Supplementary Information (SI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2024

Supporting Information

Both Zn(II) and imidazolium salt ionic liquids functionalized catalysts as efficient heterogeneous catalysts for CO_2 cycloaddition: preparation, mechanism and stability

Jingjing Sun, Yuanye Zhuang, Meng Ge, Yingying Cheng, Xia Wu*, Shiyang Bai*, Jihong Sun

Beijing Key Laboratory for Green Catalysis and Separation, College of Materials Science & Engineering, Beijing University of Technology, Beijing 100124, China.

Email: wuxia@bjut.edu.cn (Xia Wu), sybai@bjut.edu.cn (Shiyang Bai)

1. ^1H NMR

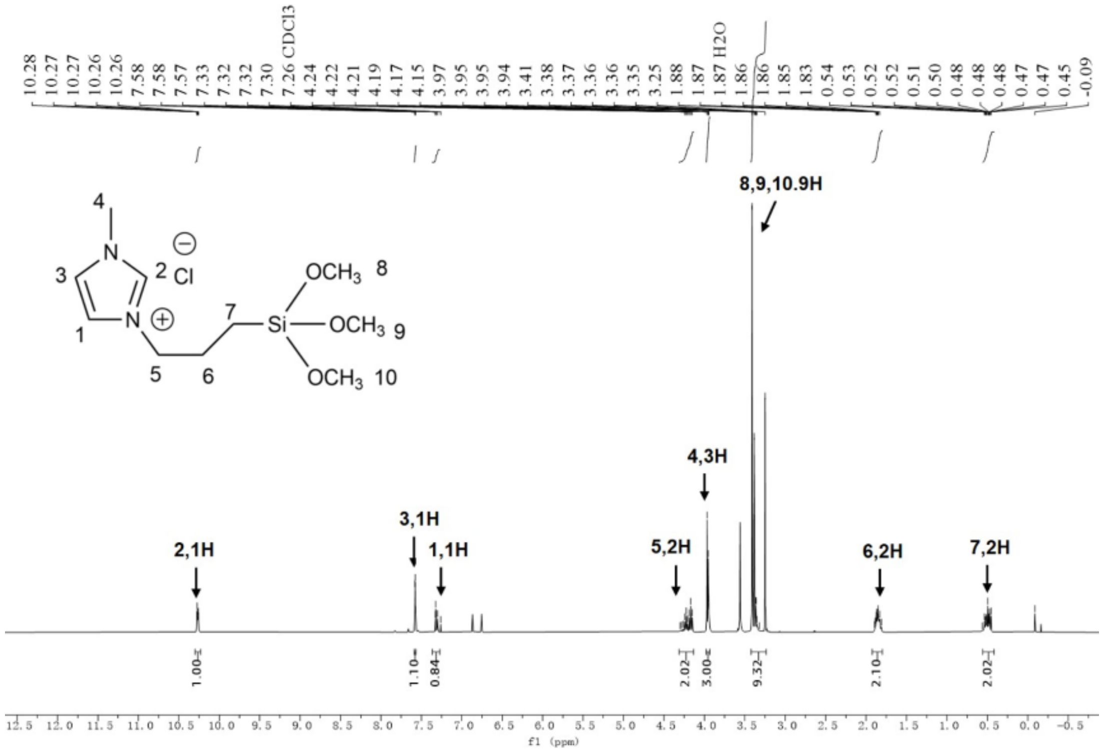

Fig. S1 The ^1H NMR spectra of ILs

ILs was confirmed by ^1H NMR spectroscopy. ^1H NMR spectra were obtained on a Bruker ASCEndTM400(AVANCE HD III) spectrometer using $CDCl_3$. The spectral data presented below are consistent with the characteristics previously reported.[1-3] ^1H NMR (400 MHz, $CDCl_3$) δ 10.30 - 10.23 (m, 1H), 7.58 (d, J = 1.7 Hz, 1H), 7.36 - 7.27 (m, 1H), 4.20 (dt, J = 22.1, 7.3 Hz, 2H), 3.98 - 3.93 (m, 3H), 3.42 - 3.24 (m, 9H), 1.92 - 1.80 (m, 2H), 0.56 - 0.42 (m, 2H).

2. X-ray diffraction patterns

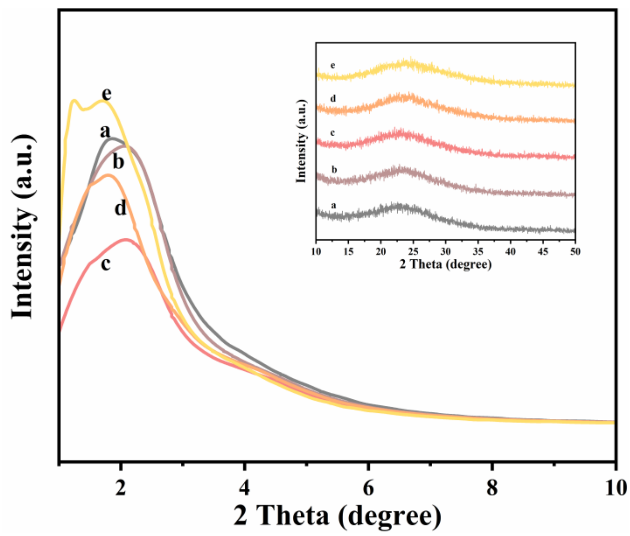

Fig. S2 Small-angle and wide-angle XRD patters of (a) Zn /BMMs-0.5%, (b) Zn/BMMs-1%, (c) Zn/BMMs-2%, (d) Zn/BMMs-4%, (e) Zn/BMMs-6%

Interestingly, the (100) crystal plane significantly shifted towards lower angles with the loading of Zn and ionic liquid, indicating the increasing of crystal plane spacing (d) composed of pores and wall thickness.

3. FT-IR spectra

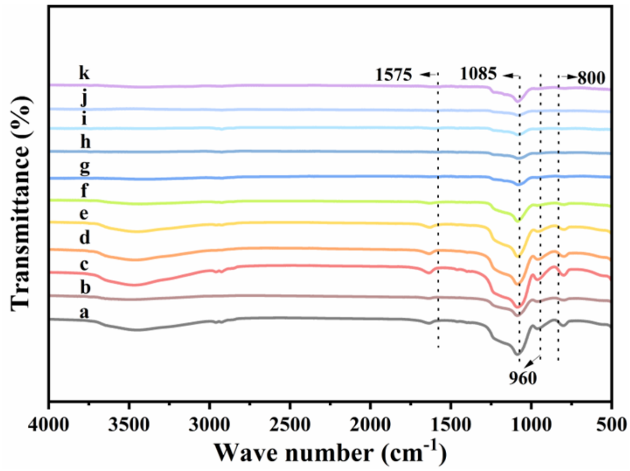

Fig. S3 FT-IR spectra of (a) BMMs, (b) Zn /BMMs-0.5%, (c) Zn/BMMs-1%, (d) Zn/BMMs-2%, (e) Zn/BMMs-4%, (f) Zn/BMMs-6%, (g) Zn/BMMs-ILs-0.5%, (h) Zn/BMM-ILs-1%, (i) Zn/BMMs-ILs-2%, (j) Zn/BMMs-ILs-4%, (k) Zn/BMMs-ILs-6%

BMMs, Zn/BMMs, and Zn/BMMs-ILs series samples are indexed by FT-IR spectroscopy in Fig. S3. The peaks at 1085 and 800 cm^{-1} in all patterns were ascribed to the bending vibration peak of Si-O-Si and the symmetrical stretching of Si-O-Si,[4, 5] respectively. The weak characteristic peak around 960 cm^{-1} corresponds to the assimilated flutter peak of Si-OH,[6] indicating a large number of Si-OH on the appearance of BMMs. In addition, a characteristic peak of imidazole appeared at 1575 cm^{-1} after loading the ionic liquid,[7] explaining that the ionic liquid had successfully grafted onto Zn/BMMs through the condensation with Si-OH on the surface. Based on the above results, indicated that Zn/BMMs-ILs material had been successfully synthesized through the in-situ synthesis method.

4. Nitrogen adsorption-desorption isotherms and pore size distribution

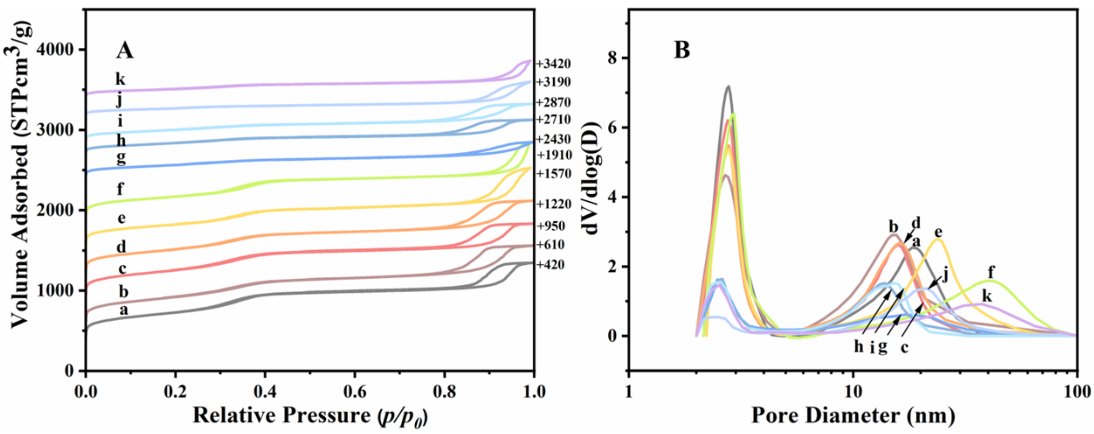

Fig. S4 N_2 adsorption-desorption isotherms (A) and corresponding pore size distributions (B) of (a) BMMs, (b) Zn /BMMs-0.5%, (c) Zn/BMMs-1%, (d) Zn/BMMs-2%, (e) Zn/BMMs-4%, (f) Zn/BMMs-6%, (g) Zn/BMMs-ILs-0.5%, (h) Zn/BMM-ILs-1%, (i) Zn/BMMs-ILs-2%, (j) Zn/BMMs-ILs-4%, (k) Zn/BMMs-ILs-6%

Table S1 Structural parameters and textural properties of all samples

Samples	2θ (°)	d (nm)	BET Surface area (m^2 /g)	Pore volume (cm^3 /g)[a]	Small mean pore (nm)[b]
BMMs	1.98	4.46	1213.0	1.6	2.8
Zn/BMMs-0.5%	1.94	4.55	1207.6	1.6	2.8
Zn/BMMs-1%	1.90	4.64	1206.4	1.5	2.7
Zn/BMMs-2%	1.84	4.80	1137.5	1.5	2.7
Zn/BMMs-4%	1.78	4.96	982.1	1.6	2.7
Zn/BMMs-6%	1.74	5.07	971.7	1.6	2.9
Zn/BMMs-ILs-0.5%	1.68	5.25	530.9	0.6	2.5
Zn/BMMs-ILs-1%	1.62	5.45	511.5	0.7	2.5
Zn/BMMs-ILs-2%	1.58	5.58	521.2	0.7	2.4
Zn/BMMs-ILs-4%	1.60	5.51	326.4	0.7	2.2
Zn/BMMs-ILs-6%	1.56	5.66	354.5	0.7	2.5

a. Estimated from the amounts adsorbed at a relative pressure (P/P_0) of 0.99.

b. The pore size distribution was calculated from the N_2 adsorption branch using the BJH method.

5. SAXS results

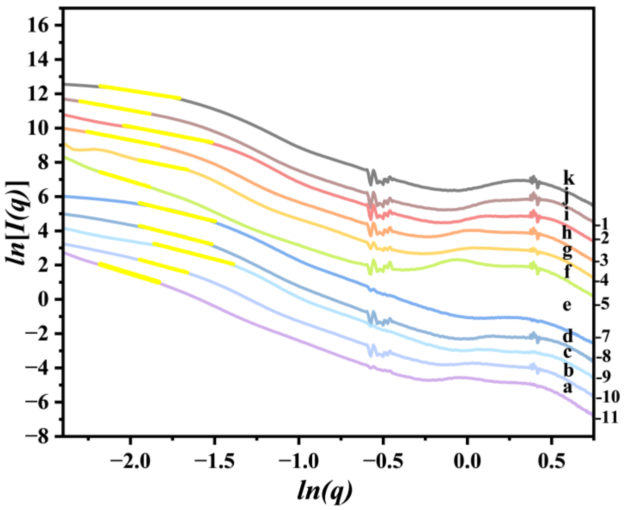

Fig. S5 Shifted scattering curves of (a) BMMs, (b) Zn/BMMs-0.5%, (c) Zn/BMMs-1%, (d) Zn/BMMs-2%, (e) Zn/BMMs-4%, (f) Zn/BMMs-6%, (g) Zn/BMMs-ILs-0.5%, (h) Zn/BMM-ILs-1%, (i) Zn/BMMs-ILs-2%, (j) Zn/BMMs-ILs-4%, (k) Zn/BMMs-ILs-6%

6. EA and AAS analysis

Table S2 Amount of ILs and Zn measured from EA and AAS

Samples	EA (wt%)			ILs (mmol/g)	Zn (mmol/g)
	C	N	H		
BMMs	--	--	--	--	0.00
Zn/BMMs-0.5%	--	--	--	--	0.09
Zn/BMMs-1%	--	--	--	--	0.15
Zn/BMMs-2%	--	--	--	--	0.25
Zn/BMMs-4%	--	--	--	--	0.37
Zn/BMMs-6%	--	--	--	--	0.44
Zn/BMMs-ILs-0.5%	13.29	3.22	2.38	1.2	0.06
Zn/BMMs-ILs-1%	12.34	3.36	2.18	1.2	0.12
Zn/BMMs-ILs-2%	12.59	3.31	2.20	1.2	0.22
Zn/BMMs-ILs-4%	13.08	3.25	2.09	1.2	0.38
Zn/BMMs-ILs-6%	14.10	4.15	2.26	1.5	0.43
BMMs-ILs	10.29	2.54	2.47	0.9	--

7. XPS spectra

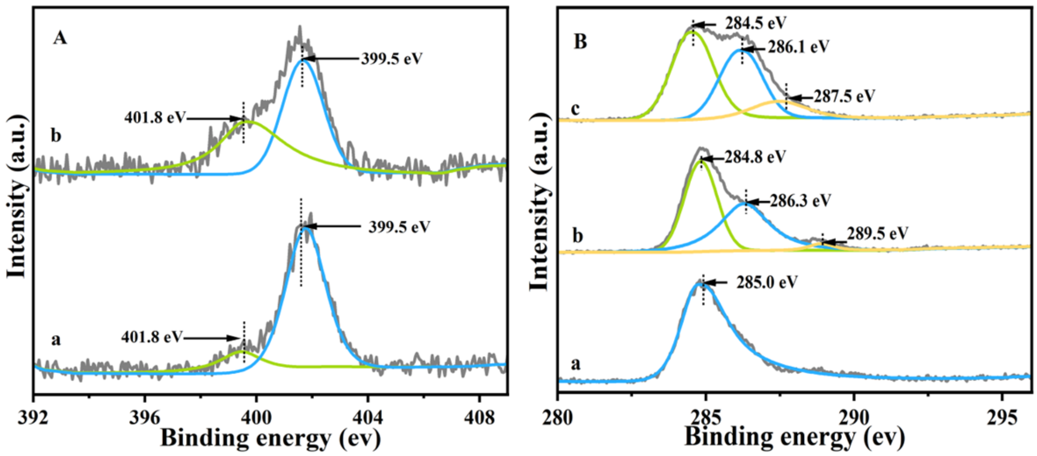

Fig. S6 XPS spectra of (A) the N 1s core level regions from (a) Zn/BMMs-ILs-4%, (b) Zn/BMMs-ILs-4%-Run5 and (B) the C 1s core level regions from (a) Zn/BMMs-4%, (b) Zn/BMMs-ILs-4% and (c) Zn/BMMs-ILs-4%-Run5

8. Reusability Study

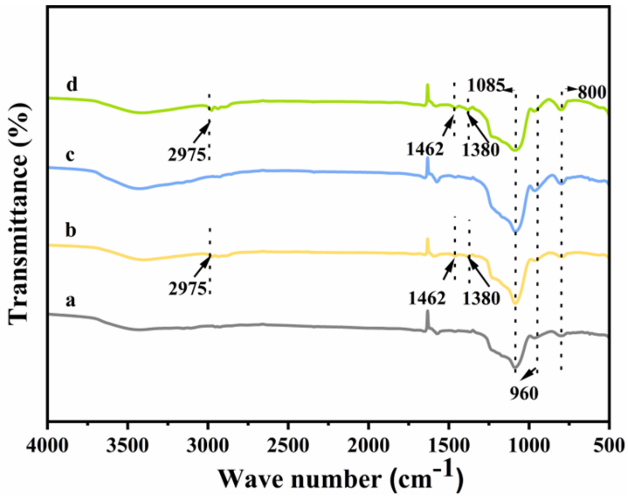

Fig. S7 FT-IR spectra of fresh and recovered catalysts (a) Zn/BMMs-ILs-4%, (b) Zn/BMMs-ILs-4%-Run5, (c)BMMs-ILs and (d) BMMs-ILs-Run5

Table S3 Zn and ILs content of reused catalysts

Samples	EA (wt%)			ILs (mmol/g)	Zn (mmol/g)
	C	N	H		
Zn/BMMs-ILs-4%-Run5	20.50	1.78	3.05	0.6	0.24
BMMs-ILs-Run5	16.95	0.63	2.46	0.2	--

References

1 I. Candel, P. Calero, R. Martinez-Manez, F. Sancenon, M. D. Marcos, T. Pardo and J. Soto, *Inorganica Chimica Acta*, 2012, **381**, 188-194.

2 M. T. Finn, C. M. Donahue, A. V. Blake, N. An, S. R. Daly and A. M. Voutchkova-Kostal, *European Journal of Inorganic Chemistry*, 2018, **2018**, 2471-2479.

3 H. Valizadeh, M. Amiri, F. Hosseinzadeh, *Dyes and Pigments*, 2012, **92**, 1308-1313.

4 L. Gao, J. Sun, L. Zhang, J. Wang and B. Ren, *Materials Chemistry and Physics*, 2012, **135**, 786-797.

5 X. Jin, Q. Wang, J. Sun, H. Panezai, S. Bai and X. Wu, *Microporous and Mesoporous Materials*, 2017, **254**, 77-85.

6 A. P. Perissinotto, C. M. Awano, D. A. Donatti, F. S. de Vicente and D. R. Vollet, *Langmuir*, 2015, **31**, 562-568.

7 S. Bai, X. Hu, J. Sun and B. Ren, *New Journal of Chemistry*, 2014, **38**, 2128-2134.