Kinetically controlled ammonia vapor diffusion synthesis of a Zn(II) MOF and its H_2O/NH_3 adsorption properties

Yang Chen, Chengyin Yang, Xiaoqing Wang, Jiangfeng Yang*, Kun Ouyang, Jinping Li*

Research Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan 030024, Shanxi, China Email: jpli211@hotmail.com

Contents

1. Comparative experiments

The comparative experiments are carried out by adding $NH_3 \cdot H_2O$ (25%) directly to adjust the pH value in synthesis of $Zn(INA)_2(H_2O)_4$. In Fig S1, the blank experiment was labeled as vial 1, which had the same reactive raw materials with original reaction while $NH_3 \cdot H_2O$ was not added; vial 2 was corresponding to that 5 μL $NH_3 \cdot H_2O$ (25%) was added to adjust the pH vale to 5; vial 3 was corresponding to that 10 μL $NH_3 \cdot H_2O$ (25%) was added to adjust the pH vale to 7.

Fig. S1 shows the reaction phenomenon and products' XRD patterns. The blank experiment in vial 1 indicates that there is not any product although the reaction is maintained for 12 h, the PXRD patterns suggest the leftover material is undissolved HINA. On the other side, the flocculent precipitate can be generated immediately while $NH_3 \cdot H_2O$ is added to reaction solution in vial 2 and 3, whose PXRD patterns are similar to that of $Zn_5(OH)_8(NO_3)_2 \cdot 2NH_3$. This phenomenon is attributed to that adding $NH_3 \cdot H_2O$ causes a huge pH value change, and $NH_3 \cdot H_2O$ reacts with Zn^{2+}, NO_3, as well as little dissolved INA^- in the upper solution, which results in the formation of $Zn_5(OH)_8(NO_3)_2 \cdot 2NH_3$ rather than $Zn(INA)_2(H_2O)_4$. Moreover, the precipitate wouldn't change to $Zn(INA)_2$ when it was heated at 150 °C for 2 h. Therefore, kinetically controlled ammonia vapor diffusion method can afford a alleviate way to adjust the reaction environment so as to synthesize $Zn(INA)_2(H_2O)_4$ crystal film rapidly.

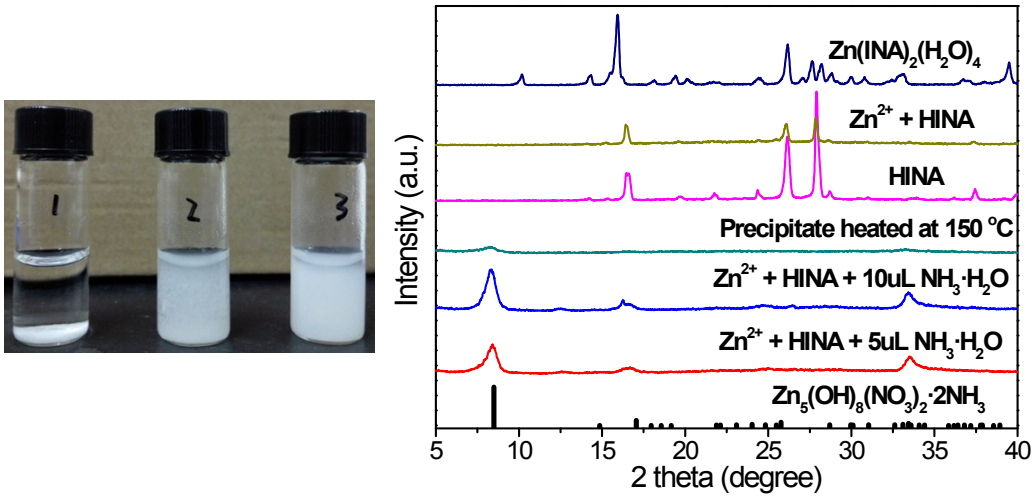


Fig. S1 Comparative experiments of adding ammonia amount and the way

2. Single crystal data of $Zn(INA)_2(H_2O)_4$

Table S1 Crystal data and structure refinement for $Zn(INA)_2(H_2O)_4$.

Empirical formula	$C_{12}H_{16}N_2O_8$ Zn
Formula weight	381.64
Wavelength (Å)	1.54184
Crystal system	Triclinic
Space group	P-1
a (Å)	6.3057(3)
b (Å)	6.8347(4)
c (Å)	9.2969(4)
α(°)	95.963(7)
β (°)	104.998(4)
γ(°)	113.213(6)
Volume ($Å^3$)	345.99(4)
Z	1
Dcalc (mg m^{-3})	1.832
Absorption coefficient (mm^{-1})	2.936
F(000)	196
θ range (°)	5.06 – 74.11
Limiting indices	-7≤ h ≤7 -8≤ k ≤8 -11≤ l ≤11
Goodness-of-fit on F^2	1.112
Final R indices [I>2σ(I)][a,b]	R_1 = 0.0267, wR_2 = 0.027
R indices (all data)[a,b]	R_1 = 0.0273, wR_2 = 0.074
Largest diff. peak and hole	0.81 and -0.82 e $Å^{-3}$

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2= [\Sigma[w (F_o^2- F_c^2)^2] /\Sigma[w (F_o^2)^2]]^{1/2}$.

Table S2 Selected bond lengths (Å) and angles (°) for $Zn(INA)_2(H_2O)_4$

Zn(1)-O(2)	2.1535(14)	C(1)-C(6)	1.520(3)	C(7)-N(2)-Zn(1)	123.20(13)
Zn(1)-O(3)	2.0983(14)	C(3)-C(9)	1.382(3)	O(5)-C(1)-C(6)	117.55(17)
Zn(1)-N(2)	2.1334(16)	C(6)-C(9)	1.390(3)	O(8)-C(1)-O(5)	126.06(18)
O(5)-C(1)	1.257(3)	C(6)-C(12)	1.388(3)	O(8)-C(1)-C(6)	116.39(17)
O(8)-C(1)	1.256(2)	C(7)-C(12)	1.389(3)	N(2)-C(3)-C(9)	123.16(18)
N(2)-C(3)	1.343(3)	C(3)-N(2)-Zn(1)	118.85(13)	C(9)-C(6)-C(1)	120.49(17)
N(2)-C(7)	1.344(3)	C(3)-N(2)-C(7)	117.71(17)	N(2)-C(7)-C(12)	122.55(18)

3. TG curve of $Zn(INA)_2(H_2O)_4$

The TG curve of $Zn(INA)_2(H_2O)_4$ is shown in Fig. S2. $Zn(INA)_2(H_2O)_4$ has a preliminary thermal stability from 30 to 80 ^oC. Furthermore, 18% weight loss occurred from 80 to 100 °C, which results from the dehydration process of $Zn(INA)_2(H_2O)_4$ to $Zn(INA)_2$. Finally, $Zn(INA)_2$ would be stable to 400 ^oC .

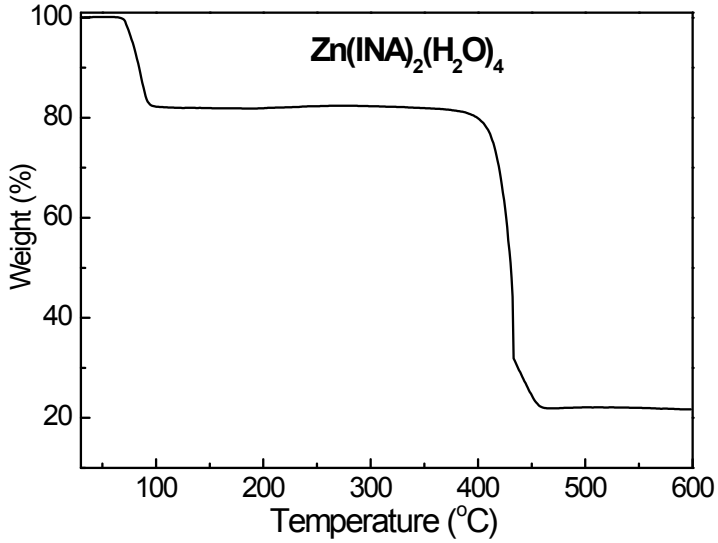


Fig. S2 TG curve of $Zn(INA)_2(H_2O)_4$

4. SEM images of $Zn(INA)_2$ and $Zn(INA)_2(H_2O)_2(NH_3)_2$.

The SEM images of $Zn(INA)_2$ and $Zn(INA)_2(H_2O)_2(NH_3)_2$ are shown in Fig. S3. $Zn(INA)_2$ was prepared by removing H_2O from $Zn(INA)_2(H_2O)_4$ whose morphology and crystal shape became ruptured. However, the morphology of $Zn(INA)_2(H_2O)_2(NH_3)_2$ became smooth when $Zn(INA)_2$ was transformed to $Zn(INA)_2(H_2O)_2(NH_3)_2$ after adsorbing H_2O and NH_3.

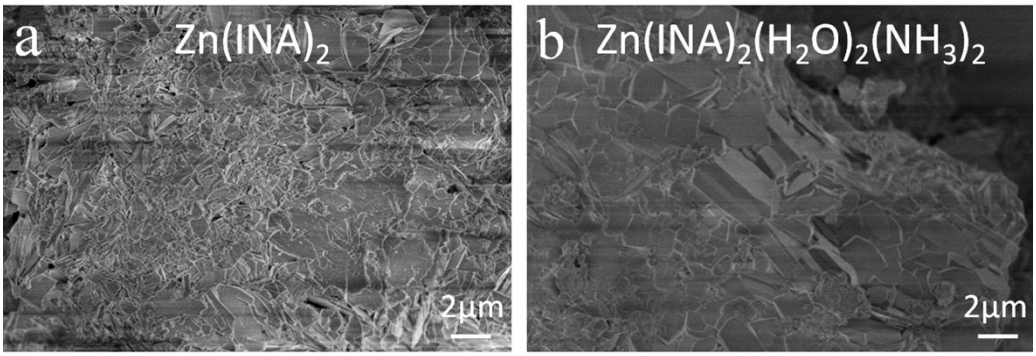


Fig. S3 SEM images of $Zn(INA)_2$ and $Zn(INA)_2(H_2O)_2(NH_3)_2$.

5. NH_3-TPD test of $Zn(INA)_2$

NH_3-TPD experiment was carried out to explain the desorption temperature of $Zn(INA)_2$ after adsorbing dry ammonia. The process of $Zn(INA)_2$ adsorbing dry ammonia gas won't result in the structure change, chemisorption of NH_3 at adsorption sites should be removal at a certain temperature. The first peak in Fig. S4 is related to the desorption of NH_3 in the range of 80–110 ^oC. Therefore, the recycle property of $Zn(INA)_2$ can be regenerated at 120 °C. The second peak is related to the decomposition of $Zn(INA)_2$ in the range of 370–460 °C, which indicates the activation temperature should be set below 350 ^oC.

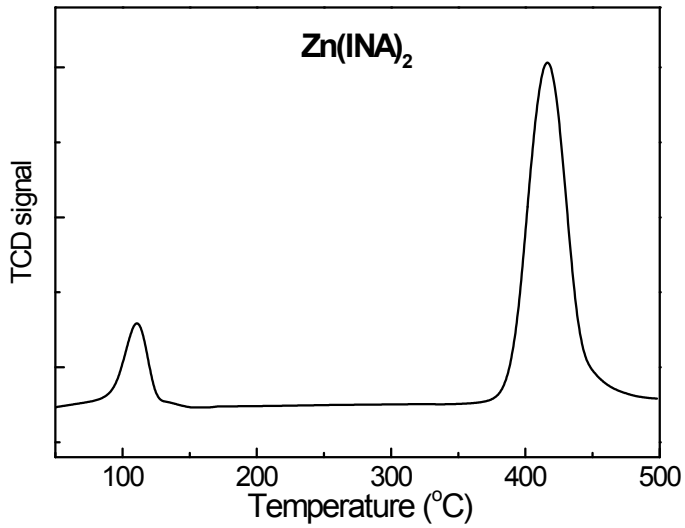


Fig. S4 NH_3-TPD curve of $Zn(INA)_2$

6. H_2O/NH_3 co-adsorption method of $Zn(INA)_2$

The H_2O/NH_3 co-adsorption method of $Zn(INA)_2$ is shown in Fig. S5. 0.3 g $Zn(INA)_2$ was added into a vial, then transferred to a bigger bottle containing 3 mL ammonia solution (25%). In the closed environment, $Zn(INA)_2$ can transform to $Zn(INA)_2(H_2O)_2(NH_3)_2$ through co-adsorption of H_2O and NH_3 at room temperature. The transformation process was accompanied by a darker color change.

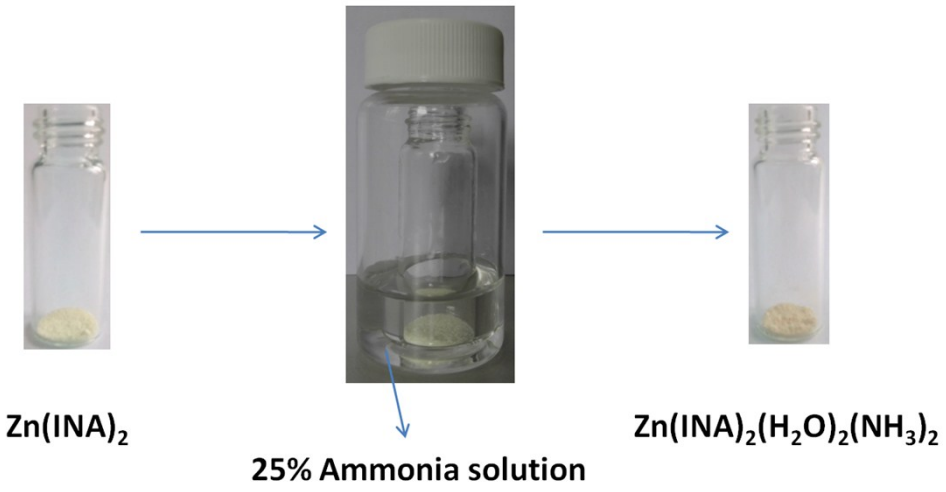


Fig. S5 The H_2O/NH_3 co-adsorption method of $Zn(INA)_2$

7. Compared PXRD patterns of $Zn(INA)_2(H_2O)_2(NH_3)_2$

The PXRD patterns of $Zn(INA)_2(H_2O)_2(NH_3)_2$, $Cu(INA)_2(H_2O)_2(NH_3)_2$ and $Zn(INA)_2(H_2O)_4$ are shown in Fig. S6. It can be observed that the main peak of PXRD patterns (about 15°) of $Zn(INA)_2(H_2O)_2(NH_3)_2$ moves to the left nearly 1° comparing to $Zn(INA)_2(H_2O)_4$, which results from its structure contains two NH_3 molecules instead of two H_2O molecules. That pattern is similar to reported $Cu(INA)_2(H_2O)_2(NH_3)_2$. Besides, Pawley refinement for the experimental PXRD data of $Zn(INA)_2(H_2O)_2(NH_3)_2$ with unit cell parameters of single crystal of $Zn(INA)_2(H_2O)_4$ and $Cu(INA)_2(H_2O)_2(NH_3)_2$ indicated that Rwp value of $Zn(INA)_2(H_2O)_2(NH_3)_2$ and $Cu(INA)_2(H_2O)_2(NH_3)_2$ is smaller than that of $Zn(INA)_2(H_2O)_4$ (Fig. S7). DFT calculation (DMol3 module implemented in Materials Studio software) also was used to speculate the structure of $Zn(INA)_2(H_2O)_2(NH_3)_2$. The results indicated that H_2O and NH_3 combined with Zn and formed a similar structure of $Cu(INA)_2(H_2O)_2(NH_3)_2$ while M-O and M-N bond lengths have changed from 2.017, 2.444 to 2.292, 2.399 (Fig. S8). Therefore, it implies that we obtain a new material by the H_2O/NH_3 co-adsorption of $Zn(INA)_2$, which is isomorphic to $Cu(INA)_2(H_2O)_2(NH_3)_2$.

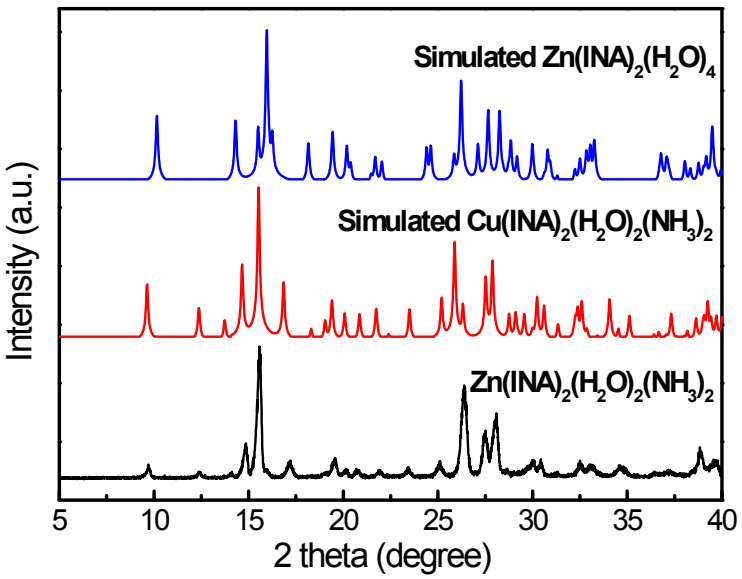
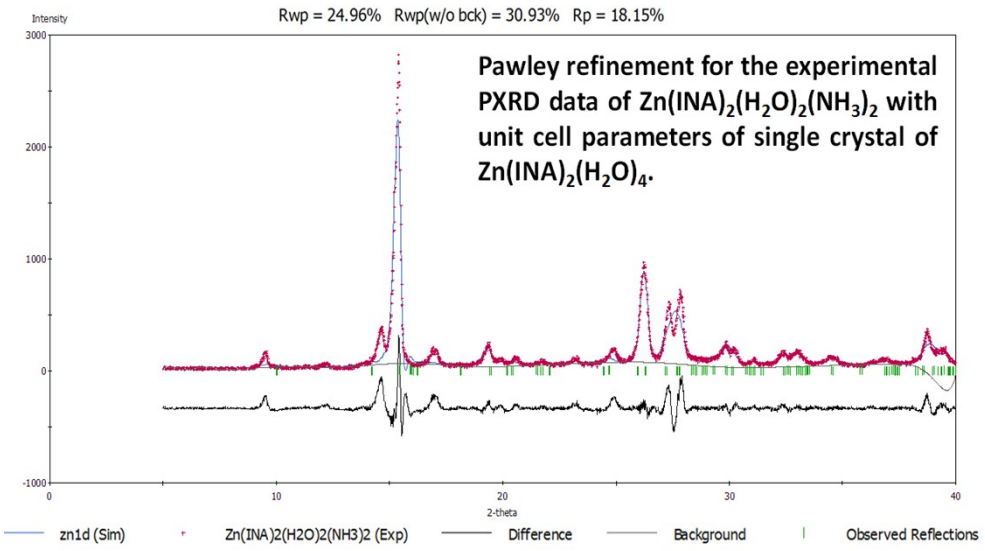
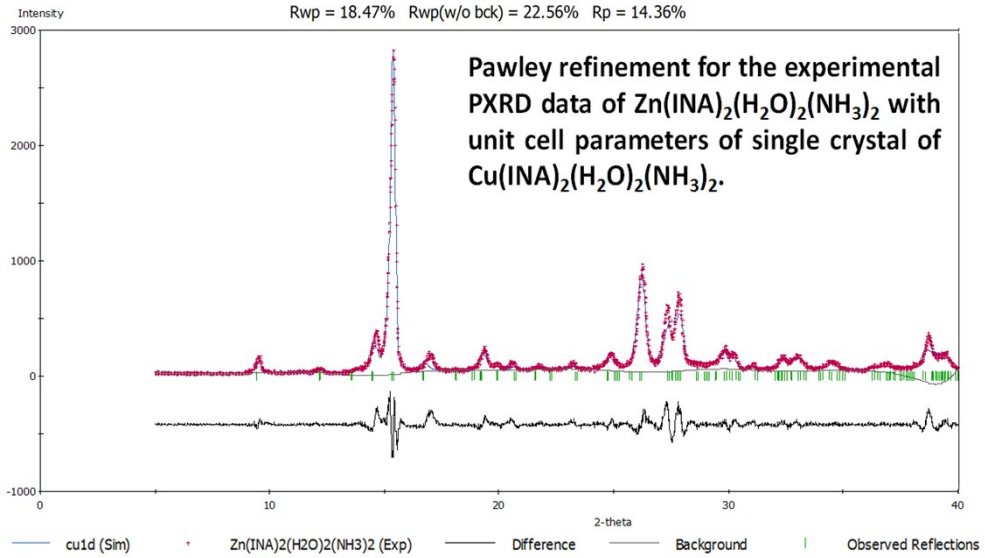


Fig. S6 The compared PXRD patterns of materials





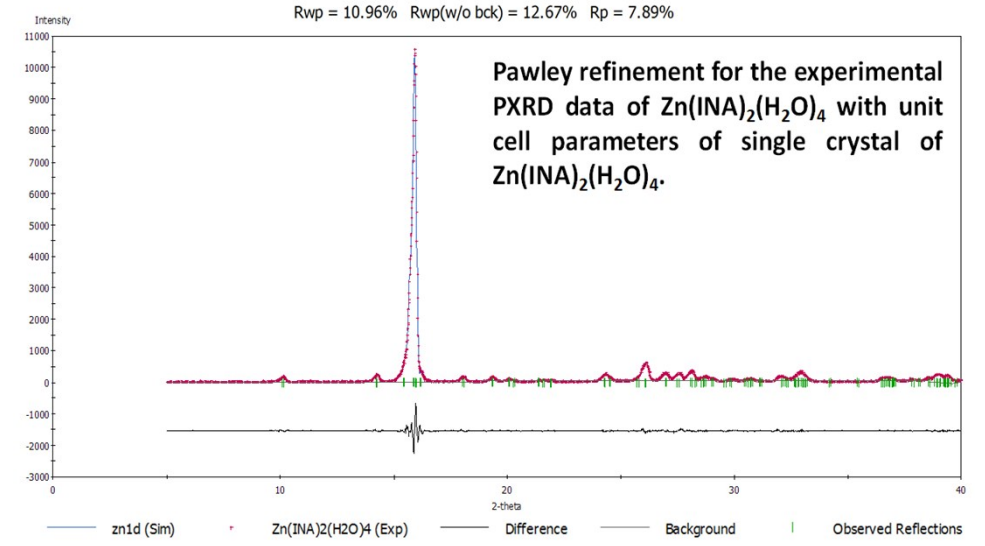


Fig. S7 Pawley refinement for the experimental PXRD data with unit cell parameters of single crystal.

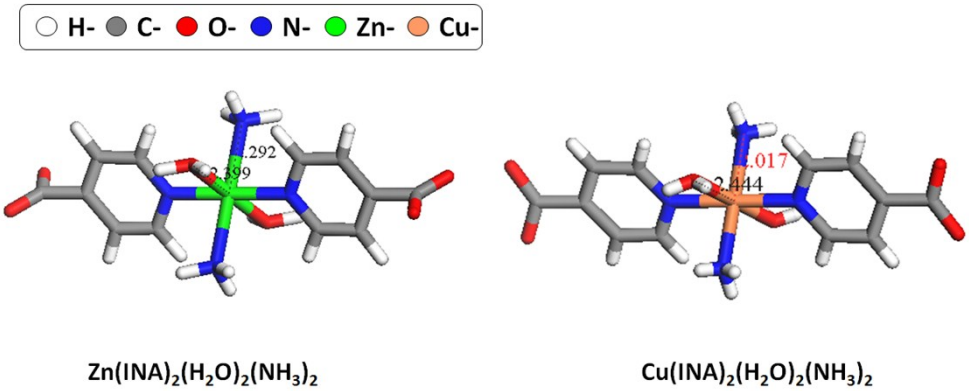


Fig. S8 Structure of $Zn(INA)_2(H_2O)_2(NH_3)_2$ speculated by DFT calculation and the comparison with $Cu(INA)_2(H_2O)_2(NH_3)_2$

8. NH_3 adsorption performance for $Zn(INA)_2$ in moist condition

Co-adsorption of H_2O and NH_3 on $Zn(INA)_2$ were tested in steam atmosphere of 4%, 8%, 12% 16% and 20% ammonia solution at 20 °C, adsorption times of 10 min, 30 min, 60 min and 120 min were investigated in each concentration case. The different H_2O/NH_3 ratios in those steam atmospheres are shown in Table S3. The co-adsorption method in H_2O/NH_3 steam atmosphere is shown in Fig. S9.

Table S3 H_2O and NH_3 steam content of different ammonia concentration at 20 °C.[1-3]

Ammonia concentration (mass)		4%	8%	12%	16%	20%
Partial pressure (kPa)	H_2O	2.07	2.12	1.84	1.78	1.62
	NH_3	3.14	7.97	13.2	20.7	30.4

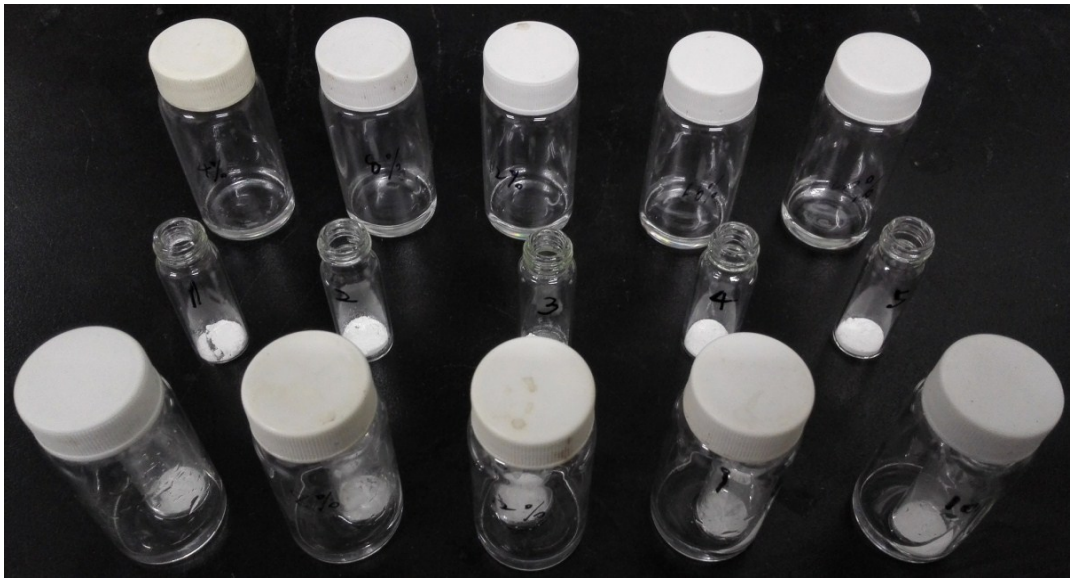


Fig. S9 Co-adsorption method in H_2O and NH_3 steam atmosphere.

Ammonia adsorption capacity in moist condition was carried out by the following method (Fig. S10), namely, the removal NH_3 from $Zn(INA)_2(H_2O)_2(NH_3)_2$ was adsorbed and further dropped by H_2SO_4 solution, then the corresponding amount of ammonia adsorption can be calculated.

Test process

1. Samples were activated at 150 °C for 6 h, weighed the mass of **m** g.

2. Activated samples were placed in different concentrations of H_2O/NH_3 vapor environment for 10, 30, 60 min, then transformed samples to 70 °C oven to removal the physisorbed H_2O and NH_3.

3. The samples were placed to the U-tube and supported by quartz wool, heating the samples to 200 °C, and maintained for 1 h, the removal gases was blown out by helium at a purge flow of 20 mL/min.

4. The removal gases was adsorbed by H_2SO_4 solution (10 mL H_2O + **x** mL H_2SO_4 solution of **c** mol/L).

5. Using methyl orange as indicator, dropping the H_2SO_4 solution to titration endpoint, the consumption of H_2SO_4 solution recorded as **y** mL.

6. Calculating the ammonia adsorption of samples was about n=**(x+y)×2c/m** mmol/g.

7. The final ammonia adsorption of samples was calculated by averaging three times. (Samples were regenerated at 150 °C for 2 h)

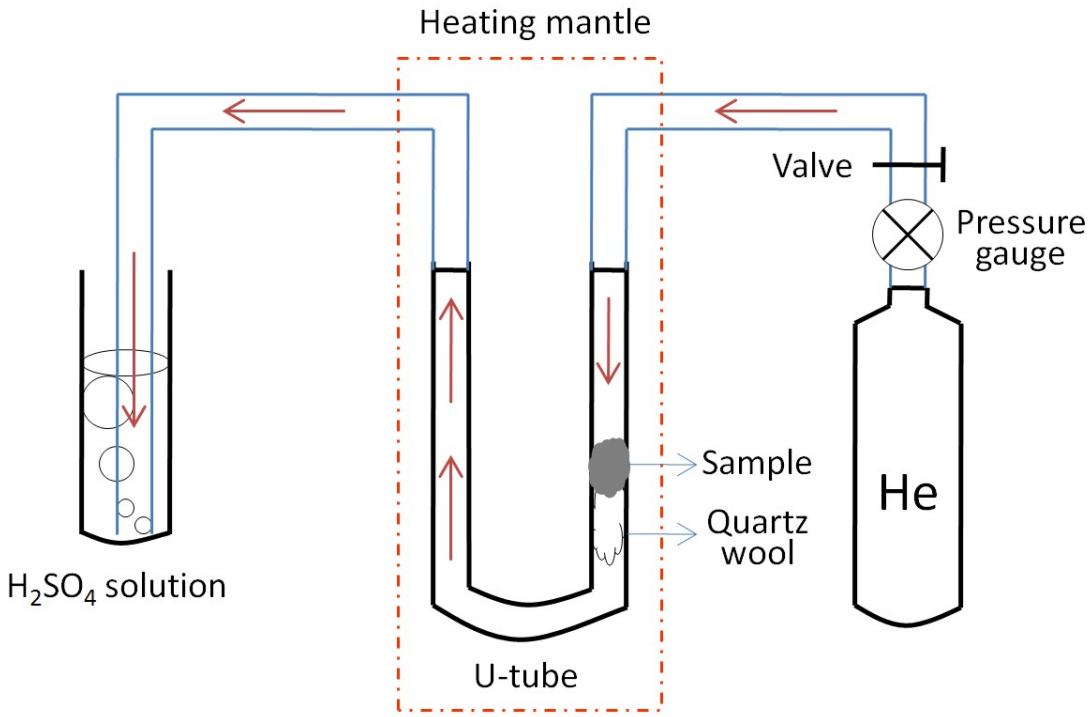


Fig. S10 Schematic diagram of ammonia adsorption capacity test

159 **Table S4** Three cycles of NH_3 adsorption amount on $Zn(INA)_2$ in moist condition at 20 °C.

Time (min)	NH_3 solution concentration (%)	NH_3 adsorption amount (mmol/g)	Average value (mmol/g)	Time (min)	NH_3 solution concentration (%)	NH_3 adsorption amount (mmol/g)	Average value (mmol/g)
10	4%	0.5	0.48	30	4%	0.88	0.88
		0.45				0.84	
		0.48				0.91	
	8%	0.74	0.77		8%	1.45	1.42
		0.8				1.39	
		0.77				1.41	
	12%	0.96	0.97		12%	1. 97	2.03
		0.94				2.07	
		1.01				2.06	
	16%	1.14	1.19		16%	2.52	2.59
		1.2				2.61	
		1.23				2.64	
	20%	1.53	1.51		20%	3.27	3.24
		1.49				3.18	
		1.51				3.26	
Time (min)	NH_3 solution concentration (%)	NH_3 adsorption amount (mmol/g)	Average value (mmol/g)	Time (min)	NH_3 solution concentration (%)	NH_3 adsorption amount (mmol/g)	Average value (mmol/g)
60	4%	3.62	3.59	120	4%	5.01	4.95
		3.57				4.97	
		3.59				4.86	
	8%	4.05	4.1		8%	5.26	5.18
		4.14				5.13	
		4.12				5.15	
	12%	4.25	4.28		12%	5.36	5.37
		4.3				5.32	
		4.28				5.43	
	16%	4.56	4.53		16%	5.64	5.72
		4.59				5.77	
		4.44				5.75	
	20%	4.88	4.82		20%	5.83	5.82
		4.74				5.75	
		4.83				5.88	

The used sample at each cycle in Table S4 was regenerated at 150 °C. The characteristic peaks of obtained material after removing H_2O and NH_3 from $Zn(INA)_2(H_2O)_2(NH_3)_2$ were consistent with that of simulated $Zn(INA)_2$ (Fig. S11). It further confirmed that $Zn(INA)_2$ material co-adsorbed H_2O and NH_3 can be regenerated at 150 °C, which suggests $Zn(INA)_2$ has reusable property for ammonia capture in moist condition.

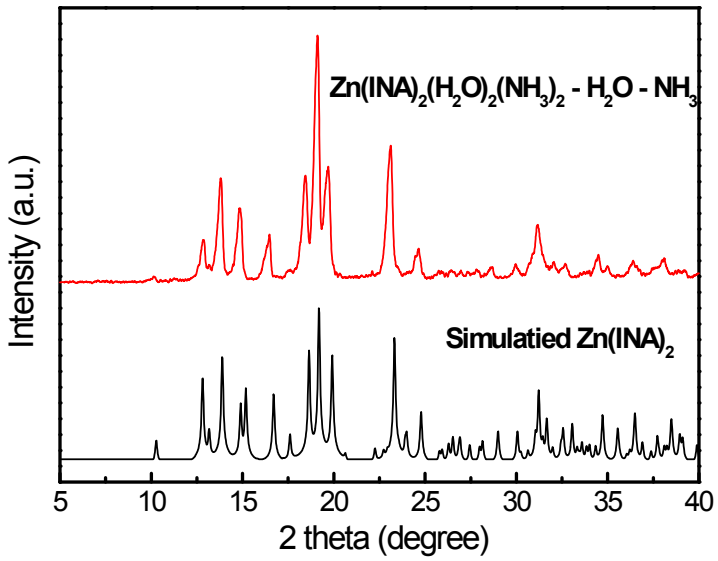


Fig. S11 The PXRD pattern of $Zn(INA)_2(H_2O)_2(NH_3)_2$ removed H_2O and NH_3 at 150 °C. ("-" means desorb)

References:

1. E. P. Perman, *Journal of the Chemical Society, Transactions*, 1901, **79**, 718-725.
2. E. P. Perman, *Journal of the Chemical Society, Transactions*, 1903, **83**, 1168-1184.
3. G. Liu, L. Ma and J. Liu, Handbook of chemistry and chemical property data (inorganic volume), *Chemical Industry Press: Beijing*, 2002.