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Mesoporous Polymeric Catalysts with Both Sulfonic Acid and Basic Amine Groups for One-pot Deacetalization-Knoevenagel Reaction

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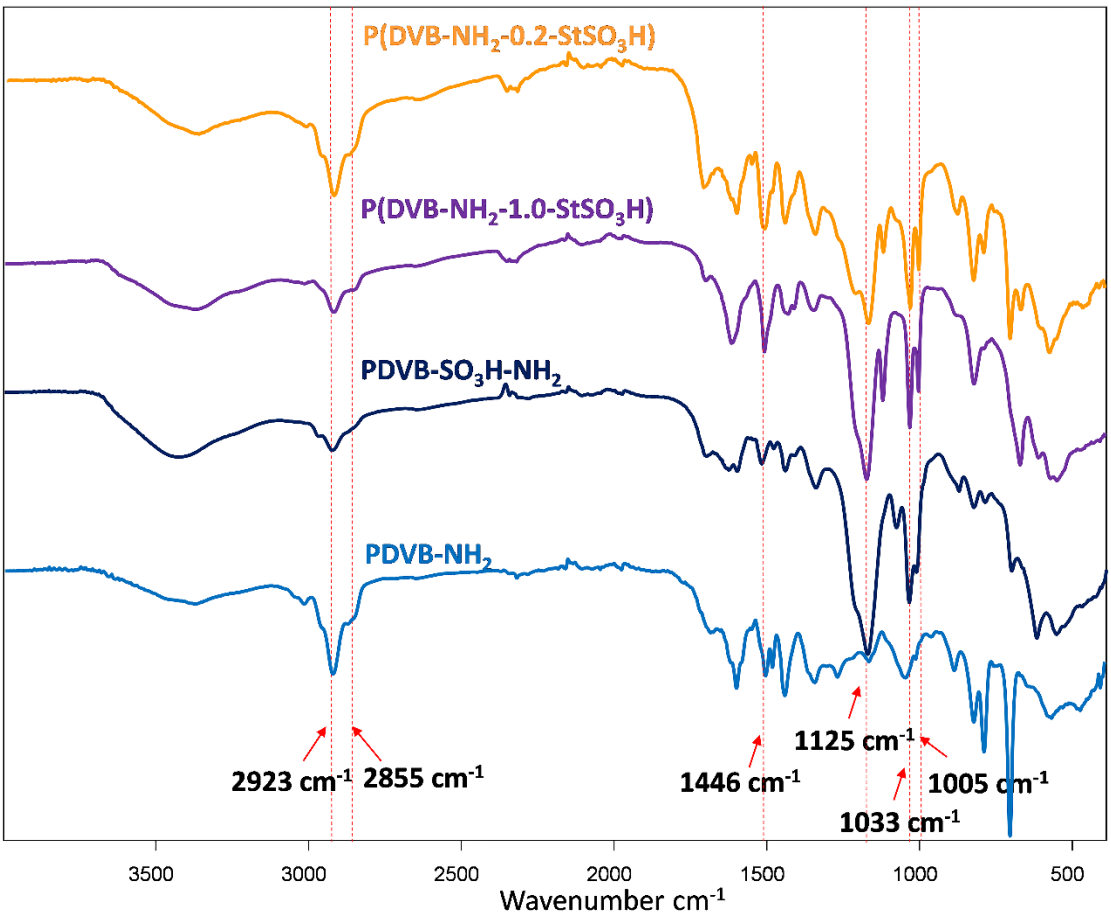


Figure S1 FT-IR spectra of P(DVB-NH_2-0.2-$StSO_3H$), P(DVB-NH_2-1.0-$StSO_3H$), PDVB-SO_3H-NH_2 and PDVB-NH_2

Table S1 Elemental analysis data of synthetic materials

Entry	C (wt%)	H (wt%)	N (wt%)	S (wt%)
P(DVB-1.0-$StSO_3H$)	68.29	7.02	0.12	6.40
P(DVB-NH_2-1.0-$StSO_3H$)	62.13	6.89	2.79	5.31
P(DVB-0.5-$StSO_3H$)	70.49	7.10	0.15	6.02
P(DVB-NH_2-0.5-$StSO_3H$)	63.56	6.91	2.81	4.95
P(DVB-0.2-$StSO_3H$)	75.15	7.54	0.10	2.56
P(DVB-NH_2-0.2-$StSO_3H$)	64.55	5.98	4.96	1.89
PDVB-SO_3H-NH_2	55.10	5.78	2.20	2.60
PDVB-NH_2	85.38	8.79	2.66	0
P(DVB-NH_2-0.5-$StSO_3H$)[a]	64.01	6.99	2.71	4.86

[a] the elemental analysis after 5 times recycles of P(DVB-NH_2-0.5-$StSO_3H$)

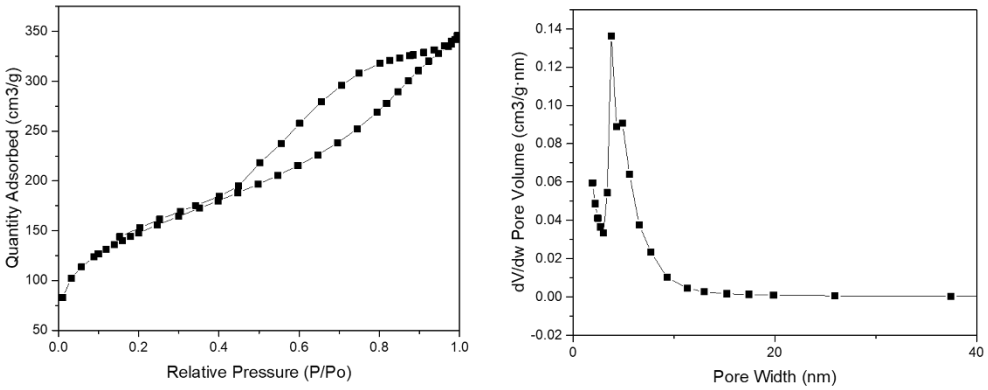


Figure S2 N_2 sorption isotherms and pore size distributions of P(DVB-NH_2-0.2-$StSO_3H$)

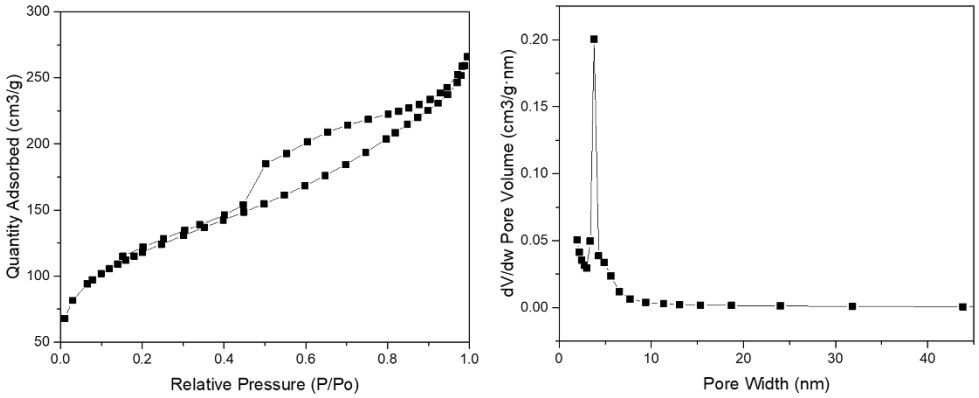


Figure S3 N_2 sorption isotherms and pore size distributions of P(DVB-NH_2-0.2-$StSO_3H$)

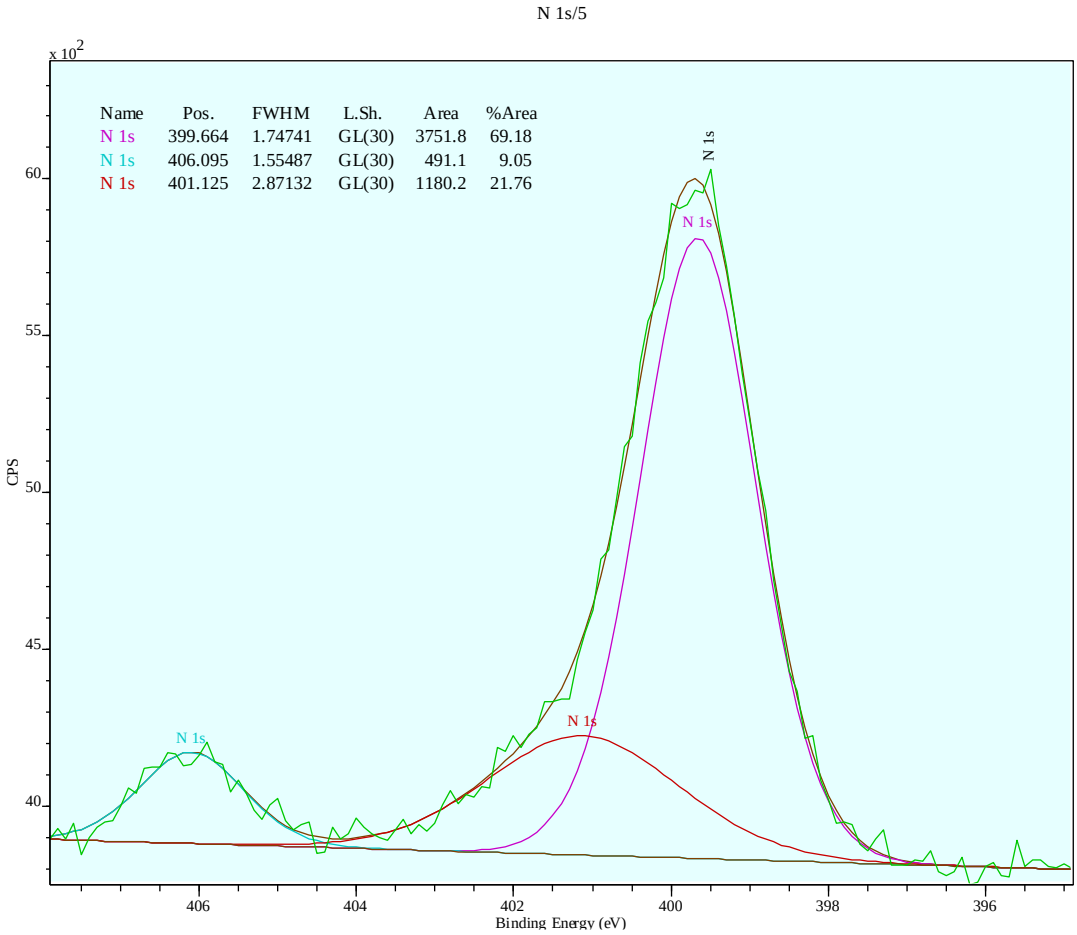


Figure S4 N1s XPS signals

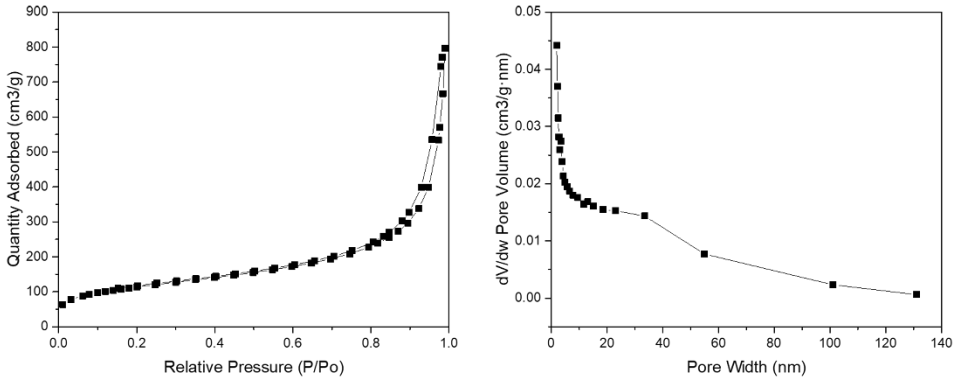


Figure S5 N_2 sorption isotherms and pore size distributions of PDVB-SO_3H-NH_2

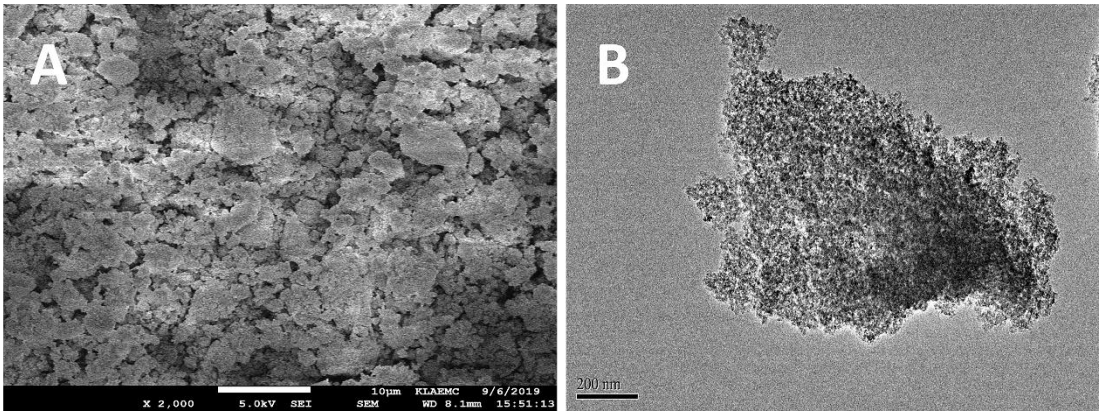


Figure S6 SEM image (A) and TEM image (B) of P(DVB-NH_2-0.5-$StSO_3H$) after recycling for 5 times.

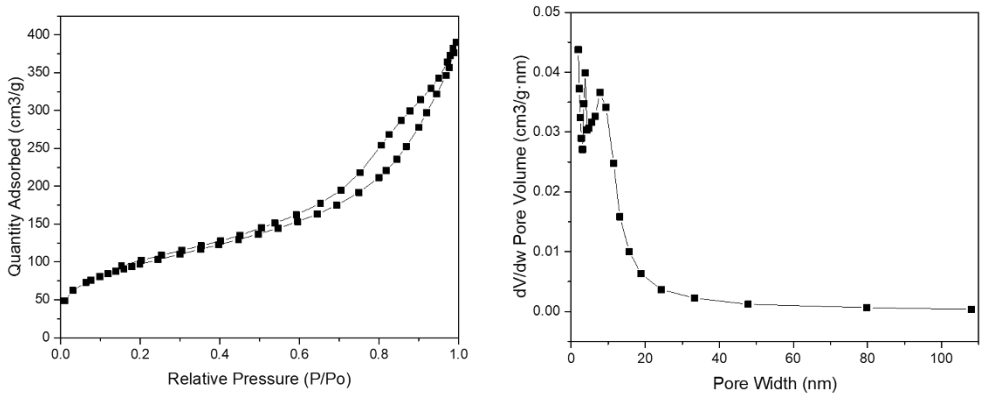
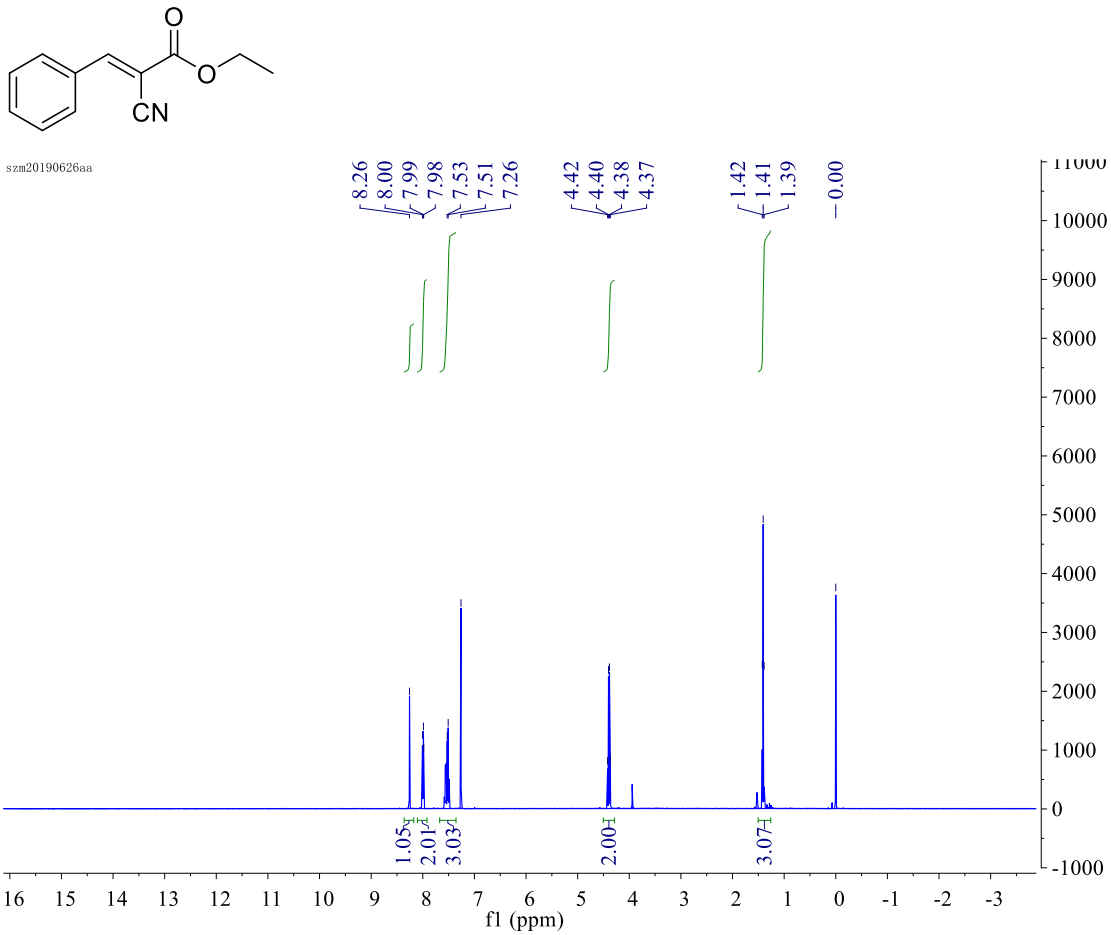


Figure S7 N_2 sorption isotherms and pore size distributions of of P(DVB-NH_2-0.5-$StSO_3H$) after recycling for 5 times.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.10 – 7.92 (m, 2H), 7.52 (d, *J* = 7.6 Hz, 3H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).

Figure S8 ^{1}H-NMR spectrum of the final product for catalytic cascade reaction.

Table S2 The activity comparison with previous works

catalysts	Number of catalytic site	S_{BET} (m^2/g)	[benzaldehyde dimethylacetal], Dose of catalyst	Reaction conditions	Yield (%)	Ref.
SAMSN-AP	0.35 mmol·g^{-1} amine 0.35 mmol·g^{-1} sulfonic acid	853	1.5 mmol, 100mg	CH_3NO_2 (1 mL), 80℃, 48 h.	97.7	*Angew. Chem. Int. Ed.* 2011, *50*, 661
PMO-SO_3H-NH_2	1.79 mmol·g^{-1} amine 1.10 mmol·g^{-1} sulfonic acid	768	1 mmol, 100mg	CH_3NO_2 (5 mL), 90℃, 20 h.	97.5	*Angew. Chem. Int. Ed.* 2010, *49*, 184
MS-A@ MS-B	0.71 mmol·g^{-1} amine 0.35 mmol·g^{-1} sulfonic acid	950	1 mmol, 20mg	toluene (3 mL), 80℃, 0.5 h.	100	*Chem. Commun.,* 2012, *48*, 10541
MS-SO_3H @MS @MS-NH_2	0.8 mmol·g^{-1} amine 0.5 mmol·g^{-1} sulfonic acid	995.7	0.5 mmol, 40mg	toluene (3 mL), 80℃, 0.5 h.	100	*J. Mater. Chem. A,* 2013, *1*, 12804
YS-NH_2@SO_3H	0.71 mmol·g^{-1} amine 0.35 mmol·g^{-1} sulfonic acid	178	0.5 mmol, 35 mg	CH_3NO_2 (5 mL), 90℃, 22 h.	＞99	*Angew. Chem. Int. Ed.* 2012, *51*, 9164
COOHAHN	0.1 mmol·g^{-1} amine	900	0.13 mmol, 30 mg	CH_3NO_2 (2 mL), 90℃, 24 h.	95	*Chem. Eur. J.* 2015, *21*, 7403
OCMN	0.25 mmol·g^{-1} acid site	400	0.5 mmol, 30 mg	toluene (3 mL), 80℃, 24 h.	96	*Sci Rep*, 2015, *5*, 12901
NH_2-GO	0.714 mmol·g^{-1} amine 1.66 mmol·g^{-1} acid site		0.5 mmol, 56 mg	toluene (5 mL), 80℃, 3 h.	95	*ACS Catal*. 2014, *4,* 394
PPAF-SO_3H-NH_2	5.12 mmol·g^{-1} amine 0.8 mmol·g^{-1} sulfonic acid	310	0.36 mmol, 20 mg	toluene (2 mL), 90℃, 1 h.	100	*Chem. Mater*. 2013, *25*, 981
MIL-101-SO_3H-NH_2		638	1 mmol, 50 mg	CH_3NO_2 (5 mL), 90℃, 24 h.	97	*Chem. Commun.,* 2012, *48*, 6151
HCP-A-B	0.85 mmol·g^{-1} amine 0.30 mmol·g^{-1} sulfonic acid	487	0.3 mmol 40 mg	CH_3NO_2 (1.5 mL), 80℃, 6 h.	96	*ACS Catal.* 2017, *7*, 3693
P(DVB-NH_2-0.5-$StSO_3H$)	**2.0 mmol g^{-1} amine 1.6 mmol g^{-1} sulfonic acid**	**251**	**1 mmol 80 mg**	**toluene (3 mL), 80℃, 24 h.**	**99**	***This work***