.8	59.1
13	56.5	53.7	55.1

Table. S 10 Glucose conversions of cycle experiments catalyzed by Cr(III)-PDVB-0.3-SSFBI

Cycle	1	2	average
1	93.7	95.3	94.5
2	91.8	89.1	90.5
3	89.1	87.3	88.2
4	88.6	90.6	89.6
5	86.1	84.7	85.4
6	84.7	81.9	83.3
7	85.9	89.1	87.5
8	83.6	82.2	82.9
9	84.1	88.9	86.5
10	86.7	83.1	84.9
11	81.9	85.1	83.5
12	85.2	83.9	84.6
13	84.7	81.9	83.3

Table. S 11 Cr(III)-PDVB-0.3-SSFBI recovery of cycle experiments

Cycle	1	2	average
1	/	/	/
2	94.5	92.1	93.3
3	93.1	96.9	95.0
4	93.6	91.8	92.7

5	90.8	93.6	92.2
6	96.3	93.5	94.9
7	96.1	93.7	94.9
8	95.8	93.8	94.8
9	91.9	95.3	93.6
10	94.3	91.2	92.8
11	90.3	92.5	91.4
12	94.3	89.9	92.1
13	86.3	90.5	88.4

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