Supporting information

Homogeneous base catalyst with high activity and stability for synthesis of dimethyl carbonate by transesterification

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Catalyst characterization

^{1}H NMR spectrum of KIm was collected on a Bruker ACF-400 NMR Spectrometer. Fourier transform infrared (IR) spectra was recorded on a Nicolet Nexus 470 spectrometer. Thermogravimetric (TG) analysis curves were obtained by the use of a thermos balance analyzer (STA-499C, NETZSCH), About 10 mg of sample was heated to 800 $^{\circ}$C with a rate of 10 $^{\circ}$C·min^{-1} under a flow of N_2 (20 mL·min^{-1}). ICP-MS testing was performed using Agilent 7700. Elemental analysis was performed at Elementar Unicube, Germany. Karl Fischer titration was performed on the catalyst and raw materials in the experiment, using 870 KF Titrino plus.

Gas chromatographic analysis condition

ZNCL-G collector type constant temperature heating magnetic stirrer was obtained from Shanghai Yuming Instrument Co., Ltd.; GC-1690 Gas Chromatograph was obtained from Hangzhou Kexiao Chemical Instrument Co., Ltd.

GC-1690 gas chromatographic analysis was used. The experimental chromatographic column was the OV-17 capillary column equipped with a hydrogen flame detector. The temperature of the column chamber was 150 °C, the temperature of the injection port was 240 °C, and the temperature of the detector was 250 °C. The chromatographic workstation adopts N2000 of Zhejiang University, and the area normalization method is used to determine the content of each com

¹H NMR spectroscopy

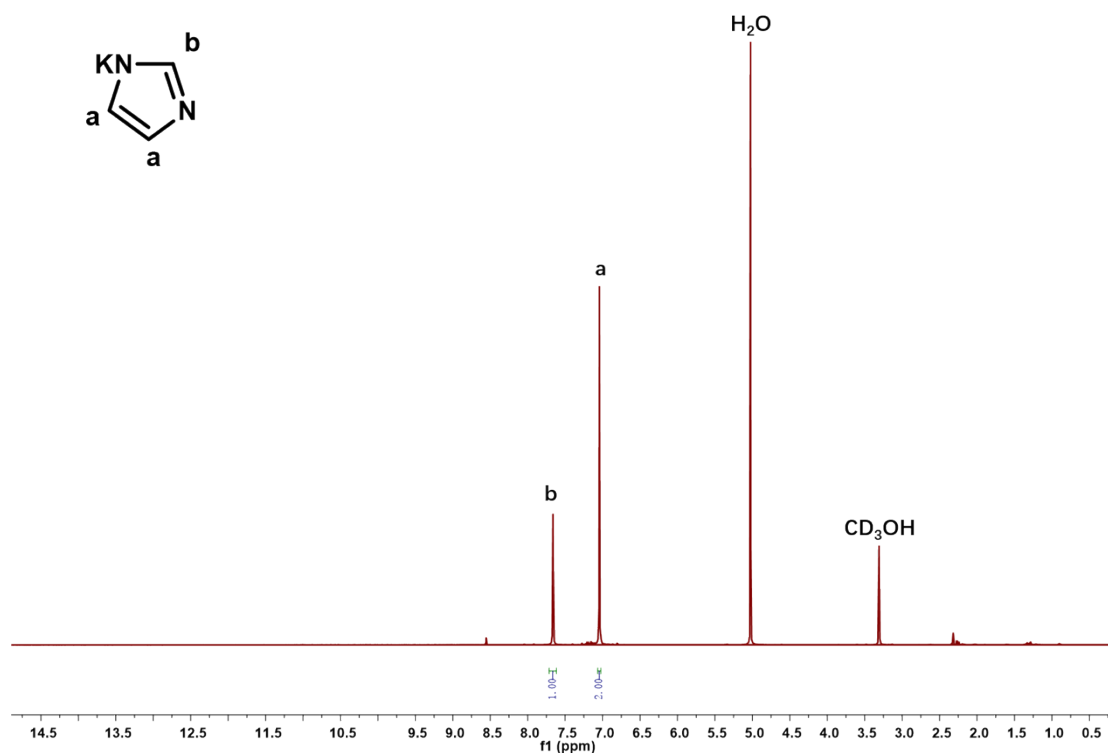Fig. S1 ¹H NMR spectrum of KIm

¹H NMR (400 MHz, CD$_3$OH) δ 7.66 (t, J = 1.1 Hz, 1H), 7.04 (d, J = 1.1 Hz, 2H).

As is shown in Fig. S1, the spectrum is basically identical with the theoretical value, which combined with the elemental analysis data (Table S1), proves the successful synthesis of KIm.
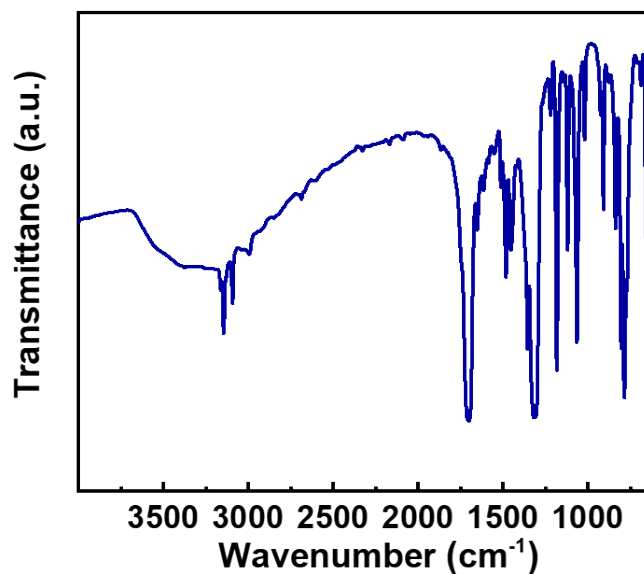
IR analysis

Fig. S2 FT-IR spectra of KIm

Fig. S2 represents the characteristic peaks of KIm. The peaks at 3145 cm^{-1} and 3094 cm^{-1} are ascribed to the stretching vibration of C-H on the unsaturated carbon of imidazole. The peak at 1699 cm^{-1} results from the stretching vibration of C=N on imidazole , the peak of C=C also appear at 1482 cm^{-1}. In addition, the in-plane bending vibration of C-N appears at 1184 cm^{-1}, the peak at 837 cm^{-1} is the C-H out-of-plane deformation vibration of imidazole; the peak at 786 cm^{-1} is the C-H in-plane bending vibration peak. [1].

Elemental analysis of KIm

Table S1 Content of each element of KIm

Element	C (wt%)	H (wt%)	N (wt%)	K (wt%)
Content	34.08	4.01	26.43	34.20

Determination of base Strength of different ionic Liquids by Hammett indicator method

The base strength of ionic liquids is determined using the Hammett indicator method, the specific steps are: the indicator is configured into 0.5 wt% anhydrous ethanol solution, and then the prepared Hammett indicator solution is added 2-3 drops to the ionic liquid, and finally the color change of the indicator is observed, and the alkali strength of the ionic liquid can be obtained.

Table S2 The Base strength of different ionic liquids

Catalyst	Bromothymol Blue	Phenolphthalein	2,4-dinitroaniline	4-Chloro-2-nitroaniline	Base strength
[BmIm]Cl	Blue	Colourless	Yellow	Yellow	$7.2<H\_<8.2$
[HmIm] Cl	Blue	Colourless	Yellow	Yellow	$7.2<H\_<8.2$
[AmIm]Cl	Blue	Colourless	Yellow	Yellow	$7.2<H\_<8.2$
[EmIm]Br	Blue	Colourless	Yellow	Yellow	$7.2<H\_<8.2$
[AmIm]Br	Blue	Colourless	Yellow	Yellow	$7.2<H\_<8.2$
[VbIm]Br	Blue	Colourless	Yellow	Yellow	$7.2<H\_<8.2$
[BmIm]Br	Blue	Colourless	Yellow	Yellow	$7.2<H\_<8.2$
[BMIm] [AcO]	Blue	Colourless	Yellow	Yellow	$7.2<H\_<8.2$
CH$_3$ONa	Blue	Red	Purplish red	Yellow	$15.0<H\_<18.4$
NaIm	Blue	Red	Purplish red	Yellow	$15.0<H\_<18.4$
KIm	Blue	Red	Purplish red	Yellow	$15.0<H\_<18.4$

GC chromatogram of the reaction mixture of methanol with PC
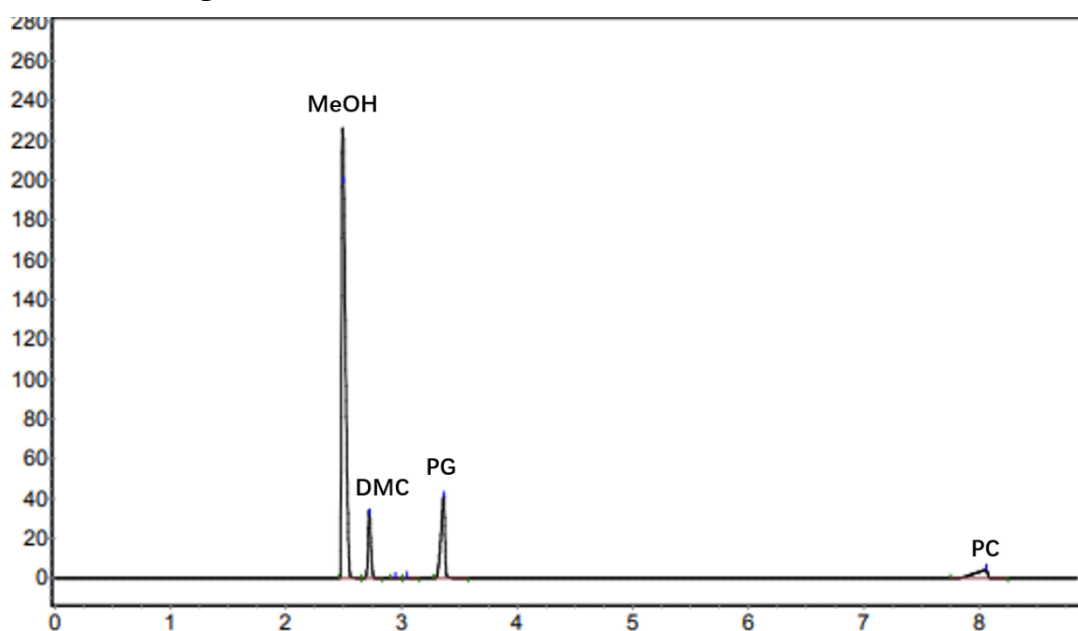

Fig. S3 GC chromatogram of the reaction mixture of methanol with PC. Reaction conditions: reaction time 3 min, reaction temperature 30 °C, catalyst amount is 0.5% of the total mass of raw materials, n(MeOH):n(PC)=10:1.

The circulation tests of KIm

During the cycle, added methanol with 20 times the molar amount of PC into the reaction solution after the last reaction, and maked the PC as fully reactive as possible. It can make the separation of catalyst and PC easier and reducing the impact of subsequent separation on the catalyst. In addition, PC is difficult to be completely removed from the reaction system by vacuum distillation. Adding excessive methanol can minimize the possibility of side reaction between PC and catalyst.

Then transferred the mixture to a rotary evaporator, removed the MeOH and DMC by vacuum distillation at 145-150 °C. At the same time, PG was almost removed completely. After evaporation, the remaining weight was weighed, the composition was analyzed, and the remaining amount of PC was calculated; the remaining mixture was used directly as the catalyst for the next cycle.

The effect of reaction conditions on the selectivity of DMC
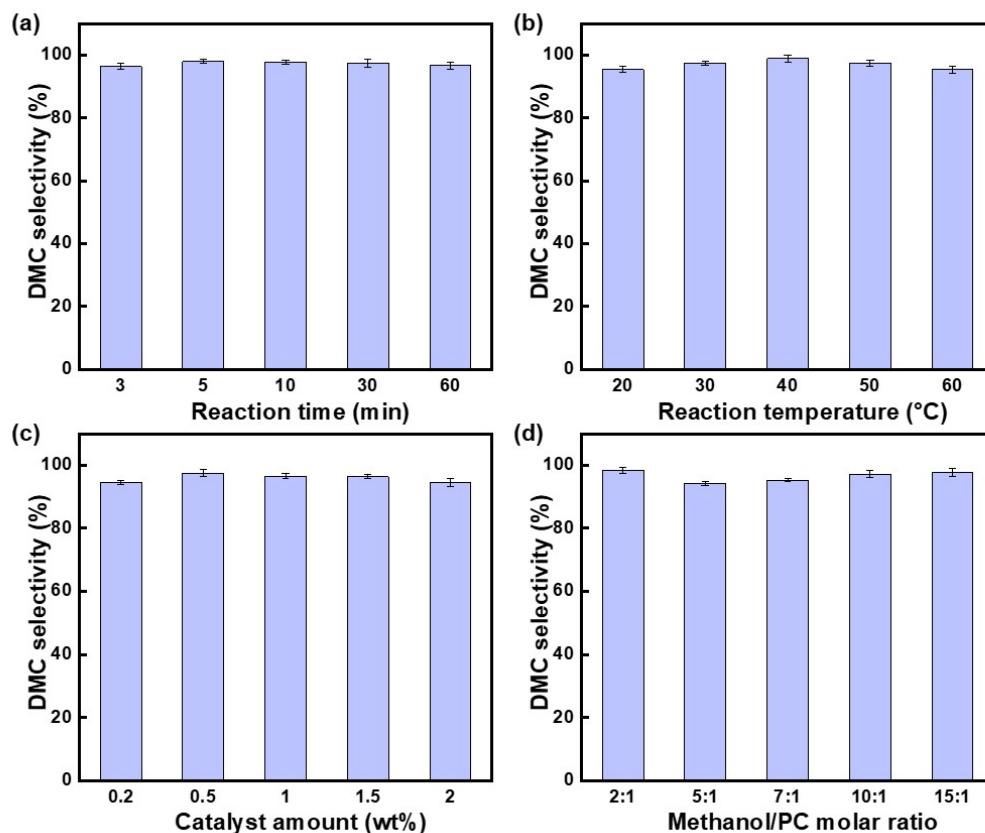

Fig. S4 (a) The effect of reaction time on the selectivity of DMC. Reaction conditions: the reaction temperature was 50 °C, catalyst amount was 0.5% of the total mass of the raw materials, and n(MeOH):n(PC)=5:1. (b) The effect of reaction temperature on the yield of DMC. Reaction conditions: the reaction time was 5 min, catalyst amount was 0.5% of the total mass of the raw materials, and n(MeOH):n(PC)=5:1. (c) Effect of catalyst amount on the yield of DMC. Reaction conditions: reaction time 5 min, reaction temperature 50 °C, n(MeOH):n(PC)=5:1. (d) Effect of MeOH/PC molar ratio on the yield of DMC. Reaction conditions: the reaction time was 5 min, the reaction temperature was 50 °C, and catalyst amount was 0.5% of the total mass of the raw materials.

The effect of catalyst cycle times on the selectivity of DMC
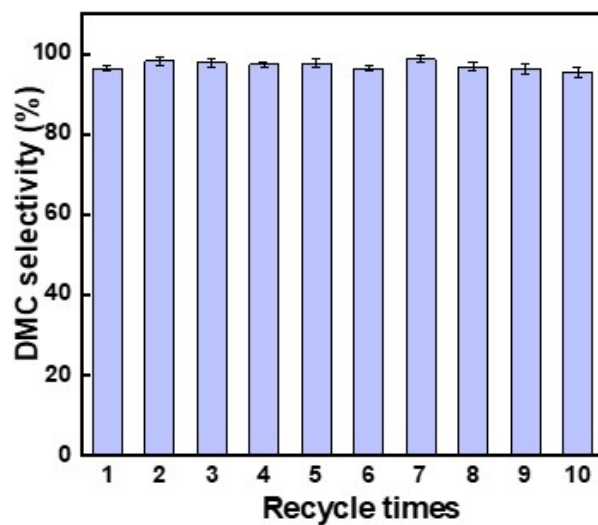

Fig. S5 Effect of catalyst cycle times on the selectivity of DMC. Reaction conditions: reaction time 3 min, reaction temperature 30 °C, catalyst amount is 0.5% of the total mass of raw materials, n(MeOH):n(PC)=10:1.

Water content of different catalysts

Karl Fischer titration was performed on the catalyst and raw materials in the experiment.

Table S3 Water Content of different materials

Materials	Average value of water content (%)
[BmIm]Cl	0.18
[HmIm] Cl	0.07
[AmIm]Cl	0.14
[EmIm]Br	0.15
[AmIm]Br	0.09
[VbIm]Br	0.12
[BmIm]Br	0.17
[BmIm] [AcO]	0.08
CH_3ONa	0.13
NaIm	0.06
KIm	0.03
PC	0.02
CH_3OH	0.02

We investigated the impact of catalysts with various water contents on the reaction, using KIm as an example. Fig. S6 depicts that the water content in the first reaction had no obvious effect on the activity of the catalyst. As demonstrated in Fig. S7, excess water content can adversely affect the cycling of the catalyst, thus the main source of catalyst loss is water contamination in the reaction system. Therefore, we have been trying to control the water contamination to reduce the deactivation of catalysts in our cycling experiments.
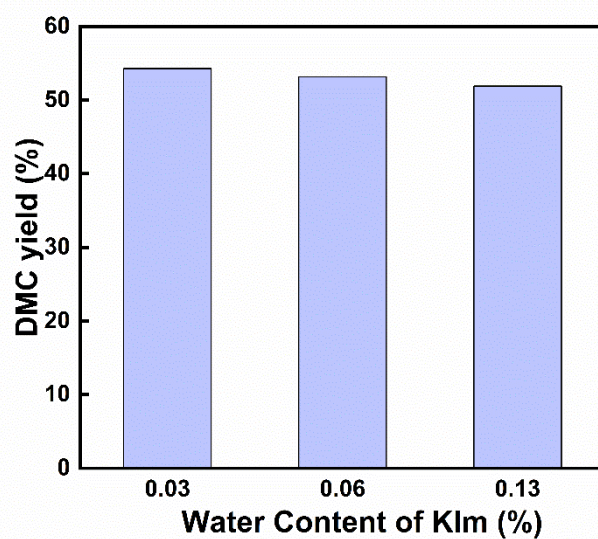
Fig. S6 Effect of different water contents on the catalytic activity of KIm. Reaction conditions: reaction time 3 min, reaction temperature 30 ^{o}C, catalyst amount is 0.5% of the total mass of raw materials, n(MeOH):n(PC)=5:1.
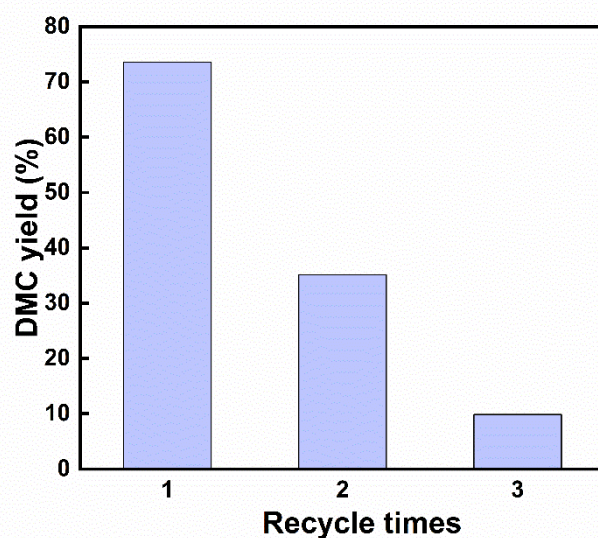

Fig. S7 Effect of higher contents on the Reusability of KIm. Reaction conditions: The water contents of KIm is 0.27%, raw materials were not dehydrated, reaction time 3 min, reaction temperature 30 °C, catalyst amount is 0.5% of the total mass of raw materials, n(MeOH):n(PC)=10:1

REFERENCES

1. S. Han, M. Luo, X. Zhou, Z. He and L. Xiong, *Industrial & Engineering Chemistry Research*, 2012, **51**, 5433-5437.