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Mesoporous acidic polymeric ionic liquids as novel solid acids for catalytic hydrolysis of ketoxime reactions

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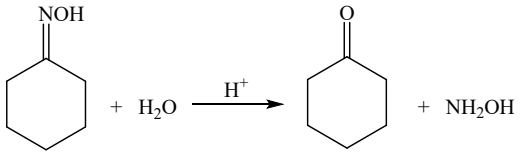
Table S1 Synthesis of various ionic liquids functionalized on polymers and catalytic performance test [a].



Sample	Cross-linking agent	ILs monomer	Anion exchange	Con. (%)[b]	Sel. (%)[c]
Poly(VPS-DVB)HSO_4	DVB	VPS	H_2SO_4	73.29	99.45
Poly(VBS-DVB)HSO_4	DVB	VBS	H_2SO_4	76.75	99.76
Poly(BuS-DVB)HSO_4	DVB	BuS	H_2SO_4	69.38	98.47
Poly(VPS-MBA)HSO_4	MBA	VPS	H_2SO_4	65.39	98.35
Poly(VBS-MBA)HSO_4	MBA	VBS	H_2SO_4	69.87	98.52
Poly(BuS-MBA)HSO_4	MBA	BuS	H_2SO_4	68.13	98.04
Poly(VBS-DVB)Cl	DVB	VBS	HCI	40.29	98.13
Poly(VBS-DVB)NO_3	DVB	VBS	HNO_3	34.54	98.48
Poly(VBS-DVB)H_2PO_4	DVB	VBS	H_3PO_4	49.26	98.65
Poly(VBS-DVB)$COOCF_3$	DVB	VBS	$COOCF_3$	19.89	98.34
Poly(VBS-DVB)SO_3CF_3	DVB	VBS	SO_3CF_3	69.37	98.41
H_2SO_4[d]	-	-	-	98.62	98.82
HCl[e]	-	-	-	99	98.58
HNO_3[f]	-	-	-	62.6	96.9
[SPIPTES]CF_3SO_3@SiO_2-5[g]	-	-	-	38.41	98.02

[a] Reaction conditions: 0.5g cyclohexanone-oxime, 2g Catalysts, 55mL H_2O, 60℃, 1h.

[b] Conversion of cyclohexanone oxime.

[c] Selectivity of hydroxylamine.

[d] Reaction conditions: 0.05mol cyclohexanone-oxime, 0.1mol H_2SO_4, 55mL H_2O, 60℃, 1h.

[e] Reaction conditions: 15.0mmol cyclohexanone-oxime, 34.5mmol HCl, 833mmol H_2O, 60℃, 1h, ref.[8]

[f] Reaction conditions: 0.02mol cyclohexanone-oxime, 0.06mol HNO_3, 100mL H_2O, 35℃, 2h, ref.[49]

[g] Reaction conditions: 0.5g cyclohexanone-oxime, 2g ILs/SiO_2 catalyst, 30 mL H_2O, 60℃, 1h, ref.[26]

Table S2 Coded Levels of Independent Factors in Box-Behnken Design [a].

Factors	Symbols	Coned levels		
		−1	0	+1
Reaction temperature (℃)	X_1	40	60	80
Catalyst amount (g)	X_2	0.5	2	3.5
Water consumption (mL)	X_3	30	55	80

[a] Reaction time:1 h, Cyclohexanone-oxime amount: 0.5 g.

Table S3 Textural parameters of samples.

Sample	BET surface area /$m^2 \cdot g^{-1}$	Pore volume /$cm^3 \cdot g^{-1}$	Pore size /nm
Poly(VBS-DVB)	18.00	0.027	10.97
Poly(VBS-DVB)HSO_4	42.25	0.065	10.92

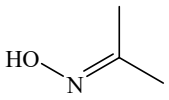
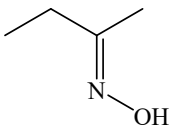
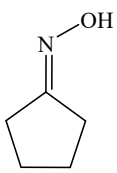
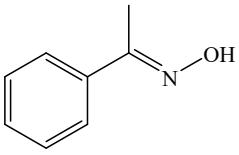
Table S4 Experimental Design and Experimental and Predicted Response Values.

Run	Experimental variables			Cyo-o conversion *Y*(%)	
	X_1	X_2	X_3	Experimental	Predicted
1	0	0	0	74.18	73.66
2	0	0	0	76.75	73.66
3	−1	−1	0	42.69	44.19
4	−1	+1	0	59.76	59.22
5	0	0	0	71.27	73.66
6	+1	0	−1	56.01	55.13
7	0	+1	+1	69.72	69.38
8	+1	+1	0	70.21	68.71
9	+1	−1	0	43.51	44.05
10	0	−1	+1	51.85	49.47
11	0	+1	−1	55.91	58.29
12	−1	0	+1	60.6	61.48
13	0	−1	−1	38.16	38.51
14	−1	0	−1	50.34	48.49
15	0	0	0	72.14	73.66
16	0	0	0	73.45	73.66
17	+1	0	+1	62.34	64.19

Table S5 ANOVA for the Fitted Polynomial Ceuadratic Model.

source	sum of squares	Df	Mean square	*F*-value	*p*-value prob ＞*F*
model	2348.02	9	260.89	41.79	＜0.0001
X_1	43.62	1	43.62	6.99	0.0333
X_2	787.85	1	787.85	126.2	＜0.0001
X_3	242.99	1	242.99	38.92	0.0004
X_1X_2	23.18	1	23.18	3.71	0.0953
X_1X_3	3.86	1	3.86	0.62	0.4574
X_2X_3	0.0036	1	0.0036	0.000567	0.9815
X_1^2	276.35	1	276.35	44.27	0.0003
X_2^2	558.20	1	558.20	89.42	＜0.0001
X_3^2	285.47	1	285.47	45.73	0.0003
residual	43.7	7	6.24		
lack of fit	25.04	3	8.35	1.79	0.2883
pure error	18.66	4	4.66		
std dev	R^2	pred R^2	adj R^2	mean	adeq precision
2.5	0.9817	0.8203	0.9582	60.55	18.344

Table S6 Hydrolytic properties of Poly(VBS-DVB)HSO_4 for different ketoxime.[a]

Entry	Substrate	Con. (%) [b]	Sel. (%) [c]
1		80.44	98.79
2		82.54	98.24
3		83.79	99.02
4		95.31	95.23

[a] Reaction conditions: 0.5g ketoxime, 2g Catalysts, 55mL H_20, 60℃, 1h.

[b] Conversion of ketoxime.

[c] Selectivity of hydroxylamine.

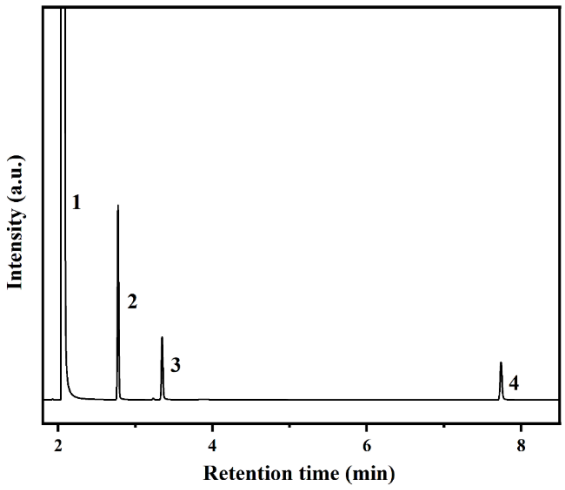


Fig S1 Gas chromatography of reaction product for the hydrolysis of cyclohexanone oxime: 1. Dichloroethane; 2. Chlorobenzene; 3. Cyclohexanone; 4. Cyclohexanone oxime.

1. Model verification and optimization

Before analyzing the 3D surfaces and contours of the regression model, the following distribution map parameter tests are usually required to determine whether the response model fitted to the system is referable and how well it fits.

1.1. Residual distribution

It could be seen from the internal normalized normal probability diagram (Fig. S2) that the residual value distribution was concentrated on the straight line of 45°, indicating that the residual distribution was in good condition and the model prediction was reasonable.

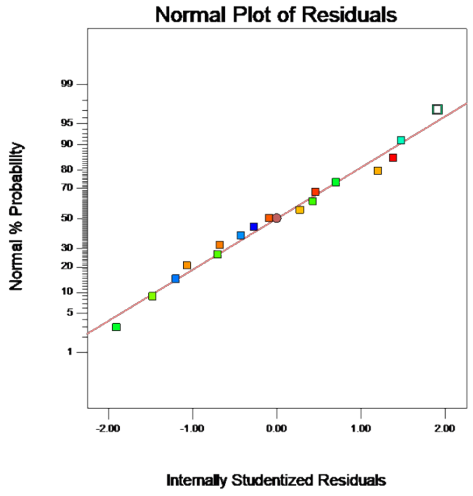


Fig. S2 Normal probability plot of residuals for cyclohexanone-oxime conversion.

1.2. Residuals and predictions

From Fig. S3, it could be seen that the distribution between the residual point and the predicted value was irregular, and there was no obvious connection, indicating that the fitting state of the model fitted well.

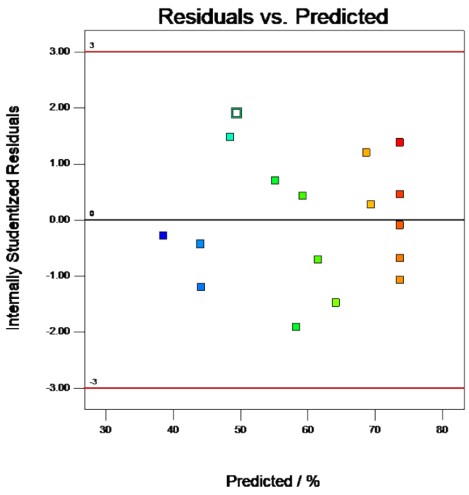


Fig. S3 Plot between residual and predicted response for cyclohexanone-oxime conversion.

1.3. Residuals and trials

It could be seen from Fig. S4 that the fluctuation range of residual difference points in the figure was between −2 and 2 with a reasonable width, and there is no obvious rule, which indicated that there was no obvious irrationality in the test data. The final output result would not deviate from individual samples.

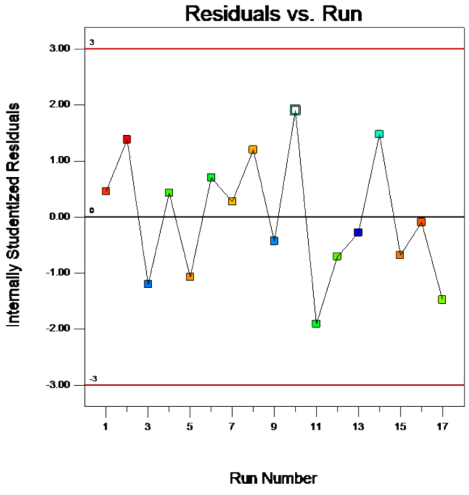


Fig. S4 Plot between Residuals and experimental response for cyclohexanone-oxime conversion.

1.4. Predicted and actual values

From Fig. S5 and S6, it can be seen that the distribution points of the predicted and actual values were close to the center of the 45° straight line, indicating that the predicted values of the system are close to the data of the experimental measurements with small deviation and good fitting model effect.

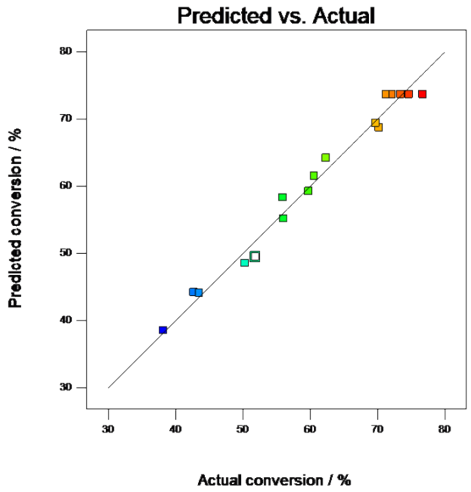


Fig. S5 Experimental values were plotted against the predicted values derived from the model.

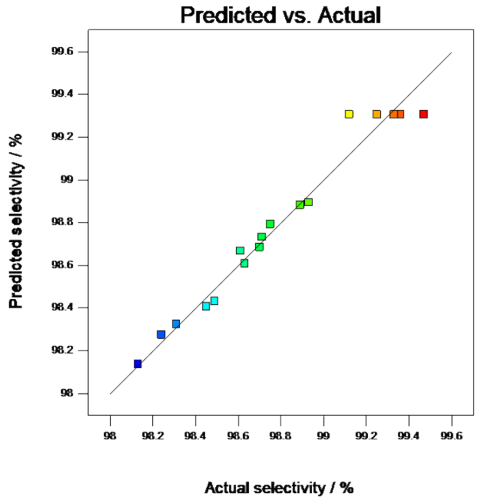


Fig. S6 Experimental values were plotted against the predicted values derived from the model.