

Templated Coordination as a Tool to Increase the Catalytic Activity of Metal–Aluminophosphates: The Case of CoAPO-11

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Preparation of CoAPO-11

Pseudoboehmite (CHALCO, China) and phosphoric acid (H_3PO_4 , 85%) were used as aluminium and phosphorus sources respectively. The CoAPO-11 was synthesized by the dynamic procedures based on the method reported in the paper¹ with the molar ratio of $\text{P}_2\text{O}_5:\text{Al}_2\text{O}_3:\text{CoO}:\text{DPA}:\text{H}_2\text{O} = 0.90:1:x:0.89:27.8$ in the mother solution, where $x = \text{CoO}:\text{Al}_2\text{O}_3 = 0.02, 0.05$ and 0.1 in this work to form different CoAPO-11 catalysts. In a typical process, di-n-propylamine (DPA) was added into the solution containing pseudoboehmite and phosphoric acid, then a given amount of Co acetate was added slowly. After stirred vigorously for 2 h, the obtained material was introduced into a stainless-steel autoclave with polytetrafluoroethylene inside, dynamically crystallized at $190\text{ }^\circ\text{C}$ with a rotating speed of 30 r/min for 16 h. The resulting mixture was filtered, washed with distilled water and then dried at $100\text{ }^\circ\text{C}$ for 12 h. The obtained raw CoAPO-11 was calcined for 6 h at $550\text{ }^\circ\text{C}$ under air atmosphere.

The APO-11 zeolite was synthesized with the molar composition of $0.9\text{P}_2\text{O}_5: \text{Al}_2\text{O}_3: 0.89\text{DPA}: 27.8\text{H}_2\text{O}$ under hydrothermal condition, the synthesis procedure is the same with that of CoAPO-11 zeolite except not adding the Co acetate. The Co/APO-11 sample was prepared by incipient wetness impregnation of APO-11 zeolite with Co acetate ($x=0.02$) and was further calcined for 6 h at $550\text{ }^\circ\text{C}$ under air atmosphere. The synthesis procedure of Co-AIPO solid is the same with that of CoAPO-11 zeolite except not adding the DPA template.

For the preparation of imidazole (MIZ) modified CoAPO-11, the synthesis procedure was the same as above with fixed $x(\text{Co content})=0.02$. Besides, imidazole was added to the solution before the dynamic crystallization, and $y= \text{MIZ}:\text{Al}_2\text{O}_3$ represented the amount of added imidazole, where $y=0.02, 0.05$ and 0.1 . We refer to these six samples as $x\text{Co}y\text{MIZ}$, where x and y is percentage of $\text{CoO}/\text{Al}_2\text{O}_3$ and $\text{MIZ}/\text{Al}_2\text{O}_3$ respectively.

Characterization of CoAPO-11

The X-ray diffraction (XRD) patterns were obtained with a Rigku X-ray diffractometer equipped with high-speed array detection system using Cu $K\alpha$ radiation (40 KV and 30 mA), using a scanning rate of 10°min^{-1} in the range of 5° to 85° . The electronic state of the metals in the CoAPO-11 samples was determined using a Shimadzu UV-visible spectrometer (UV-2100) in DR mode. N_2 isotherms at 77 K were measured in a Micromeritics TriStar 3020 instrument. The samples were evacuated at 573 K for 6 h prior to measurement. The elemental data were collected by a S8 TIGER X-ray fluorescence (XRF) Spectrometer. Electron paramagnetic resonance (ESR) spectra were obtained from a Bruker EMX-10/12 ESR Spectrometer. Thermal-gravity/differential scanning calorimetry (TG/DSC) profiles were detected by a NETZSCH (DSC/DTA-TG) STA 449 F5 Jupiter from 50 to $850\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C/min}$ in an air environment with flowrate of 50 mL/min . For H_2 -temperature programmed reduction (TPR), 30.0 mg sample was placed in a quartz reactor as a shallow packed bed, pretreated in a high purity N_2 at $300\text{ }^\circ\text{C}$ for 2 h and cooled down to $200\text{ }^\circ\text{C}$. After the gas was switched to 5.0%

H₂/N₂, the temperature was starting to target 900 °C at the rate of 5 °C/min and the H₂-TPR patterns were recorded with a thermal conductivity detector. Scanning electron micrographs (SEM) were obtained using a Hitachi S-4800 microscope. Transmission electron microscope (TEM) measurements of the catalysts were carried out using a JEM-2100 electron microscope with a field emission source, operated at an accelerating voltage of 200kV. Fourier Transform Infrared (FTIR) spectra were recorded with a Nicolet 6700 instrument, using conventional IR cells connected to a gas handling system, under static conditions. Experimentally, pressed disks of pure solid powders (10 mg) were thermally treated within the IR cell at 573 K under vacuum (10-4mmHg) for 0.5 h. Pyridine was introduced at 323 K, and spectra were recorded after evacuation at increasing temperatures (423 K). For a quantitative analysis of the Brønsted and Lewis sites, the C≡N-B vibration at 1545 cm⁻¹ with extinction coefficient of ε(B)=1.67 cm/μmol, and C≡N-L vibration at 1455 cm⁻¹ with extinction coefficient of ε(L)=2.22 cm/μmol were used referred to the literature.² Solid state NMR experiments were performed on a Bruker Avance III 400 MHz spectrometer with 4 mm H/X/Y MAS probe at room temperature with a rotor spinning rate of 12 kHz. ¹³C NMR signal was monitored via cross-polarization (CP). The ¹H-¹³C CPMAS NMR spectra were recorded using 50 kHz RF field on ¹³C, 4096 scans, recycle delay of 2s, and a contact time of 2ms. The operating frequencies for ²⁷Al NMR and ³¹P NMR were 161.98MHz and 104.26MHz respectively.

Catalytic skeletal isomerization of n-butene

Skeletal isomerization of n-butene to isobutene was performed on a continuous flow fixed-bed reactor at atmospheric pressure, and 1-butene with purity of pure 99.99% was used as feed gas. Typically, 0.1 g (40–60 mesh) of the catalyst was activated under flowing N₂ at 400 °C for 2 h. And then changed to the feed gas at the same temperature to conduct the reaction. The reaction products were analyzed on-line by a gas chromatograph (Shimadzu GC-14C) equipped with a capillary column (50m×0.53mm×20μm, KB-Al₂O₃/Na₂SO₄) and FID.

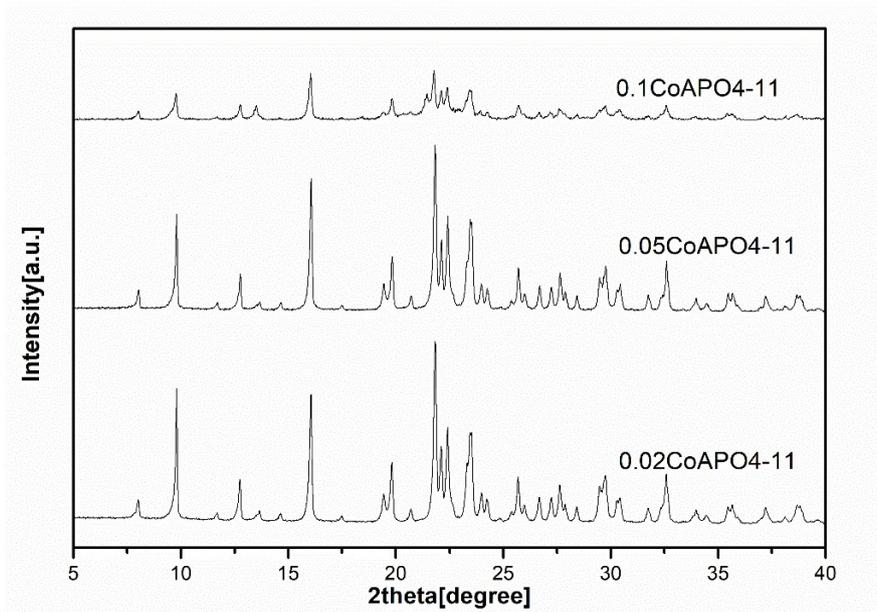


Fig. S1. XRD patterns of CoAPO-11 with different amount of Co contents

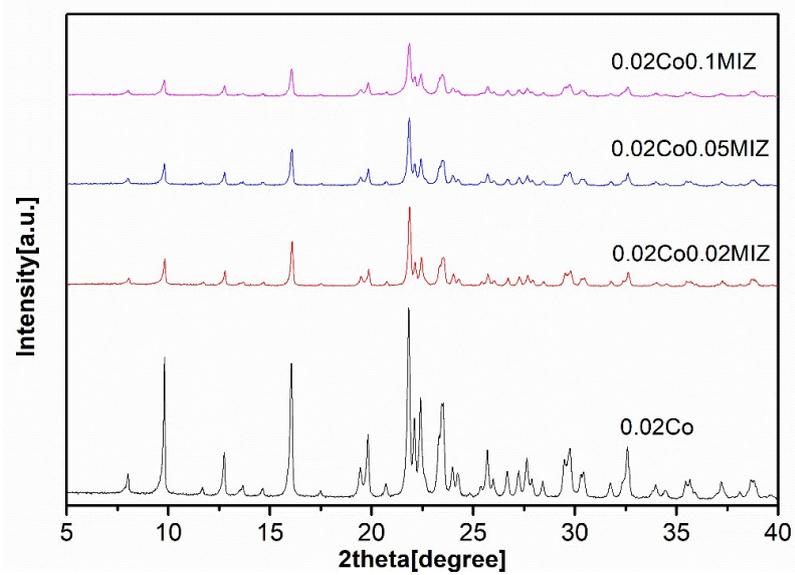


Fig. S2. XRD patterns of CoAPO-11 with different amount of imidazole

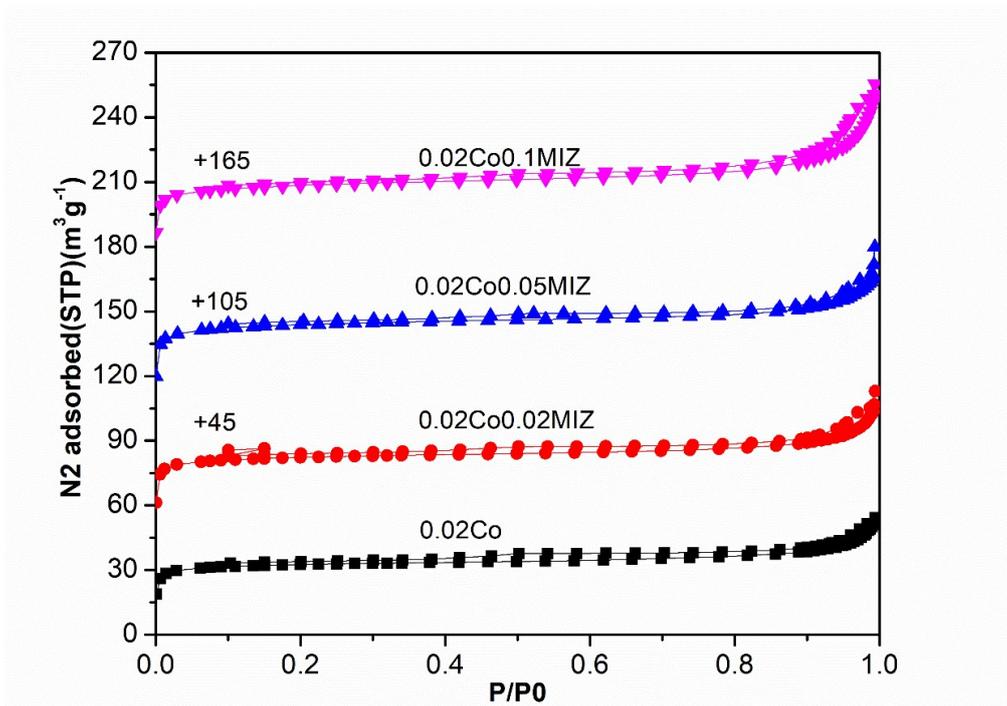


Fig. S3. Nitrogen adsorption–desorption isotherms of CoAPO-11 with different amount of imidazole.

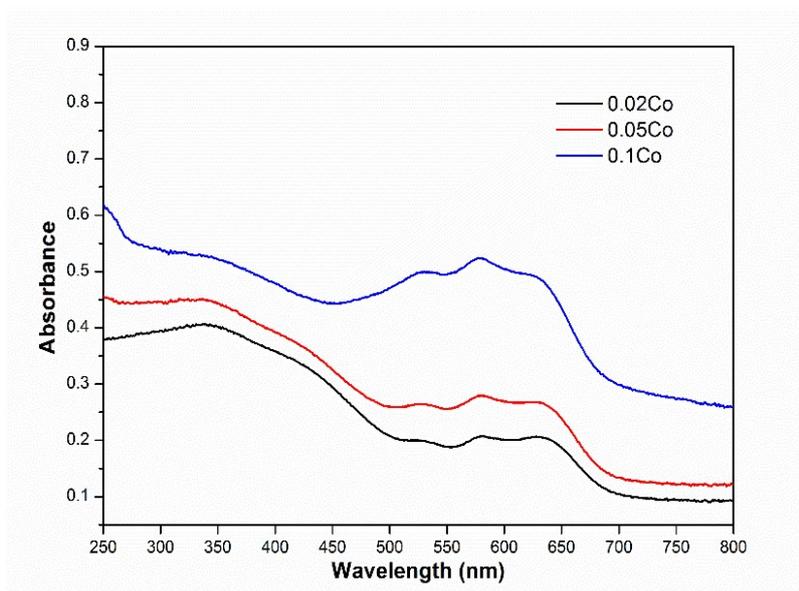


Fig. S4. UV-visible spectra of CoAPO-11 with different amount of Co species

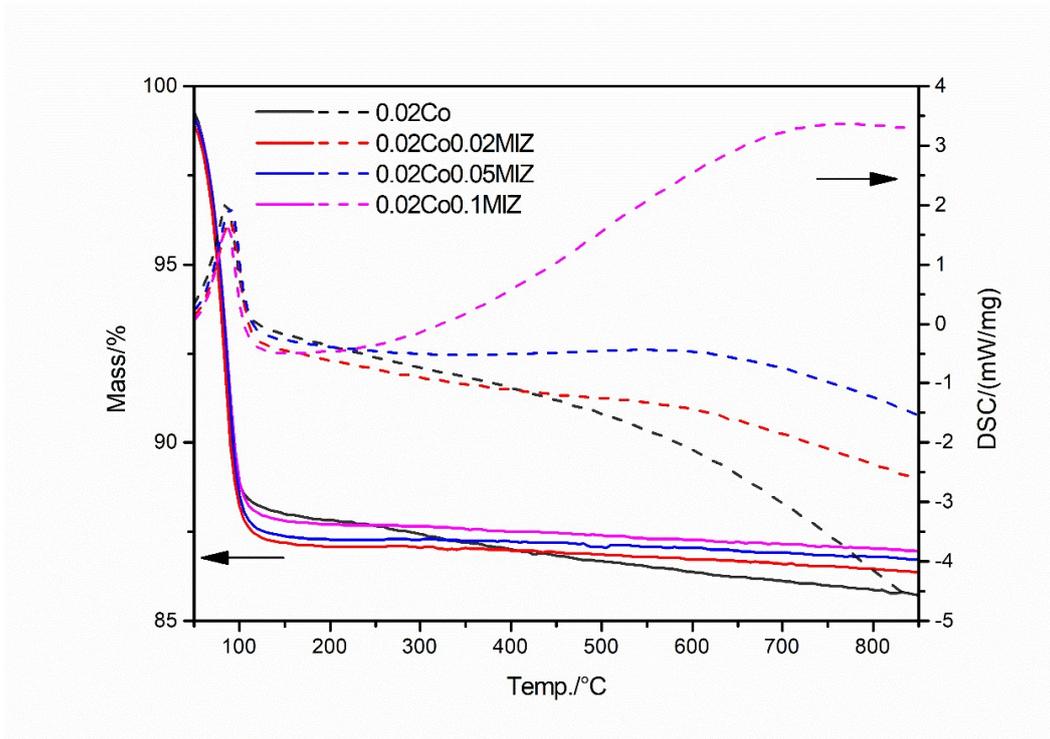


Fig. S5. TG-DSC curve of CoAPO-11 with different amount of imidazole.

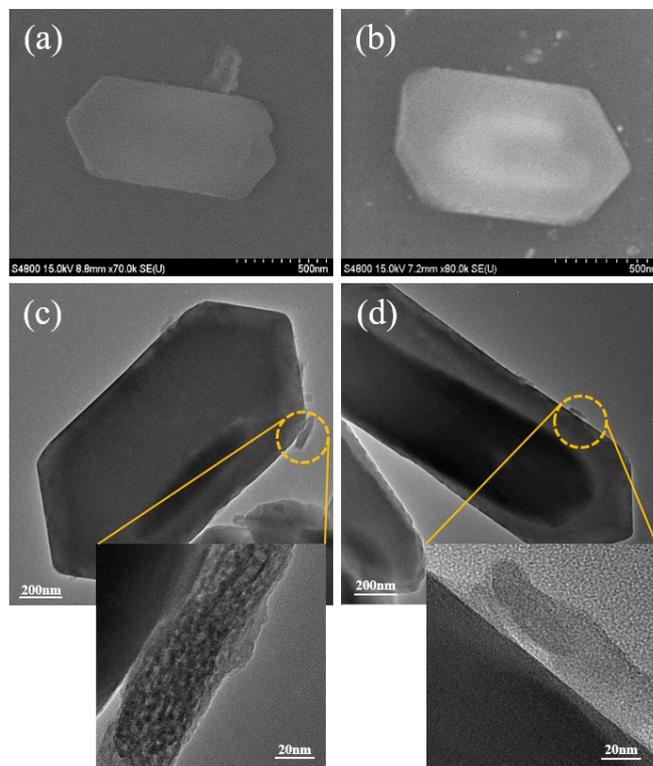
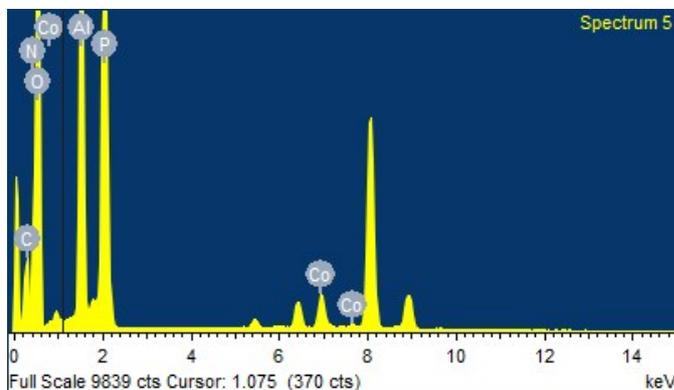


Fig. S6. SEM images of (a) 0.02Co and (b) 0.02Co0.05MIZ samples and TEM images of (c) 0.02Co and (d) 0.02Co0.05MIZ samples.

EDS element analysis of imidazole modified CoAPO-11 samples

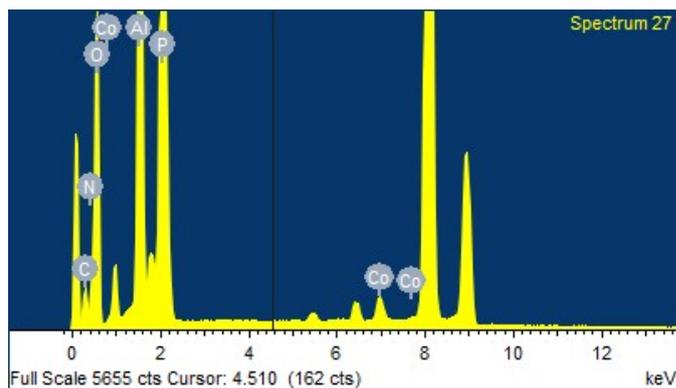
1.0.02Co

Element	Weight%	Atomic%
C K	3.27	6.30
N K	1.51	2.49
O K	25.33	36.69
Al K	30.79	26.44
P K	35.77	26.76
Co K	3.34	1.31
Totals	100.00	



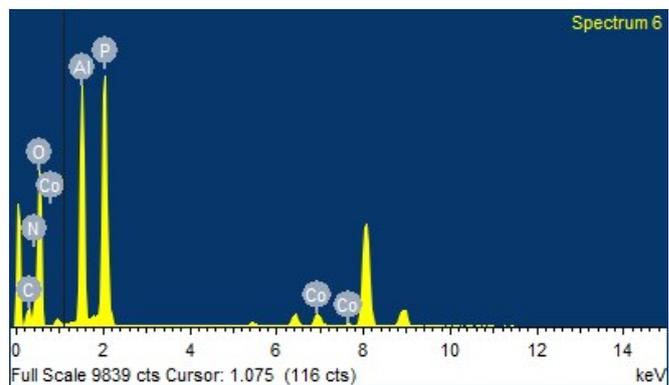
2.0.02Co0.02MIZ

Element	Weight%	Atomic%
C K	3.17	5.69
N K	1.27	1.96
O K	36.48	49.24
Al K	27.25	21.81
P K	29.11	20.30
Co K	2.72	1.00
Totals	100.00	



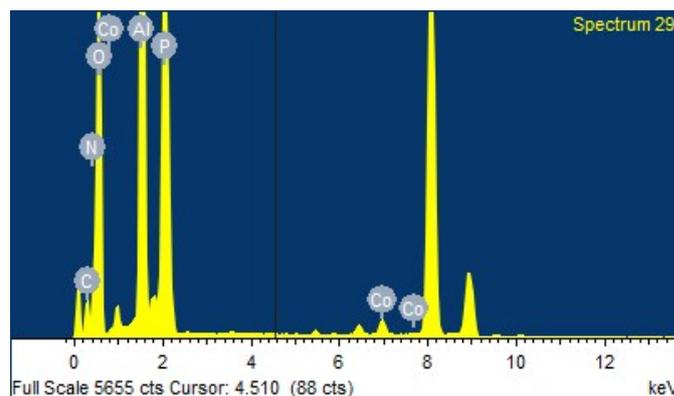
3.0.02Co0.05MIZ

Element	Weight%	Atomic%
C K	2.07	4.37
N K	0.00	0.00
O K	15.91	25.23
Al K	32.92	30.95
P K	47.12	38.59
Co K	1.98	0.85
Totals	100.00	



4.0.02Co0.1MIZ

Element	Weight%	Atomic%
C K	2.29	4.46
N K	0.00	0.00
O K	26.53	38.78
Al K	31.39	27.21
P K	38.42	29.01
Co K	1.37	0.54
Totals	100.00	



Cobalt incorporation analysis of 0.02Co0.05MIZ sample during crystallization by solid NMR

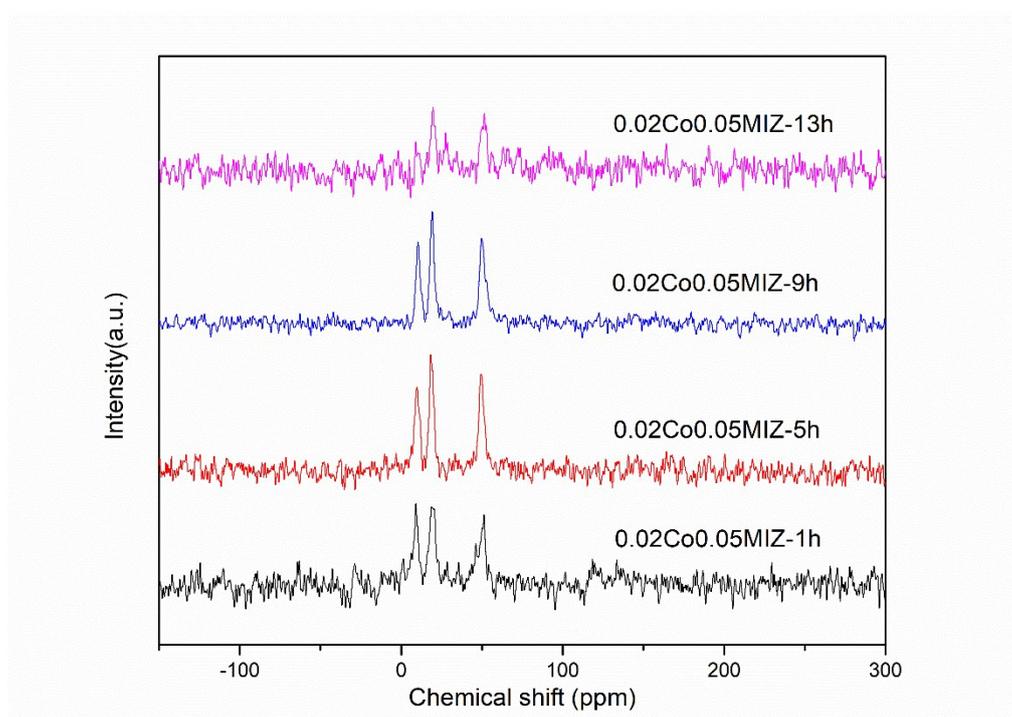


Fig. S7. ^{13}C solid-state NMR spectrum of as-synthesized 0.02Co0.05MIZ sample crystallized in 1 h, 5 h, 9 h and 13 h respectively

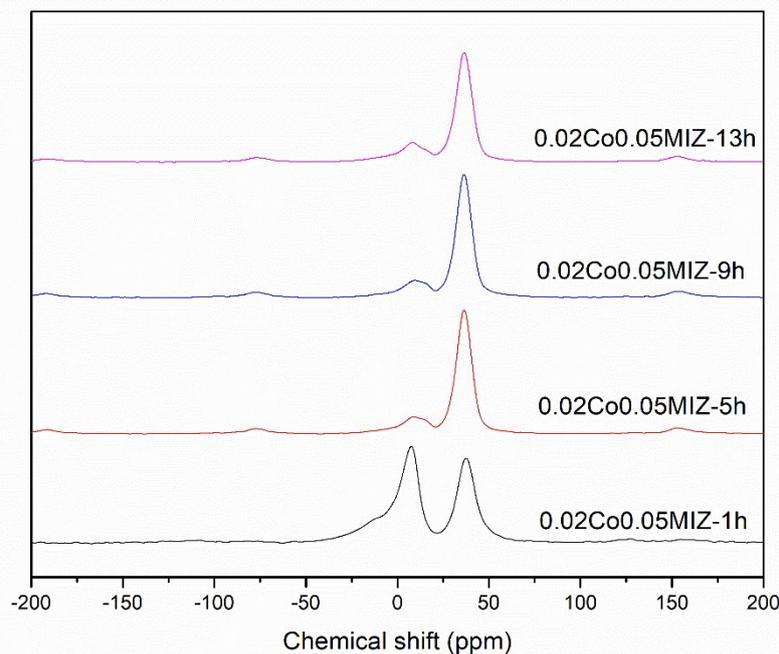


Fig. S8. ^{27}Al solid-state NMR spectrum of as-synthesized $0.02\text{Co}0.05\text{MIZ}$ sample crystallized in 1 h, 5 h, 9 h and 13 h respectively

As shown by ^{13}C solid-state NMR spectrum of as-synthesized $0.02\text{Co}0.05\text{MIZ}$ sample in different crystallization stage in Fig. S7, the major three peaks were assigned to the three different carbons in di-n-propylamine, but no obvious peaks corresponding to the imidazole could be observed probably due to the relatively slight addition of imidazole. ^{27}Al and ^{31}P solid-state NMR spectrum in Fig. S8 and Fig. S9 further confirmed the incorporation of Co during the zeolite's crystallization. Table S1 further provided the calculated $P(n\text{Co})$ populations change while Co isomorphous substitution into the zeolitic framework.

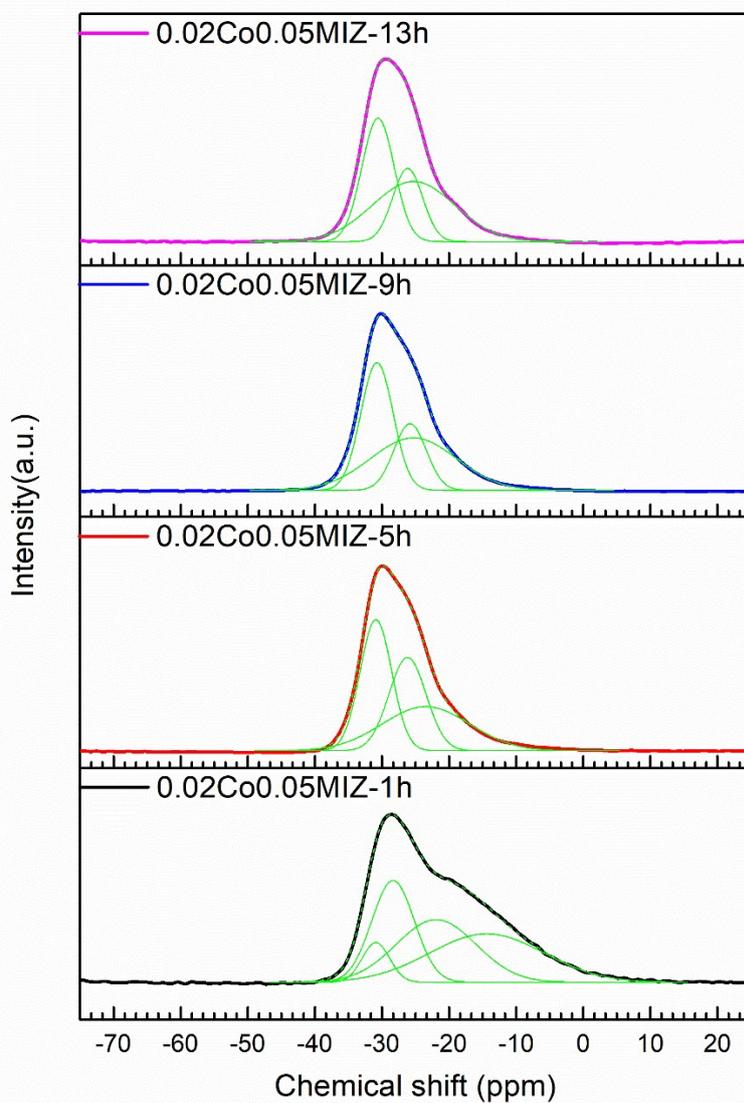


Fig. S9. ^{31}P solid-state NMR spectrum of as-synthesized $0.02\text{Co}0.05\text{MIZ}$ sample crystallized in 1 h, 5 h, 9 h and 13 h respectively

Table S1. Different $\text{P}(n\text{Co})$ populations deduced from ^{31}P NMR Spectra (INMR) of $0.02\text{Co}0.05\text{MIZ}$ sample with different crystallization time

Sample	I_{NMR}			
	P(0Co)	P(1Co)	P(2Co)	P(3Co)
0.02Co0.05MIZ-1h	0.1570	0.4030	0.2481	0.1918
0.02Co0.05MIZ-5h	0.4882	0.3475	0.1643	0
0.02Co0.05MIZ-9h	0.5171	0.2702	0.2126	0
0.02Co0.05MIZ-13h	0.4805	0.2851	0.2344	0

FT-IR spectra of the hydroxyl region

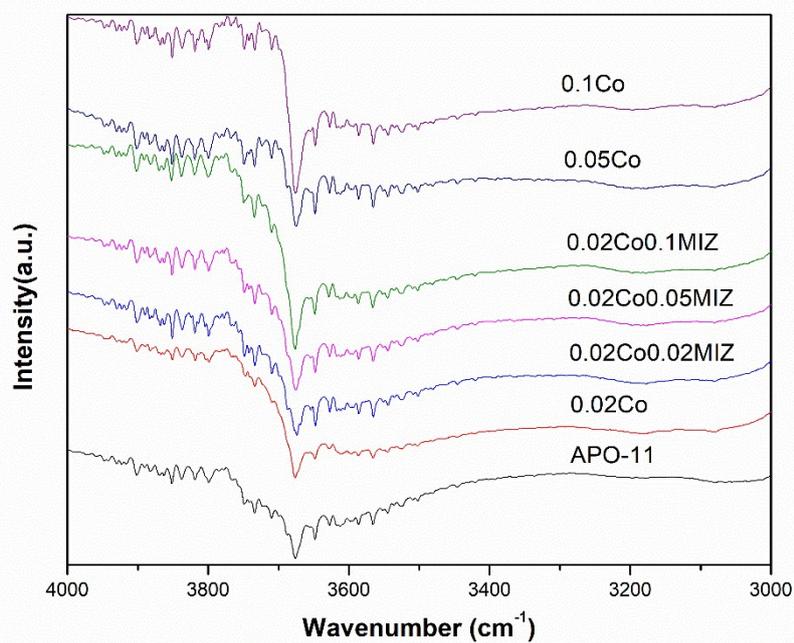


Fig. S10. FT-IR spectra of APO-11 and different CoAPO-11 samples

References

1. J. í. Dečec̃ek, J. í. C̃ejka and B. Wichterlová, *Appl. Catal., B*, 1998, **15**, 233-240.
2. C. A. Emeis, *J. Catal.*, 1993, **141**, 347-354.