# Electronic Supporting Information (ESI)

## Ultrafine Rh nanoparticles confined by nitrogen-rich covalent

### organic frameworks for methanolysis of ammonia borane

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# **Table of Contents**

#### **Experimental section**

- Figure S1 SEM images of PC-COF and Rh/PC-COF
- Figure S2 TEM images of Rh/PC-COF with different ratios of mixed-solvents
- Figure S3 TEM images of Rh NPs without support
- Figure S4 TEM images of Rh/PC-COF with different loadings of Rh
- Figure S5 FTIR spectra of PC-COF, piperazine, and cyanuric chloride
- Figure S6 FTIR spectra of Rh/PC-COF catalysts with different loading of Rh
- Figure S7 XRD patterns of PC-COF and Rh/PC-COF catalysts
- Figure S8 BET analysis of PC-COF and Rh/PC-COF
- Figure S9 GC spectrum for generated gas of AB methanolysis
- Figure S10 AB methanolysis over Rh/PC-COF with different loadings of Rh
- Figure S11 AB methanolysis over Rh/PC-COF with different solvents
- Figure S12 AB methanolysis over Rh/PC-COF with different Rh concentrations
- Figure S13 AB methanolysis over Rh/PC-COF with different AB concentrations
- Figure S14 Powder XRD patterns of Rh/PC-COF before and after durability test
- Figure S15 Typical SEM and TEM images of Rh/PC-COF after five runs
- Figure S16 AB methanolysis catalyzed by the filtrate of active catalyst
- Table S1 CHN OEA of as-synthesized PC-COF
- Table S2 ICP-AES results of different catalysts
- Table S3 Catalytic activities of different catalysts for methanolysis of AB

#### References

#### **Experimental Section**

#### Characterization

Powder X-ray diffraction (XRD) patterns were carried out with X-ray diffractometer of Rigaku RINT-2200, using graphite monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54$  Å) at a scanning rate of 4°/min. An inductively coupled plasma (ICP) spectrophotometer (Varian, 725-ES) was used to determine the chemical components of the assynthesized catalysts after the sample digested by microwave. Organic element analysis (OEA) was carried out on an EA3000 elemental analyzer (Euro EA3000, Euro Vector, Milano, Italy). The Brunauer-Emmett-Teller (BET) equation method was used to analyze the specific surface areas, on the basis of nitrogen adsorptiondesorption isotherms which was recorded on a BELSORP-mini II at 77 K. Fouriertransfer infrared spectroscopic (FT-IR) spectroscopy were carried out on a Thermo Nicolet 870 instrument with the KBr discs in the 500-4000 cm-1 region. X-ray photoelectron spectroscopy (XPS) analyses were carried out on an ESCALAB 250XI X-ray photoelectron spectrometer using an Al Ka source. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images and energy-dispersive X-ray spectroscopy (EDS) mapping analyses were recorded on SU-8020 and JEM-2100 with Super-X EDS system under operating voltages of 300 kV. GC analysis was carried out on a FULI GC-9790II gas chromatography equipped with a TCD system and a TDX-01 chromatographic column (FULI Anal. Instrument Ltd., Wenling, China): oven temperature at 60 °C and detector temperature at 120 °C.

#### Synthesis of PC-COF

PC-COF was synthesized by a modified solution-processed condensation polymerization of piperazine and cyanuric chloride.<sup>S1</sup> Typically, piperazine (36 mmol),  $K_2CO_3$  (72 mmol), and 1,4-dioxane (100 mL) were added into a 250 mL three-necked round flask where the mixture was stirred for 1 h. A solution of 1,4dioxane (100 mL) and cyanuric chloride (24 mmol) were added into above solution by drops for 3 h under the ice-water bath condition. Then, the reaction mixture was maintained at 333 K for 3 h and 378 K for 48 h. After the completion of reaction, the product was isolated by filtration and washed several times with 1,4-dioxane, deionized water, and ethanol. The obtained white powder was dried at 313 K for 12 h in a vacuum oven, affording PC-COF with the yield of around 87%.

#### Synthesis of Rh@PVP and Rh NPs

For comparison, Rh NPs stabilized by PVP (denoted as Rh@PVP) were synthesized using the same in-situ reduction method as for Rh/PC-COF. The pure Rh NPs were also synthesized by in-situ reduction method with AB as a reductant.

#### Leaching test of Rh/PC-COF

A leaching test of Rh/PC-COF catalyst was performed for the methanolysis of AB. After the first run of catalytic methanolysis, the suspension in reaction flask was filtered and the filtrate was transferred in another reaction flask. After adding 1 mL mixed-solvent ( $V_{MeOH}/V_{DCM}=2/1$ ) containing AB (31.8 mg, 1 mmol), the hydrogen generation from methanolysis of AB was recorded as described above. Additionally, the filtrate obtained by filtrating the reaction mixture was also analyzed by ICP-OES for the Rh leaching test.

#### **Calculation methods**

The turnover frequency (TOF) is based on the amount of Rh atoms, which was calculated from the equation below:

$$TOF = \frac{n_{H_2}}{n_{Rh} \cdot tmin} = \frac{PatmVH2/RT}{n_{Rh} \cdot tmin}$$

In the equation,  $n_{H_2}$  is the total mol of generated H<sub>2</sub> (P<sub>atm</sub> is 101.325 kPa, R is 8.3145 m<sup>3</sup>·Pa·mol<sup>-1</sup>·K<sup>-1</sup>, and T is 298 K),  $n_{Rh}$  is the total mole number of Rh atoms in catalyst, and  $t_{min}$  is the completion time of the reaction in minute.

The apparent activation energy  $(E_a)$  of AB methanolysis was calculated from the equation below:

#### lnk = lnA - Ea/RT

The values of rate constant k at different temperatures are calculated from the slope of the linear part of each plot when the conversion reaches 50%.



Figure S1 Typical SEM images of (a) PC-COF and (b) Rh/PC-COF.



**Figure S2** TEM images of 1.91 wt% Rh/PC-COF and the corresponding size distribution of Rh nanoparticles with different solvents: (a) MeOH, (b) MeOH/DCM 2/1, (c) MeOH/DCM 1/1, and (d) MeOH/DCM 1/2.



Figure S3 TEM images of Rh NPs without support.



**Figure S4** TEM images of Rh/PC-COF and the corresponding size distribution of Rh nanoparticles with different loading of Rh: (a) 0.96 wt%, (b) 1.91 wt%, (c) 3.82 wt%, (d) 5.73 wt%, and (e) 7.64 wt%; (f) Mean diameters and standard deviations of Rh NPs synthesized with different loading of Rh.



Figure S5 FTIR spectra of PC-COF, piperazine, and cyanuric chloride.



Figure S6 FTIR spectra of Rh/PC-COF catalysts with different loadings of Rh.



**Figure S7** Powder XRD patterns of (a) PC-COF and Rh/PC-COF catalysts with different loadings of Rh, (b) Enlarged XRD pattern of PC-COF.



Figure S8 (a)  $N_2$  adsorption/desorption isotherms of PC-COF and 1.91 wt% Rh/PC-COF; (b) Pore size distribution curves of PC-COF and 1.91 wt% Rh/PC-COF.



Figure S9 GC spectrum for evolved gas of AB methanolysis.



**Figure S10** (a) Time course plots of  $H_2$  generation for methanolysis of AB over Rh/PC-COF with different loadings of Rh at 298 K and (b) The corresponding TOF values.



**Figure S11** Time course plots of  $H_2$  generation for methanolysis of AB over Rh/PC-COF with different solvents.



**Figure S12** Time course plots of  $H_2$  generation for the methanolysis over Rh/PC-COF at 298 K: (a) Different catalyst concentrations and (b) ln [Rh] vs. ln k plot.



**Figure S13** Time course plots of  $H_2$  generation for the methanolysis over Rh/PC-COF at 298 K: (a) Different AB concentrations and (b) ln [AB] vs. ln k plot.



**Figure S14** Powder XRD patterns of the as-synthesized Rh/PC-COF catalyst before and after durability tests.



**Figure S15** Typical (a) SEM and (b) TEM images of 1.91 wt% Rh/PC-COF after five runs. The inset of (b) is the corresponding distribution histogram of Rh NP size.



Figure S16 Time course plots of  $H_2$  generation for the methanolysis catalyzed by the filtrate obtained from filtration of active catalyst after the first run of catalytic methanolysis.

Samples	N (wt%)	C (wt%)	H (wt%)	Total (wt%)
PC-COF	39.47	52.40	6.36	98.23
Theoretical	41.17	52.94	5.88	100

 Table S1 CHN OEA of as-synthesized PC-COF.

Enter	Catalyst	Rh loading (wt%)	
1	0.96 wt% Rh/PC-COF	0.95	
2	1.91 wt% Rh/PC-COF	1.90	
3	3.82 wt% Rh/PC-COF	3.78	
4	5.73 wt% Rh/PC-COF	5.64	
5	7.64 wt% Rh/PC-COF	7.53	

 Table S2 ICP-AES results of different catalysts.

Catalyst	Temp. (K)	TOF(min <sup>-1</sup> )	$E_{\rm a}({\rm kJ/mol})$	Ref.
Rh/PC-COF	298	505	31.8	This Work
Rh-PRO/C	298	411	38.2	S2
AgPd alloy	298	366.4	37.5	S3
Ru@PCC-2	298	304		S4
HPRhS	298	292		S5
Rh/nanoAl <sub>2</sub> O <sub>3</sub>	298	218	48	S6
Rh/CC3-R-homo	298	215		S7
Pd@RCC3	298	176		S8
Rh/nanoSiO <sub>2</sub>	298	168	62	S9
Rh/nanoHAP	298	147	56	S10
Rh/nanoCeO <sub>2</sub>	298	144	64.6	S11
Ru/MMT	298	118	23.8	S12
Pd/GNS	298	101	46	S13
Ru/graphene	298	99.4	54.1	S14
PVP-stabilized Ru	298	67	58	S15
Cu48Pd52 alloy/C	298	53.2		S16
Cu <sub>36</sub> Ni <sub>64</sub> /Graphene	298	49.1	24.4	S17
Co <sub>48</sub> Pd <sub>52</sub> /C	298	27.7	25.5	S18
Cu@Cu <sub>2</sub> O@CuO/C	298	24	67.9	S19
PVP-stabilized Pd	298	22.3	35	S20

Table S3 Catalytic activities of different catalysts for methanolysis of AB.

PVP-stabilized Ni	298	12.1	62	S21
Co-Ni-B	298	10		S22

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