Electronic Supplementary Information

Metalated carbon nitrides as base catalysts for efficient catalytic hydrolysis of carbonyl sulfide

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Experimental materials

All the regents used are analysis grades without further purification. Melamine ($C_3H_6N_6$, 99%) were purchased from Sigma-Aldrich. Activated carbon, LiCl (99%), NaCl(99%), KCl(99%), RbCl(99%) and CsCl (99%) were purchased from China Sinopharm Chemical reagent Co. Ltd.. All the regents were used without further purification.

Experimental Section

Synthesis of PCN: PCN was prepared by direct thermal polymerization of melamine in the air. In a typical synthesis, Melamine (10g) was thermal heated to 600 ° C for 2 h at a rate of 5 °C min^{-1} in a muffle furnace. The final products were collected after the temperature cooled down to the room temperature.

Synthesis of X-MPCN: The metalation of PCN was achieved by a simple method of treatment of PCN materials with alkali chloride (LiCl, NaCl, KCl, RbCl and CsCl) at 600℃ with N_2 atmosphere.Typically, 2 g PCN (synthesized-above) was ground with 10 g alkali chloride (*e. g.*, KCl) in a mortar. Then, the resultant mixture was heated to 600 °C for 2 h at a rate of 5 °C min^{-1} in a tube furnace with N_2 flow rate of 200 mL/min. After it was cooled to

room temperature, the product was washed with deionized water several times to remove the overmuch alkali chloride (eg, KCl). This sample is denoted as X-MPCN (eg, K^+-MPCN).

Synthesis of K^+/PCN: For comparison, the PCN material loaded with a certain amount of K^+ was also prepared by impregnation method. Typically, 286.5 mg KCl and 2 g PCN powders were mixed together in 10 mL of water. Then, after stirred for 10 min, the mixture was evaporated with a water vapor. The obtained solid is denoted as K^+/PCN.

Synthesis of K^+/AC: the AC material loaded with a certain amount of K^+ was also prepared by impregnation method. Typically, 286.5 mg KCl and 2 g AC powders were mixed together in 10 mL of water. Then, after stirred for 10 min, the mixture was evaporated with a water vapor. The obtained solids is denoted as K^+/AC.

Characterization: Transmission electron microscopy (TEM) was obtained by Zeis 912 microscope. The CO_2 adsorption capacity of the samples were measured by CO_2 adsorption collected at 273 K using an ASAP 2020 instrument (Micromeritics, USA). The nitrogen adsorption–desorption isotherms were collected at 77 K using Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. Powder X-ray diffraction (XRD) measurements were performed on Bruker D8 Advance diffractometer with Cu K*a1* radiation (λ = 1.5406 Å). Fourier transformed infrared (FTIR) spectra were recorded on BioRad FTS 6000 spectrometer. X-ray photoelectron spectroscopy (XPS) data were obtained on Thermo ESCALAB250 instrument with a monochromatized Al Kα line source (200 W).

Carbon dioxide temperature programmed desorption (CO_2-TPD): CO_2-TPD was carried out on an AutoChem II 2920 Micromeritics Chemisorption Analyzer (USA). Before measurements, the samples were first activated at 300 °C for 1 h under a N_2 atmosphere.

After the temperature was reduced to 50 °C, the samples were swept by CO_2 for 1 h. Thereafter, N_2 with flow rate of 30 mLmin^{-1} was switched again to the sample, and after reaching a stable baseline. Subsequently, the temperature was gradually increased to 350 °C with a ramping rate of 10 °C/min to obtain the CO_2-TPD curves.

Raman measurements: The Raman measurements were performed on a Renishaw in Via Raman System 1000 with a 312 nm Nd: YAG excitation source at room temperature.

In situ FTIR measurements : In situ FTIR spectroscopic studies were performed on a Thermofisher Nicolet IS50 equipped with a liquid nitrogen cooled MCT-A detector. Before the measurement, the K^+-MPCN sample was treated at 300 °C for 1h under N_2 atmosphere to remove the adsorbed contaminants. Then the FTIR spectrum of the K^+-MPCN sample at 25°C was first collected as the background prior to any CO_2 introduction. After CO_2 introduction, the FTIR spectra were obtained by subtracting the background. The measurements were performed at room temperature of around 25°C.

DFT Calculations: DFT calculations were carried out using the Vienna ab initio simulation package (VASP5.3).[1] The Perdew−Burke−Ernzerhof (PBE) exchange-correlation functional was used within the spin-polarized generalized gradient approximation (GGA).[2] A plane-wave basis set was employed within the framework of the projector augmented-wave (PAW) method.[3] In order to get accurate results, the cutoff was set to 450 eV. A Gaussian smearing was used with a smearing width of 0.1 eV. Geometry relaxations were carried out until the residual forces on each ion were smaller than 0.02 eV/Å. We first relaxed a single unit cell of PCN. Then, a single Li, Na, K , Rb, or Cs atom was introduced into PCN. The van der Waals (vdW) correction was included by using the DFT-D2 approach.[4]

Evaluation of catalytic activity: The hydrolysis of COS over catalyst was performed in a fixed-bed reactor at atmospheric pressure. 0.2 g catalyst was used. At steady state, a mixture gas of N_2 containing COS (100 ppm) and H_2O (250 ppm)was introduced into the reactor at a total flow rate of 50 mL/min. The concentration of COS in the reactor effluent was monitored on-line by a gas chromatograph (Fuli GC-9790II) equipped with a flame photometric detector. The conversion of COS was determined by analyzing the initial and the current temperature-peak areas of COS in the GC. In this study, the COS conversion was calculated as follows:

COS conversion (%) = $(C_0 - C_T) / C_0 \times 100$

where C_0 and C_T are the peak area of COS at temperatures of 20° C and 80°C, respectively.
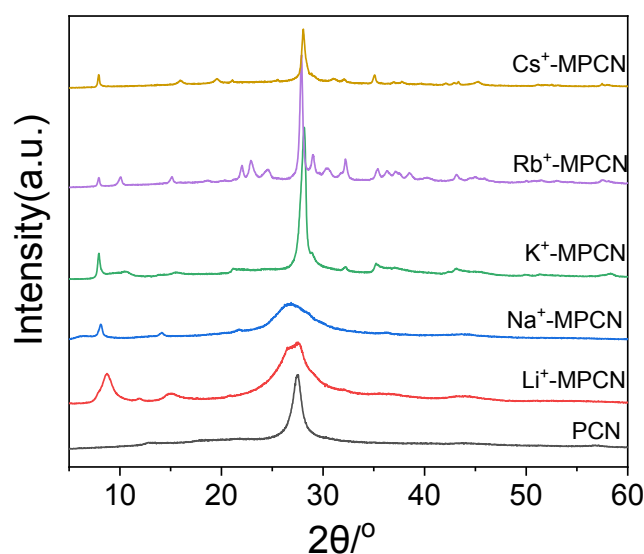
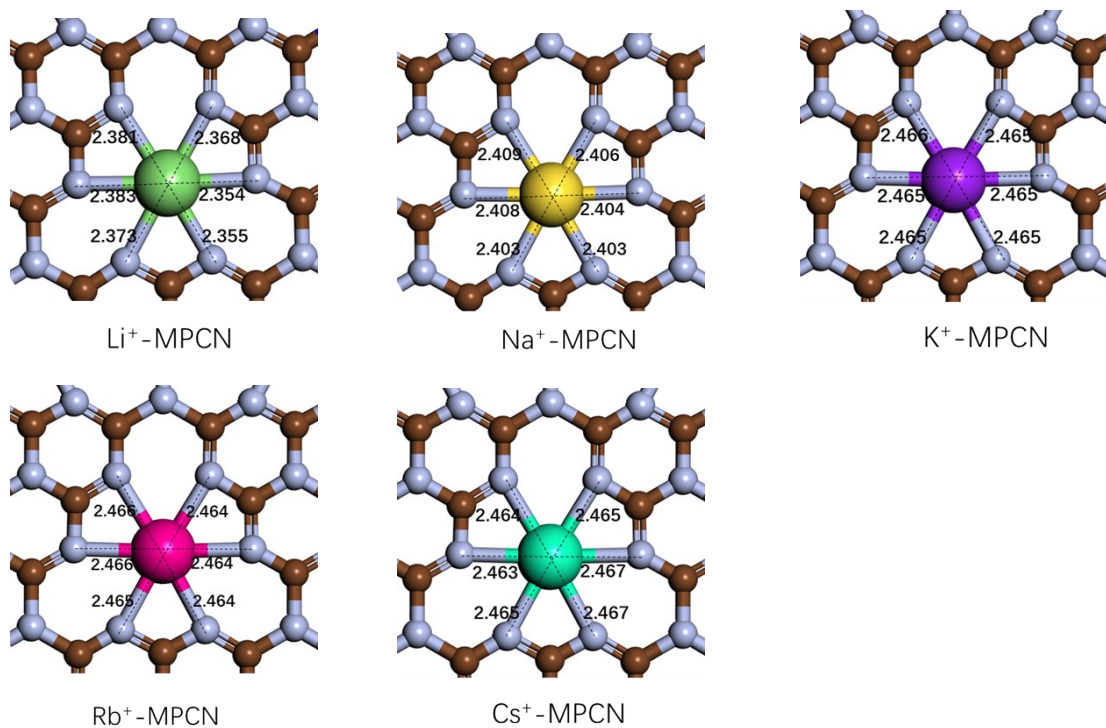**Fig. S1** Powder XRD patterns of K^+-MPCN and PCN

Fig. S2 The molecular models of X-MPCN samples.

Table S1 The adsorption energy and Bader charge of alkali metal ion in the X-MPCN structure.

	Li$^+$-MPCN	Na$^+$-MPCN	K$^+$-MPCN	Rb$^+$-MPCN	Cs$^+$-MPCN
Adsorption energy (eV)	-3.22	-3.17	-2.01	-1.04	-5.00
Bader charge (|e|)	0.996	0.995	0.754	0.757	0.887
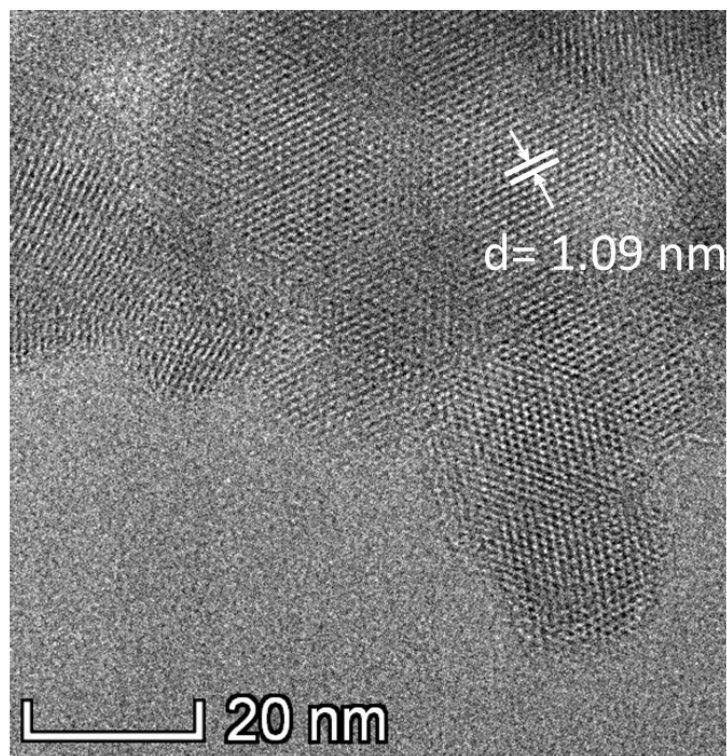
Fig. S3 High-resolution transmission electron microscopy (HRTEM) image of K^+-MPCN sample.
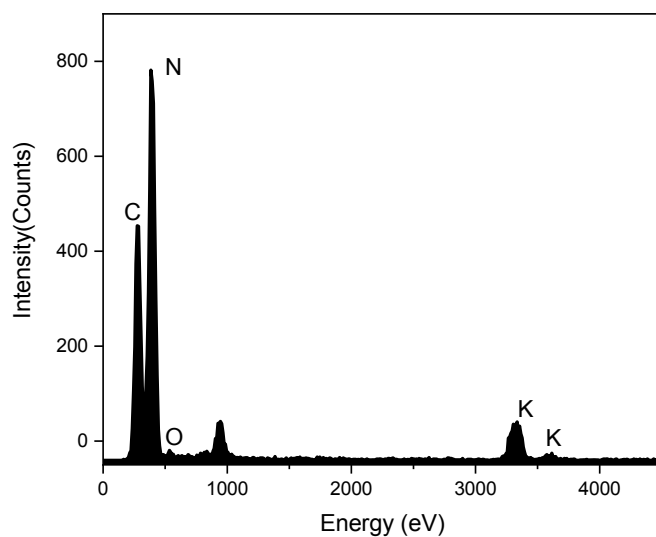
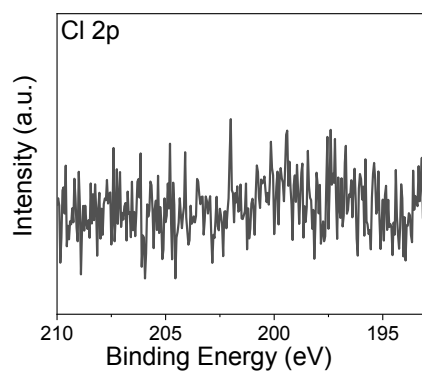**Fig. S4** Energy dispersive X-ray (EDX) analysis of K^+-MPCN sample.

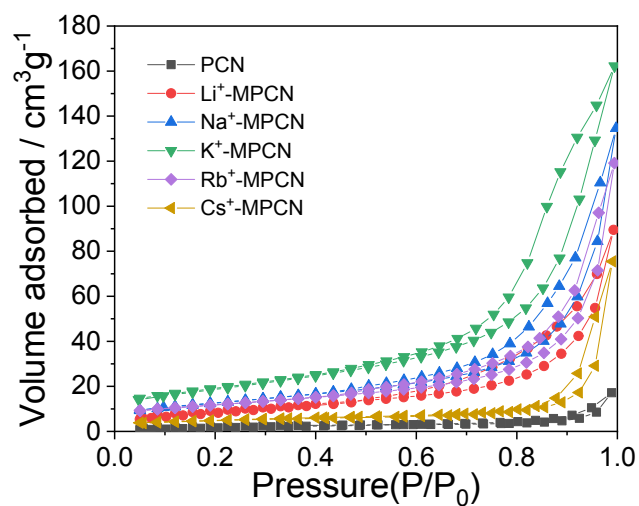**Fig. S5** Cl 2p high-resolution XPS spectrum of K⁺-MPCN sample.

Fig. S6 N$_2$-sorption isotherms collected at 77 K of X-MPCN and PCN samples.

Table S2 Physicochemical properties of X-MPCN and PCN samples from Nitrogen adsorption-desorption and CO_2 adsorption analysis.

Sample	Surface area cm^2g^{-1}	Pore volume cm^3g^{-1}	CO_2 adsorption cm^3g^{-1}
Li^+-MPCN	26	0.12	34
Na^+-MPCN	31	0.14	37
K^+-MPCN	38	0.16	61
Rb^+-MPCN	29	0.12	45
Cs^+-MPCN	16	0.08	42
PCN	8	0.03	7

Table S3 Content of alkali metal on X-MPCN, K^+/AC and K^+/PCN analysis by ICP.

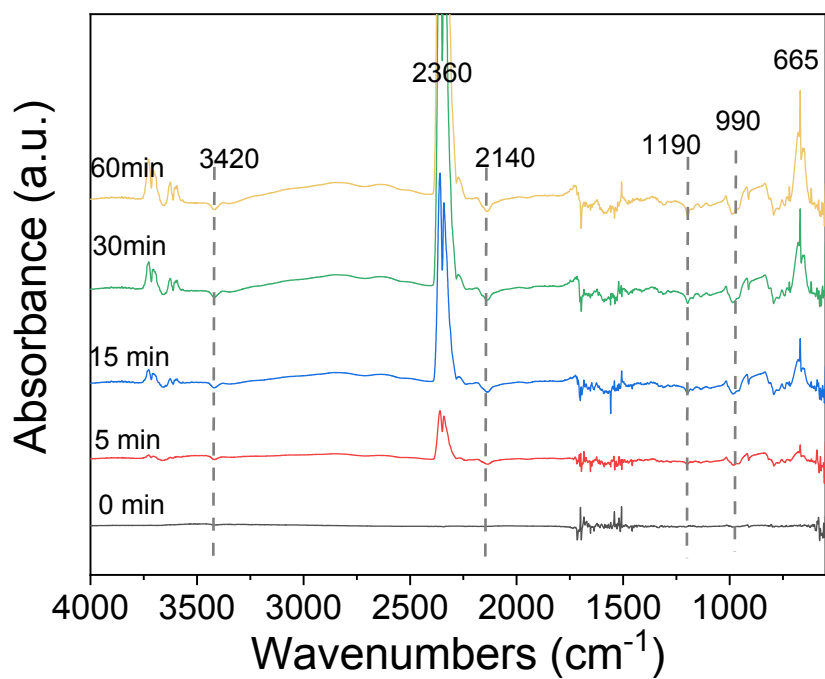| Sample	Li（wt.%)	Na（wt.%)	K（wt.%)	Rb (wt.%)	Cs (wt.%)
Li^+-MPCN	1.6				
Na^+-MPCN		4.9			
K^+-MPCN			8.0		
K^+-MPCN$_{recycle\ 1}$			7.8		
K^+-MPCN$_{recycle\ 2}$			7.7		
Rb^+-MPCN				17.3	
Cs^+-MPCN					25.7
K^+/PCN			8.1		
K^+/AC			8.0		

Fig. S7 In situ FTIR spectra for the adsorption of CO_2 on K^+-MPCN.
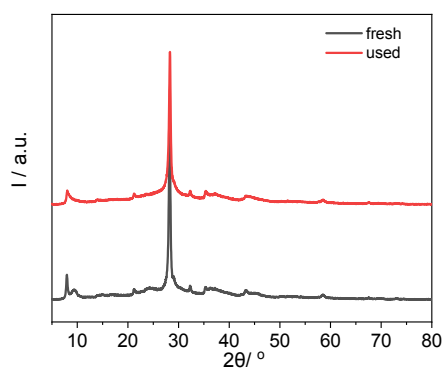

Fig. S8 Powder XRD patterns of K^+-MPCN sample before and after the COS hydrolysis reaction.
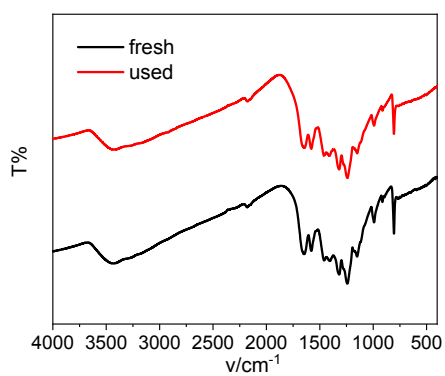

Fig. S9 FT-IR spectra of K^+-MPCN sample before and after the COS hydrolysis reaction.
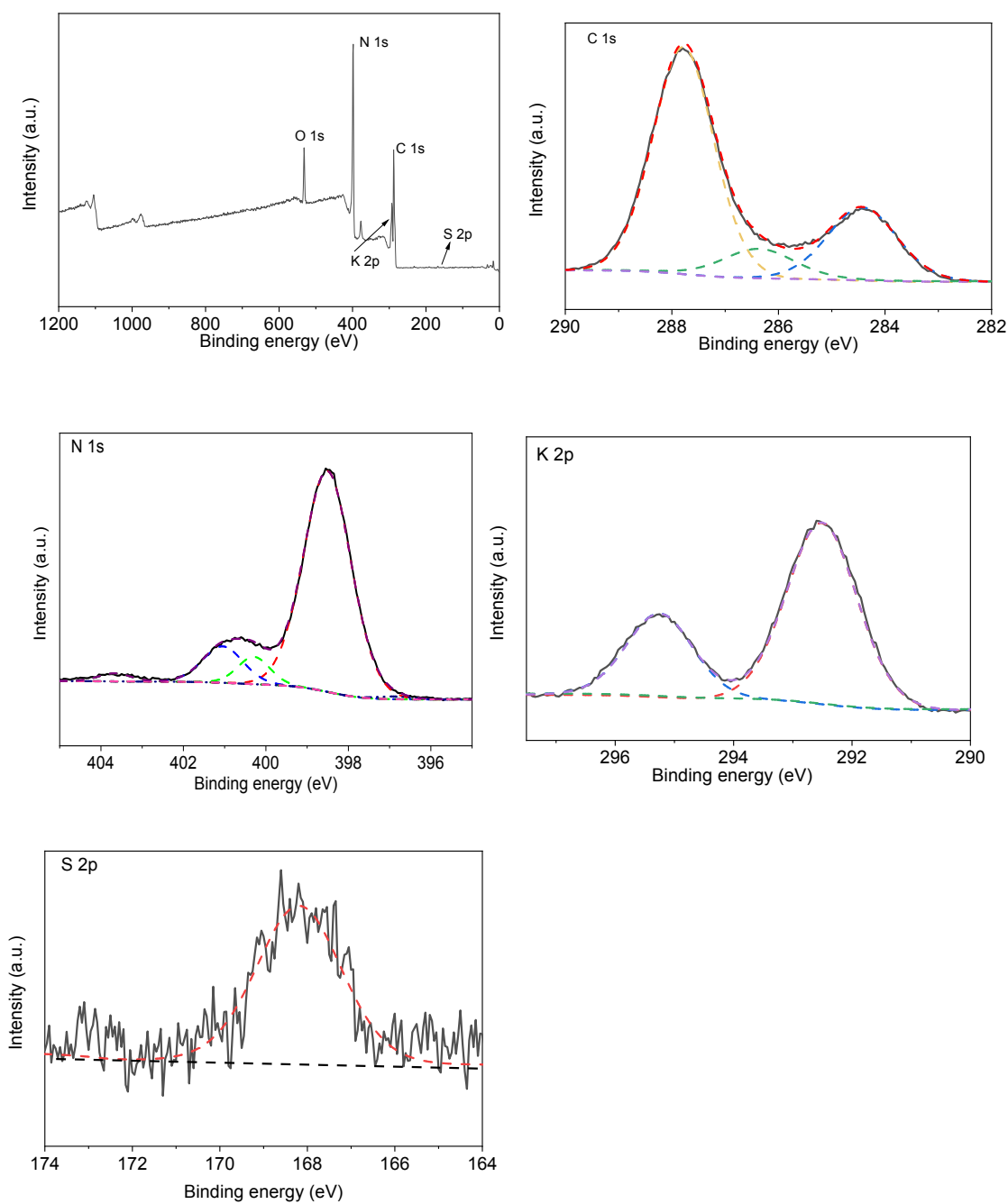
Fig. S10 Survey and XPS analysis of of K⁺-MPCN sample after the COS hydrolysis reaction.

References

1. G. Kresse and J. Furthmüller, Phys. Rev. B, 1996, 54, 11169-11186.
2. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865-3868.
3. G. Kresse and D. Joubert, Phys. Rev. B, 1999, 59, 1758-1775.
4. S. Grimme, J. Comput. Chem., 2006, 27, 1787-1799.