Water-Induced Gaseous Formaldehyde Decomposition Using Ruthenium Organic Crystalline

Yangbin Shen,[,a] Ying Xu,[a] Ting Zhang,[b] Yulu Zhan,[c] and Chunxian Guo[*,a]*

[a] Institute of Materials Science and Devices, School of Materials Science and Engineering, Suzhou University of Science and Technology， Suzhou 215009, China

[b] School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 20024, China

[c] Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

CONTENTS

SI-1. Chemicals and Materials.

All chemicals are commercial and used without further purification unless specified. Ethanol (C_2H_5OH, Tianjing Baishi Chemical Industry Co., Ltd, >99.7%), 2,3,5,6-tetramethyl-1,4-phenylenediamine (Shanghai Aladdin Biochemical Technology Co., Ltd., 98%),3,3',5,5'-tetramethylbenzidine (TMB) ($C_{16}H_{20}N_2$, Shanghai Aladdin Biochemical Technology Co., Ltd, >99%),4,4-methylenebis(2,6-diethylaniline) ($C_{21}H_{30}N_2$, Shanghai Bide Pharmatech Co., Ltd, 98%),4,4'-diaminodiphenylmethane ($C_{13}H_{14}N_2$, Shanghai Macklin Biochemical Co., Ltd, 97%), 4,4'-methylenebis(2-methylaniline) ($C_{15}H_{18}N_2$, Shanghai Bide Pharmatech Co., Ltd, 98%), dichloro(p-cymene)ruthenium(II) dimer ($C_{20}H_{28}Cl_4Ru_2$, Energy Chemical Reagent. Co., Ltd., 98%), paraformaldehyde (Shanghai Macklin Biochemical Co., Ltd, 96%), air (Suzhou Jinhong Gas Co., Ltd, containing 21% O_2 and 79% N_2), nitrogen (N_2, Suzhou Jinhong Gas Co., Ltd, ≥99.999%), carbon dioxide (CO_2, Suzhou Jinhong Gas Co., Ltd, ≥99.99%), formaldehyde (CH_2O, Shanghai Macklin Biochemical Co., Ltd., 37%), disodium hydrogen phosphate (Na_2HPO_4, Sinopharm Chemical Reagent. Co., Ltd., >99%), sodium phosphate monobasic (NaH_2PO_4, Sinopharm Chemical Reagent. Co., Ltd. >99%), sodium hydroxide (NaOH, Sinopharm Chemical Reagent. Co., Ltd.,> 96%), boric acid (H_3BO_3, Shanghai Macklin Biochemical Co., Ltd.,>99.5%), potassium periodate ($KIO4$, Shanghai Meryer Chemical Technology Co., Ltd, 98%), 4-Amino-3-hydrazino5-mercapto-1,2,4-triazole (AHMT) ($C_2H_6N_6S$, Shanghai Acmec Biochemical Co., Ltd, 98%), ultrapure water is prepared by Thermo PureLab Ultra Genetic.

SI-2. Preparation of the Ru-MOFs.

The novel ruthenium organic crystalline particles were creatively prepared through the coordination reaction between the [Ru(p-Cymene)Cl$_2$]$_2$ and aniline-containing ligands. Take Ru-DAPM$_2$ preparation for example, 198 mg 4,4'-diaminodiphenylmethane (1 mmol) is dissolved in 10 mL ethanol at 60 ℃, then transfer 306 mg [Ru(p-Cymene)Cl$_2$]$_2$ (0.5 mmol) in ethanol solution. The [Ru(p-Cymene)Cl$_2$]$_2$ will dissolve in hot ethanol at 60 ℃ rapidly. Then yellow insoluble Ru-DAPM$_2$ powder will be produced in several minutes. At last, yellow suspension is filtered by filter membrane and washed with hot ethanol after 12 hours reaction. The other four kinds of ruthenium organic crystalline particles are prepared by similar process, could be employed for hydrogen production from formaldehyde decomposition both in water and moist air.
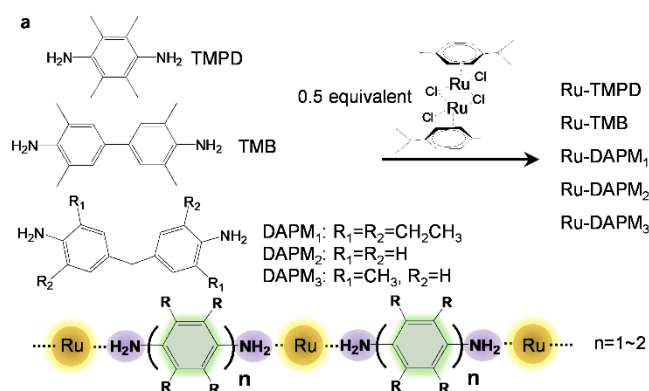
Scheme 1. Preparation of Ruthenium Organic Crystalline Particles.

SI-3. Characterization and Physical Measurements.

The scanning electron microscope images (SEM) were recorded on Quanta FEG 250. The transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded on the Talos F200X, Thermo Scientific. The UV-Vis spectrum analysis was carried out by UV-Vis spectrometer (UV-2600 Shimadzu). Powder X-ray diffraction (XRD) patterns of samples were recorded with Bruker D8 X-ray diffractometer using Cu-Kα radiation (40 kV and 10 mA). The XPS analysis was determined by the Escalab 250Xi spectrometer. The ruthenium content of the catalysts was determined by Agilent 720 ICP-OES. Gas chromatography experiments were performed on GC-G5 chromatograph (Beijing Persee General Instrument Co., Ltd). The gas chromatograph (GC) has the flame ionization detector, thermal conductivity detector and methanizer. The column of GC is TDX-1 (3 m*3 mm). The system used N_2 as a carrier gas. Although the TCD could give the detection signal of high concentration of CO_2, CH_4 and CO, but it shows poor sensitivity. The methanizer is necessary for improving the sensitivity of FID for CO_2 and CO detection. So we detect and quantify the H_2 by TCD of this GC, detect and quantify the CH_4 by FID of this GC, detect and quantify the CO_2 and CO by FID and methanizer of this GC. The FTIR data were detected by Nicolet iS 50 (Nicolet Instrument Co. USA). The surface areas of the Ru-MOFs were determined by the Brunauer-Emmett-Teller (BET) method, based on the amount of N_2 adsorbed at pressures of $0.005 < P/P_0 < 0.998$. The pore size distributions and average pore diameter of the catalyst were analyzed by the BJH nitrogen adsorption and desorption method (Quantachrome Instruments).

The transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded on the Talos F200X, Thermo Scientific. The samples were dispersed on the silicon slice. The SEM images were recorded on the Quanta FEG 250. The EDS and mapping are analyzed by Oxford Instruments.
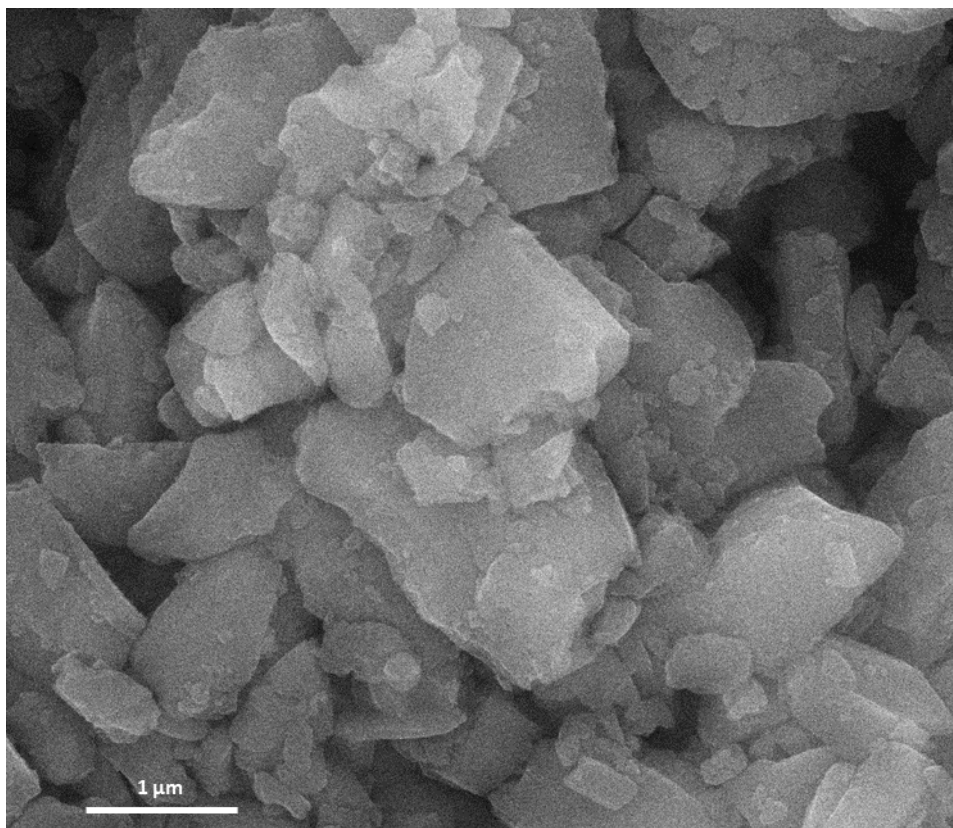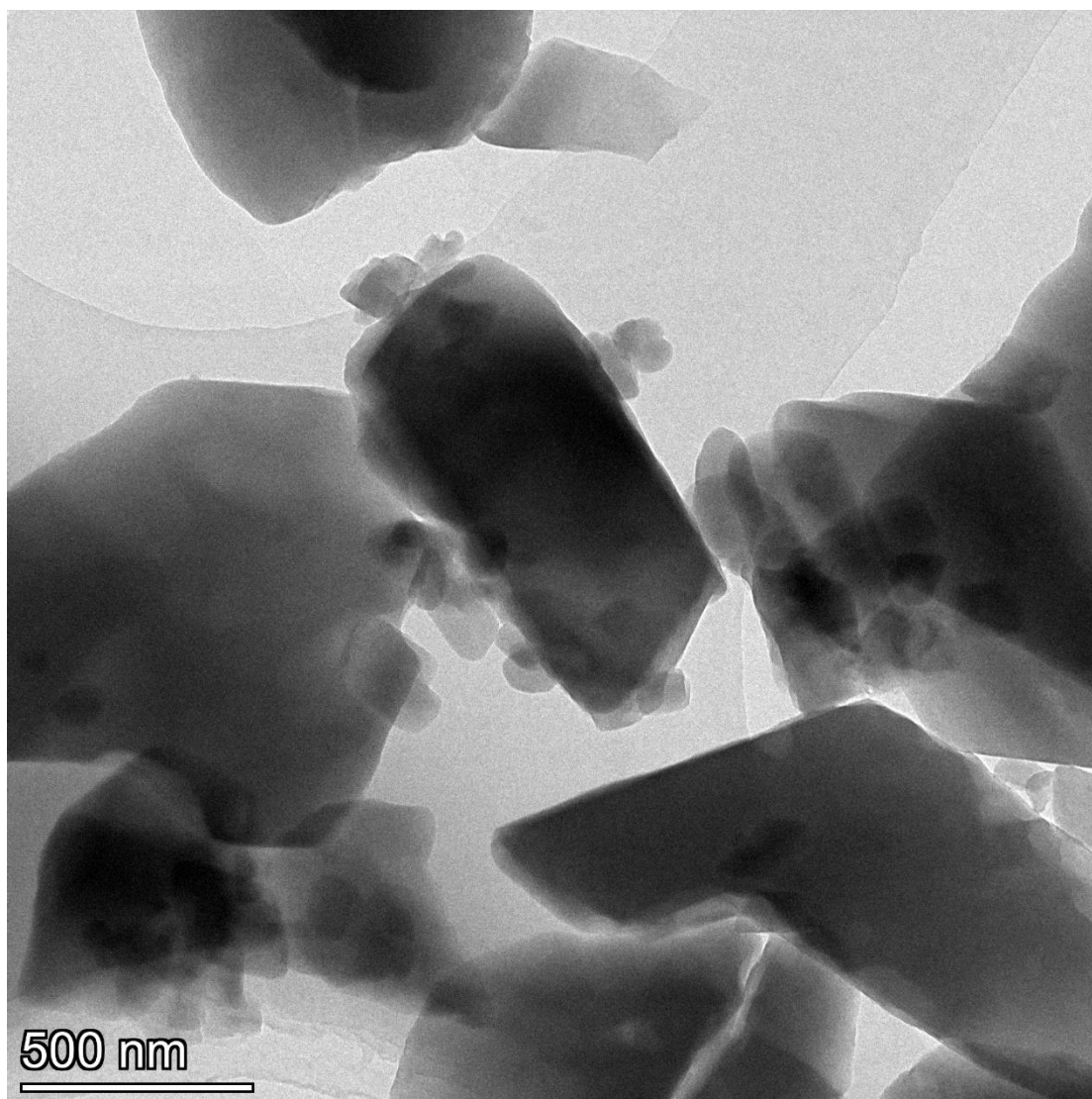

Figure S 1. SEM Images of Ru-DAPM$_2$.
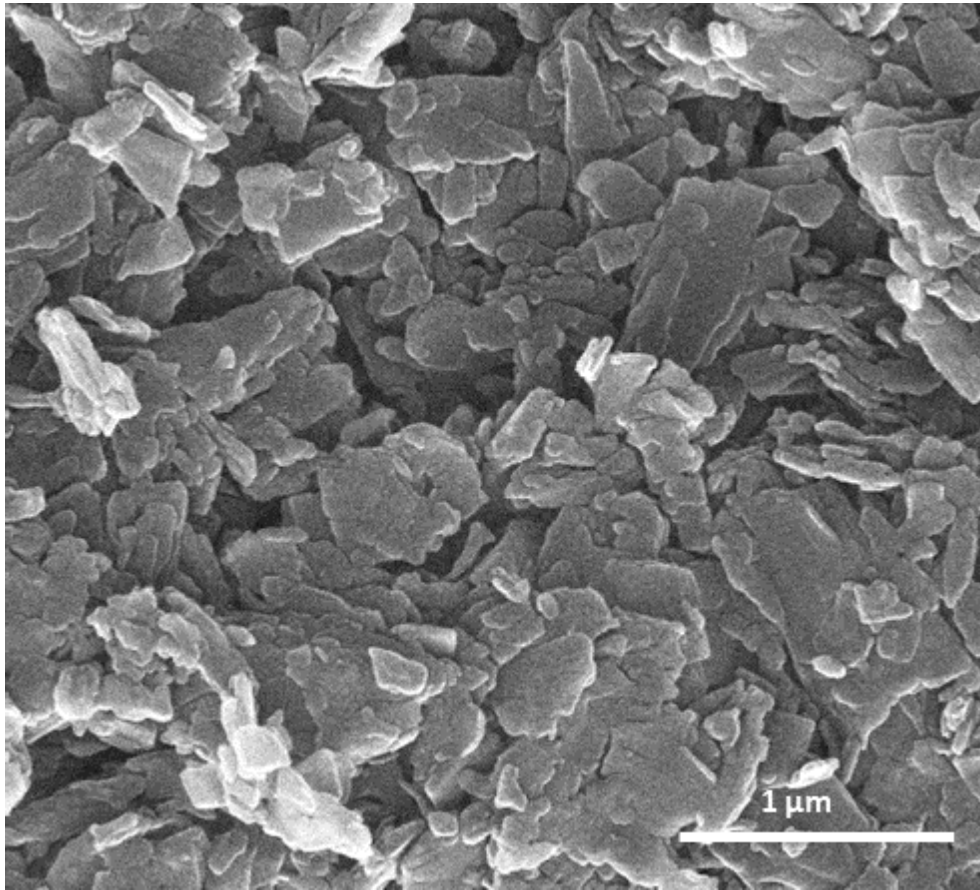
Figure S 2. TEM Images of Ru-DAPM$_2$.

Figure S 3. SEM Images of Ru-TMB.
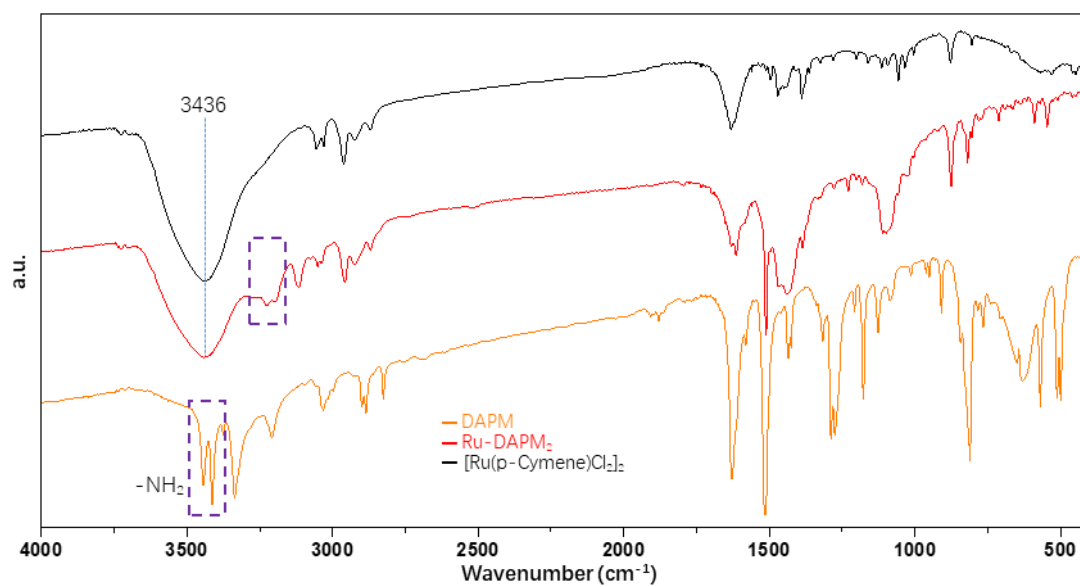
Figure S 4. TEM Images of Ru-TMB.

Figure S 5. FTIR Spectrum of DAPM, Ru-DAPM$_2$ and [Ru(p-Cymene)Cl$_2$]$_2$.

The pore size distributions and average pore radius of the catalysts were analyzed by the BJH nitrogen adsorption and desorption method (Quantachrome Instruments). All the ruthenium organic crystalline has microporous structure.
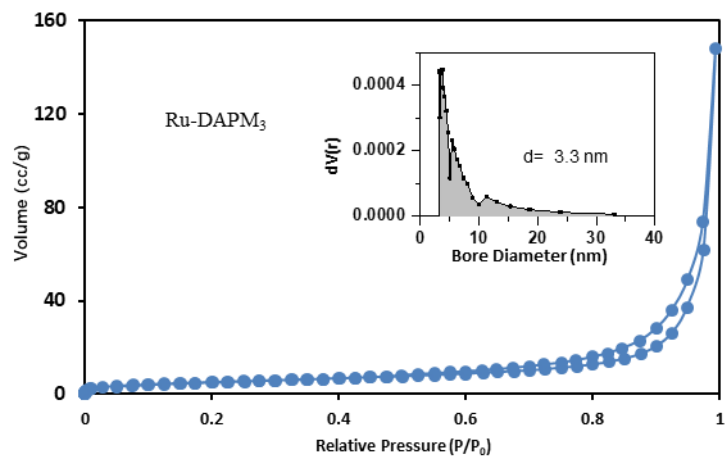

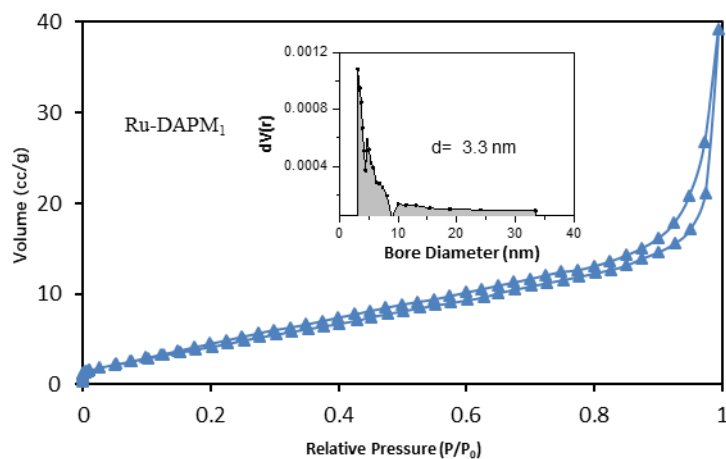**Figure S 6**. BET Analysis and Pore Size Distribution of Ru-DAPM$_3$.

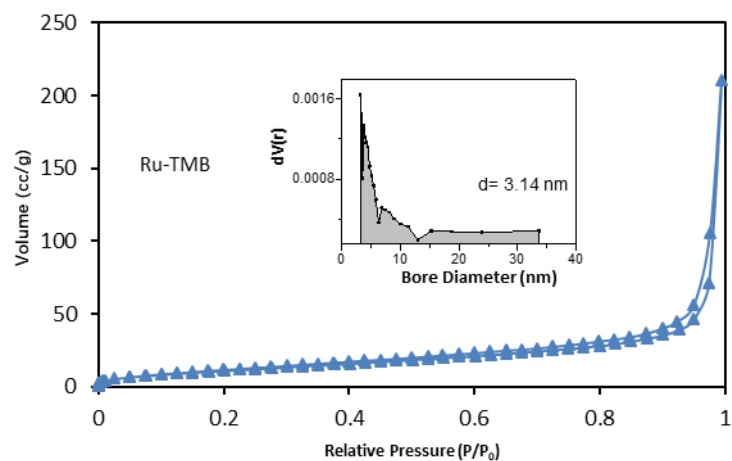**Figure S 7**. BET Analysis and Pore Size Distribution of Ru-DAPM$_1$.

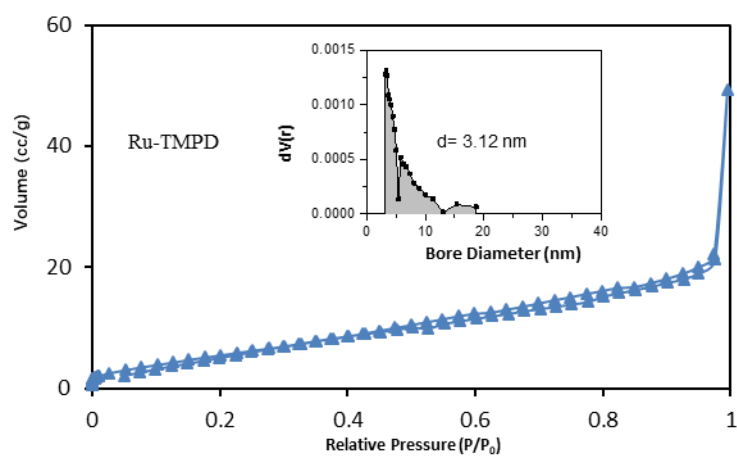**Figure S 8**. BET Analysis and Pore Size Distribution of Ru-TMB.

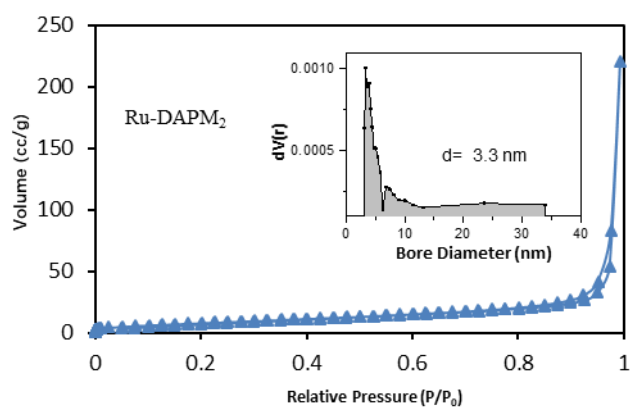**Figure S 9**. BET Analysis and Pore Size Distribution of Ru-TMPD.

Figure S 10. BET Analysis and Pore Size Distribution of Ru-DAPM$_2$.

SI-4. Formaldehyde decomposition in water.

Typically, 10mL 4 M formaldehyde water solution was stirred by magnetic bar in 25mL flask. Then, 6 mg ruthenium organic crystalline were added into the solution after the flask been heated to the preset temperature. The flask was connected to a U-tube containing colored solution. Then blow nitrogen into the total device for more than 10 minutes, replaced the air inside. The U-shaped tube was used for measuring the volume of the generated gas during formaldehyde and water catalytic reforming. The gas was analyzed by gas chromatography.

TOF Calculations for HCHO decomposition. Hydrogen production from formaldehyde water reforming is a complicated process, it contains formaldehyde water shift reaction and formic acid decomposition. The Ru(p-Cymene) group has been confirmed effective for formaldehyde-water shift reaction and formic acid decomposition. Little carbon dioxide was detected by GC during the initial 30 minutes of reaction, so we calculated the TOF of formaldehyde decomposition based on the chemical **Reaction (1)**.

$$HCHO + H_2O \rightarrow HCOOH + H_2 \qquad \qquad \textbf{Reaction (1)}$$

The TOF was calculated by **Equation 1**. The water vapor was neglected.

$$TOF = \frac{V_{H2}/(t*V_{m,20°C})}{n_{(Ru)}} \qquad \qquad \textbf{Equation 1}$$

V_{H2} was the volume of hydrogen which is generated during the initial 0.5 hours, t was 0.5 h. $n_{(Ru)}$ was the molar number of ruthenium, which was determined by Agilent 720 ICP-OES. The $V_{m,20°C}$ was calculated by van der Waals equation of hydrogen.[1]

$$V_{m,20°C} = \frac{RT}{p} + b - \frac{a}{RT} = 24 \text{ L/mol} \qquad \qquad \textbf{Equation 2}$$

R is 8.3145 m^3 Pa mol^{-1} K^{-1}, T is 293.15 K, p is 101325 Pa, b is $26.7×10^{-6}$ $m^3 \cdot mol^{-1}$, a is $2.49×10^{-10}$ $Pa \cdot m^3 \cdot mol^{-2}$.

The catalyst also shows high catalytic selectivity for HCHO-H_2O decomposition. As exhibited in the **Figure S 11**, trace carbon monoxide will be produced during HCHO-H_2O decomposition.
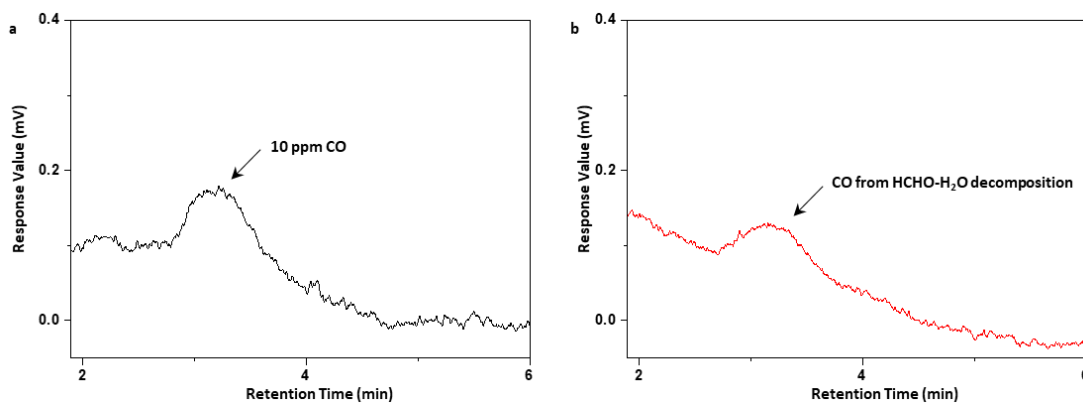
Figure S 11.Gas Chromatogram of CO using the FID Detectors and Methanizer. (a) 10 ppm CO sample. (b) generated CO during HCHO-H$_2$O decomposition by Ru-TMPD.

We also carry out the formaldehyde-water decomposition in a fixed-bed reactor at 110 ℃. 30 mg catalysts were mixed with 500 mg quartz sand (80 mesh), then the mixture is loaded in a fixed-bed reactor. 3 M formaldehyde-water solution was vaporized and injected into reactor at 110 ℃. Outlet gas of the reactor was cooled down to room temperature, and gas flow rate was recorded by a flowmeter. At last, the TOF was calculated by catalyst dosage, gas flow rate and gas content.

Table S 1. Catalytic Activity of Ruthenium Organic Crystalline for Formaldehyde-Water Decomposition at 110 ℃.

Entry	Catalysts	TOF (h^{-1})
1	Ru-TMPD	5800
2	Ru-TMB	5510
3	Ru-DAPM$_1$	4890
4	Ru-DAPM$_2$	7720
5	Ru-DAPM$_3$	7120

SI-5. Gaseous Formaldehyde decomposition.

1. Gaseous Formaldehyde Decomposition in Moist Nitrogen.

Typically, blow high-purity nitrogen into a bottle at 25 °C, the bottle contains 10 wt% HCHO formaldehyde solution. The gas mixture will outflow through the bottle outlet, and will blow into a quartz tube with an inner diameter of 5 mm. The gas contains formaldehyde, nitrogen and water vapor. 30 mg catalysts were mixed with 500 mg quartz sand (80 mesh), then the mixture is loaded in a quartz tube. Gaseous formaldehyde decomposition was carried out by blowing gaseous mixture through a fixed-bed quartz reactor after the tube is heated to the preset temperature. The outlet gas is connected to a gas flowmeter. The total flow rate was 50 mL/min, corresponding to a weight hourly space velocity (WHSV) of 100000 mL g^{-1} h^{-1}.
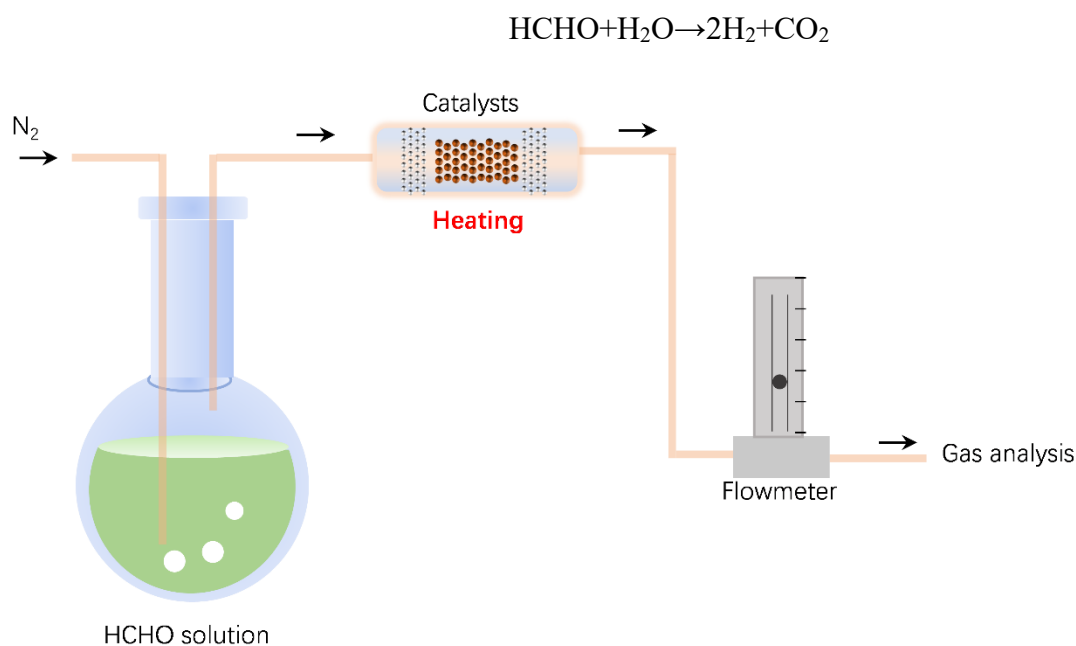
$$HCHO+H_2O \rightarrow 2H_2+CO_2$$

Figure S 12. Diagram of Gaseous Formaldehyde Decomposition in Moist Nitrogen.

50 ppm commercial gaseous formaldehyde is also employed for formaldehyde decomposition in moist nitrogen. This gas contains 50 ppm gaseous formaldehyde (diluted in N_2). We blow formaldehyde-contained nitrogen through a bottle, the bottle contains pure water at 50 ℃. The gas doesn't blow through liquid water, but could take away water vapor. The gas mixture will outflow through the bottle outlet, and will blow into a quartz tube with an inner diameter of 5 mm. The gas

contains formaldehyde, nitrogen and water vapor. 30 mg catalysts were mixed with 500 mg quartz sand (80 mesh), then the mixture is loaded in a quartz tube. Gaseous formaldehyde decomposition was carried out by blowing gaseous mixture through a fixed-bed quartz reactor after the tube is heated to 90 ℃. The outlet gas is connected to a gas flowmeter. The total flow rate was 50 mL/min, corresponding to a weight hourly space velocity (WHSV) of 100000 mL $g^{-1} h^{-1}$. The inlet and outlet formaldehyde concentration are determined by AHMT spectrophotometric method.[2-3]

Table S 2. 50 ppm Formaldehyde Catalytic Conversion by Ruthenium Organic Crystalline at 90 ℃.

Entry	Catalysts	Conversion Rate
1	Ru-TMPD	83%
2	Ru-TMB	82%
3	Ru-DAPM1	70%
4	Ru-DAPM2	94%
5	Ru-DAPM3	89%

2.Gaseous Formaldehyde Catalytic Oxidation in Dry Air.

Paraformaldehyde is easy to be decomposed in air. As exhibited in **Figure S 13**, paraformaldehyde start to be decomposed obviously at 50 ℃.
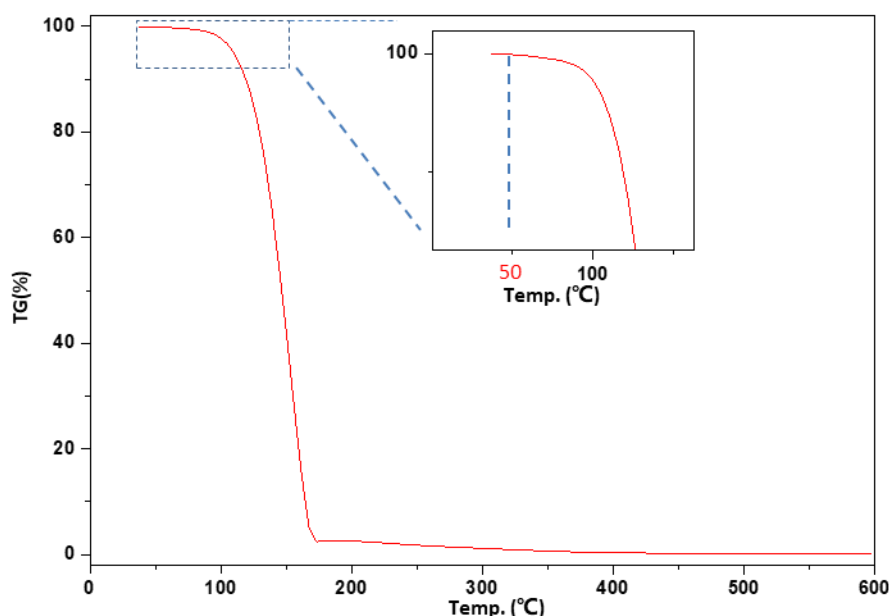

Figure S 13. TGA of paraformaldehyde.

Gaseous HCHO was generated by flowing air through 5 g dry paraformaldehyde in a round-bottomed flask.[3-4] The gas mixture will outflow through the bottle outlet, and will blow into a quartz tube with an inner diameter of 5 mm. The gas contains formaldehyde, nitrogen and oxygen. 30 mg catalysts were mixed with 500 mg quartz sand (80 mesh), then the mixture is loaded in a quartz tube. Gaseous formaldehyde catalytic oxidation was carried out by blowing gaseous mixture through a fixed-bed quartz reactor after the tube is heated to the preset temperature. The outlet gas is connected to a gas flowmeter. The total flow rate was 50 mL/min, corresponding to a weight hourly space velocity (WHSV) of 100000 mL $g^{-1} h^{-1}$.
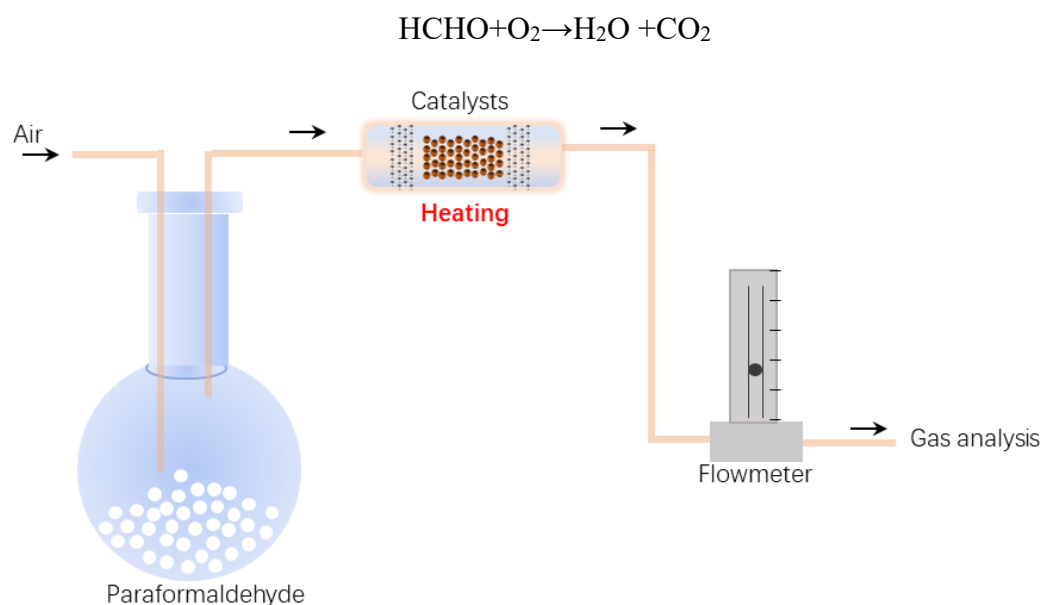
$$HCHO+O_2 \rightarrow H_2O +CO_2$$

Figure S 14. Diagram of Gaseous Formaldehyde Catalytic Oxidation in Dry Air.

3. Gaseous Formaldehyde Decomposition in Moist Air.

Typically, blow air into a bottle at 25 °C, the bottle contains 10 wt% HCHO formaldehyde solution. The gas mixture will outflow through the bottle outlet, and will blow into a quartz tube with an inner diameter of 5 mm. The gas contains formaldehyde, nitrogen, oxygen and water vapor. 30 mg catalysts were mixed with 500 mg quartz sand (80 mesh), then the mixture is loaded in a quartz tube. Gaseous formaldehyde decomposition was carried out by blowing gaseous mixture through a fixed-bed quartz reactor after the tube is heated to the preset temperature. The outlet gas is connected to a gas flowmeter. The total flow rate was 50 mL/min, corresponding to a weight hourly space velocity (WHSV) of 100000 mL $g^{-1} h^{-1}$.
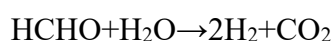
$$HCHO+H_2O \rightarrow 2H_2+CO_2$$
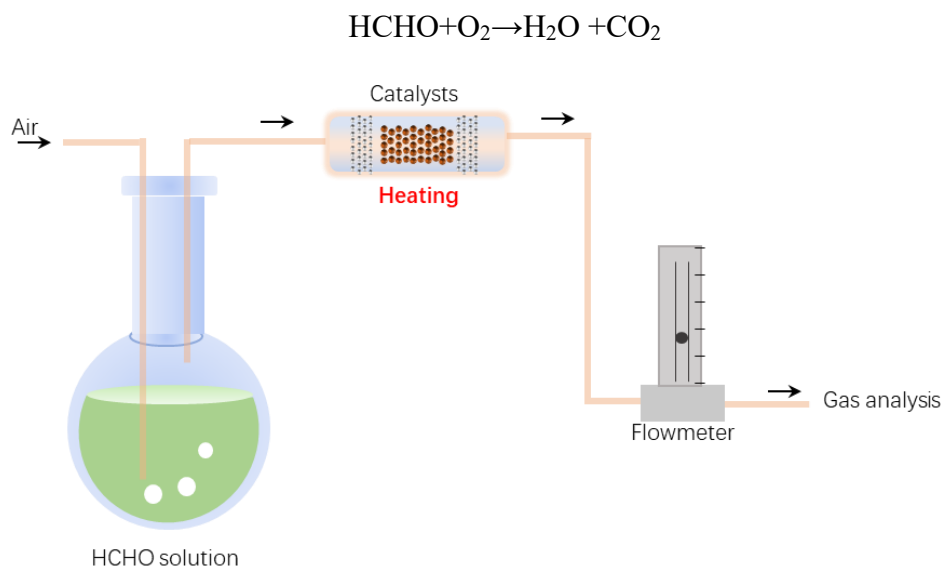
$$HCHO+O_2 \rightarrow H_2O +CO_2$$

Figure S 15. Diagram of Gaseous Formaldehyde Decomposition in Moist Air.

Typically, blow air into a bottle at 40 °C, the bottle contains 20 wt% HCHO formaldehyde solution. The gas mixture will outflow through the bottle outlet, and will blow into a quartz tube with an inner diameter of 5 mm. The gas contains formaldehyde (612 ppm), nitrogen, oxygen and water vapor. 30 mg catalysts were mixed with 500 mg quartz sand (80 mesh), then the mixture is loaded in a quartz tube. Gaseous formaldehyde decomposition was carried out by blowing gaseous mixture through a fixed-bed quartz reactor after the tube is heated to the preset temperature. The outlet gas is connected to a gas flowmeter. The total flow rate was 50 mL/min, corresponding to a weight hourly space velocity (WHSV) of 100000 mL $g^{-1} h^{-1}$.

$$HCHO+H_2O \rightarrow 2H_2+CO_2$$
$$HCHO+O_2 \rightarrow H_2O +CO_2$$
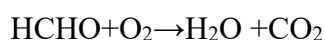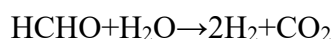
4. Formaldehyde Removal Efficiency

Formaldehyde removal efficiency was calculated as follows:

HCHO conversion = ([HCHO]$_{in}$ – [HCHO]$_{out}$)/[HCHO]$_{in}$ * 100%

where HCHO conversion, [HCHO]$_{in}$, and [HCHO]$_{out}$ represent the formaldehyde removal efficiency and the inlet and outlet HCHO concentrations, respectively. Its inlet and outlet formaldehyde concentration are determined by AHMT spectrophotometric method.[2-3]

Typically, the outlet gas stream is bubbled through 15 mL boric acid solution (0.5 wt.%) for 5

minutes, the gas velocity is 50 mL/min. Formaldehyde will be collected in the solution, dilute the solution to 100 mL with boric acid solution. Then 2 mL NaOH solution (20 wt.%) and 2 mL AHMT solution (0.5 wt.%) are added into 8 mL of diluted solution, shake the mixture solution for 10 s and stay reaction for 15 min under dark condition. Finally, 2 mL (0.75 wt.%) KIO_4 solution and 1 mL boric acid solution added into the mixture solution. HCHO concentration in the gas stream was then determined by measuring the absorbance at 550 nm with UV-Vis spectrophotometer. The HCHO conversion was calculated based on its concentration change. The equation of this method was shown in **Figure S 16**.
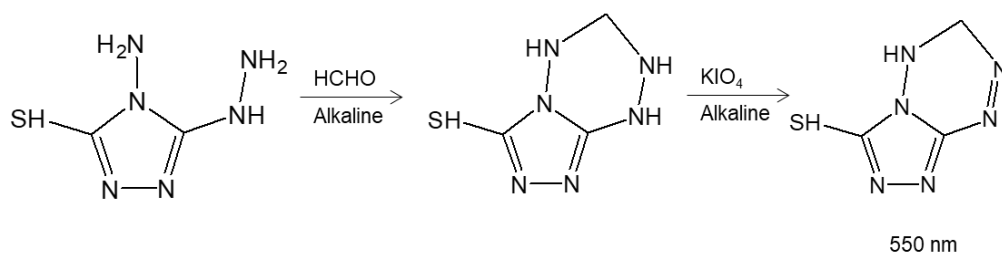

Figure S 16. Mechanism of the AHMT Method for HCHO Detection.

For low- concentration formaldehyde (< 10 ppm) detection, the outlet gas stream is bubbled through 10 mL boric acid solution (0.5 wt.%) for 5 minutes, the gas velocity is 50 mL/min. Formaldehyde will be collected in the solution, mix 0.8 mL solution with 0.2 mL NaOH solution (20 wt.%) and 0.2 mL AHMT solution (0.5 wt.%), and shake the mixture solution for 10 s. Then stay reaction for 15 min under dark condition. Finally, 0.2 mL (0.75 wt.%) KIO_4 solution and 0.1 mL boric acid solution added into the mixture solution. HCHO concentration in the gas stream was then determined by measuring the absorbance at 550 nm with UV-Vis spectrophotometer.

SI-6. Hydrogen Selectivity Analysis

We study the catalytic selectivity by product analysis during formaldehyde decomposition. Both formaldehyde oxidation and formaldehyde-water decomposition could produce carbon dioxide, but hydrogen is the exclusive product through formaldehyde-water decomposition. So hydrogen selectivity could be used for evaluating the catalytic pathway during formaldehyde decomposition. As the catalyst dosage is much higher than the formaldehyde, we consider intermediate products formic acid is also decomposed completely.

$$HCHO + H_2O \rightarrow 2H_2 + CO_2 \qquad \text{Reaction 1}$$

$$HCHO + O_2 \rightarrow H_2O + CO_2 \qquad \text{Reaction 2}$$
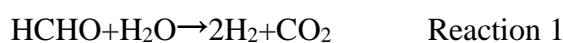
The ratio of H_2 selectivity was calculated according to the generation of H_2 and CO_2, which was determined by a GC-G5 (Beijing Persee General Instrument CO. Ltd). The gas chromatography was equipped with TDX-1 column, Porapak Q column, FID, TCD and methanizer, N_2 as carrier gas. No carbon products other than CO_2 were detected.

$$H_2 \text{ selectivity} = 0.5 * [H_2]_{out} / ([HCHO]_{in} - [HCHO]_{out}) * 100\%$$

Where $[H_2]_{out}$, $[HCHO]_{in}$ and $[HCHO]_{out}$ represent the outlet H_2, inlet and outlet HCHO concentrations respectively.

SI-7. Reaction Mechanism

1. Water and Methanediol Detection by ATR-FTIR.

We analyze the formaldehyde decomposition process by ATR-FTIR, it is crucial for us to propose catalytic mechanism and explain the catalytic selectivity in moist air. We find vapor will be adsorbed on the Ru-DAMP$_2$ when the moist air blows through it. Ru-DAMP$_2$ provide suitable volume for moisture condensation and enrichment in its micropore, which cause the FTIR absorption peak shift from 3436 cm^{-1} to 3400 cm^{-1} gradually. 3400 cm^{-1} is the characteristic absorption peak of O-H vibration in liquid water. The gaseous formaldehyde will dissolve in water, react with water, and form methanediol in micropore spontaneously.[5] Methanediol has broad band at 3000–3700 cm^{-1} in water, which could be attributed to the O–H stretching modes of two OH groups. It is difficult to explicitly attribute the broad band at 3000–3700 cm^{-1} to given molecular interactions between $CH_2(OH)_2$ and H_2O at the present stage.[6] While the FTIR spectrum have changed from 3000–3700 cm^{-1}, which may cause by $CH_2(OH)_2$ and H_2O. The weak peaks at 1022 cm^{-1} is caused by O–C–O stretching vibration of $CH_2(OH)_2$.
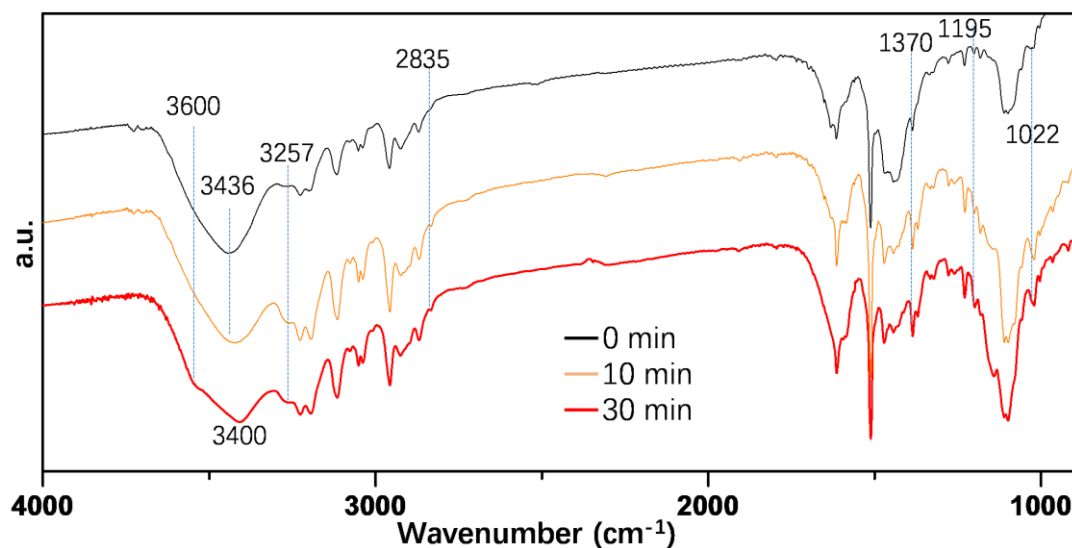

Figure S 17. ATR-FTIR Spectrum Variety of Ru-DAMP$_2$ during Reaction.

We employ ATR-FTIR for detecting the intermediate products and catalyst intermediate. 30 mg catalysts were analyzed during gaseous formaldehyde decomposition in moist air. The catalysts were encapsulated and fixed in a CaF$_2$ flow cell. The formaldehyde-contained moist air will blow into the

flow cell at 50 ℃. The catalyst was analyzed every 10 minutes.

2. Water Detection by XPS.

The XPS measurements were conducted via Escalab 250Xi spectrometer. The Ru-DAMP$_2$ have microporous structure, could adsorbed water vapor from moist air. The water could be stable in this ruthenium organic crystalline. **Figure S 18** and **Figure S 19** exhibit the binding energy of O 1s in the DAMP$_2$ after it exposes to moist air, the O 1s is belong to the absorbed water in the micropore of DAMP$_2$. It is a typical binding energy of O 1s in water.[7]
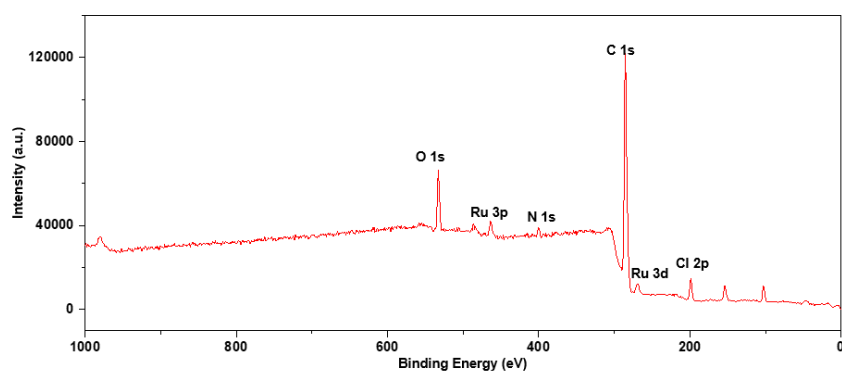

Figure S 18. XPS Analysis of Ru-DAMP$_2$ after Exposure to Moist Air.
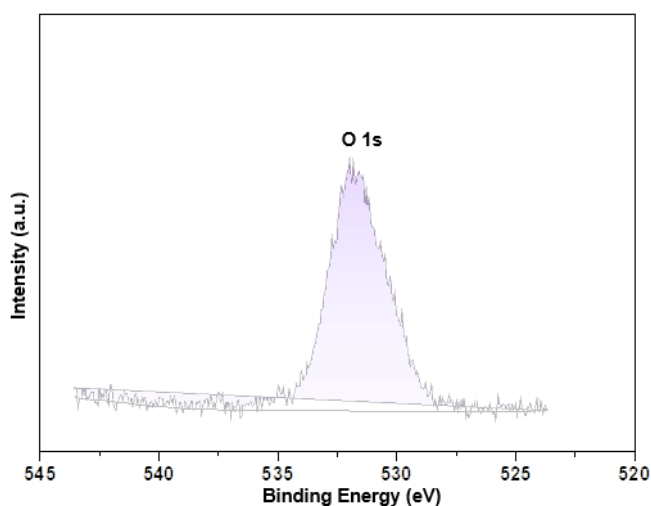

Figure S 19. O 1s of Ru-DAMP$_2$ after Exposure to Moist Air.

References

(1)   Wang, Z.; Lu, S. M.; Li, J.; Wang, J.; Li, C.   Unprecedentedly High Formic Acid Dehydrogenation Activity on An Iridium Complex with An N,N'-diimine Ligand in Water. *Chemistry–A European Journal* **2015,** 21 (36), 12592-12595.

(2)   Xu, D.; Zhu, R.; Xie, D.; Xie, Y.; Wu, H.; Mei, Y.   Amine-Containing Resin for Coating with Excellent Formaldehyde Removal Performance. *Industrial & Engineering Chemistry Research* **2021,** 60 (29), 10674-10682.

(3)   Ou, C.-C.; Chen, C.-H.; Chan, T.-S.; Chen, C.-S.; Cheng, S.   Influence of pretreatment on the catalytic performance of Ag/CeO2 for formaldehyde removal at low temperature. *J. Catal.* **2019,** 380, 43-54.

(4)   Ji, J.; Lu, X.; Chen, C.; He, M.; Huang, H.   Potassium-modulated delta-MnO2 as robust catalysts for formaldehyde oxidation at room temperature. *Appl. Catal.B-Environ* **2020,** 260.

(5)   Heim, L. E.; Schloerer, N. E.; Choi, J.-H.; Prechtl, M. H. G.   Selective and mild hydrogen production using water and formaldehyde. *Nat. Commun.* **2014,** 5.

(6)   Chen, Y.-F.; Chu, L.-K.   Infrared Characterization of Isotopic Analogues of Methanediol in Aqueous Solution. *The Journal of Physical Chemistry A* **2022,** 126 (32), 5302-5309.

(7)   Ogasawara, H.; Brena, B.; Nordlund, D.; Nyberg, M.; Pelmenschikov, A.; Pettersson, L. G. M.; Nilsson, A.   Structure and bonding of water on Pt(111). *Phys. Rev. Lett.* **2002,** 89 (27), 276102.