

Supporting Information

Hydrogen Generation from s-Trioxane and Water Catalytic Reforming: A Solid Organic Hydrogen Carrier

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SI-1 Calculations for Table 1

The gas volume generating from the hydrogen carrier in **Table S1** is calculated by the following chemical equations. Take methanol for example, its density is 0.79 g/cm³ at room temperature, according to the **Equation S2**, 1 cm³ methanol will generate 2376 mL gas at 20°C. Theoretically, 75% of the generating gas is hydrogen. The density of s-trioxane is 1.17 g/cm³, according to the **Equation S4**, 1 cm³ s-trioxane will generate 2808 cm³ gas, and 66.7% is hydrogen.



Table S1. Parameters of representative organic molecules for hydrogen storage

Hydrogen carriers	State at r.t.	boiling point(°C)	Density (g/cm ³)	Volumetric density (g/L)	Gravimetric density (wt%)	Volume of gas from 1 cm ³ substrate (cm ³)	H ₂ content of evolved gas
HCHO	gas	-19.5	/	54.36	6.67	1956cm ³	66.7%
CH ₃ OH	liquid	64.7	0.79	98.75	12.5	2376cm ³	75%
HCOOH	liquid	100.8	1.22	53.04	4.34	1273cm ³	50%
C ₃ H ₆ O ₃	solid	114.5	1.17	78.09	6.67	2808cm ³	66.7%
H ₂ O	liquid	100	1	111.1	11.1	2000cm ³	66.7%

SI-2 Synthesis of catalysts in Table 2 and 3

The catalysts [Cp*IrCl₂]bpym, [Cp*IrCl₂]₂bpym, Cp*IrCl₂(ppy), [Cp*RhCl₂]bpym, [IrCp*Cl₂]₂, [RhCp*Cl₂]₂ in **Table 2** were prepared according to our previous works,

and the detailed process could refer to these literatures.¹⁻³

Synthesis of $[\text{Cp}^*\text{RhCl}_2]_2\text{bpym}$. This catalyst was prepared by stirring a 1:1 mixture of $[\text{RhCp}^*\text{Cl}_2]_2$ and 2,2'-bipyrimidine in methanol for 4 hours. During the reaction, the $[\text{Rh}(\text{Cp}^*)(\text{Cl})_2]_2$ would dissolved in methanol gradually, accompanied by red solution formed. The red product would be gained after the methanol removed by the rotary evaporation apparatus. The product should be washed with diethyl ether before using.⁴(Yield: 79% based on $[\text{RhCp}^*\text{Cl}_2]_2$).

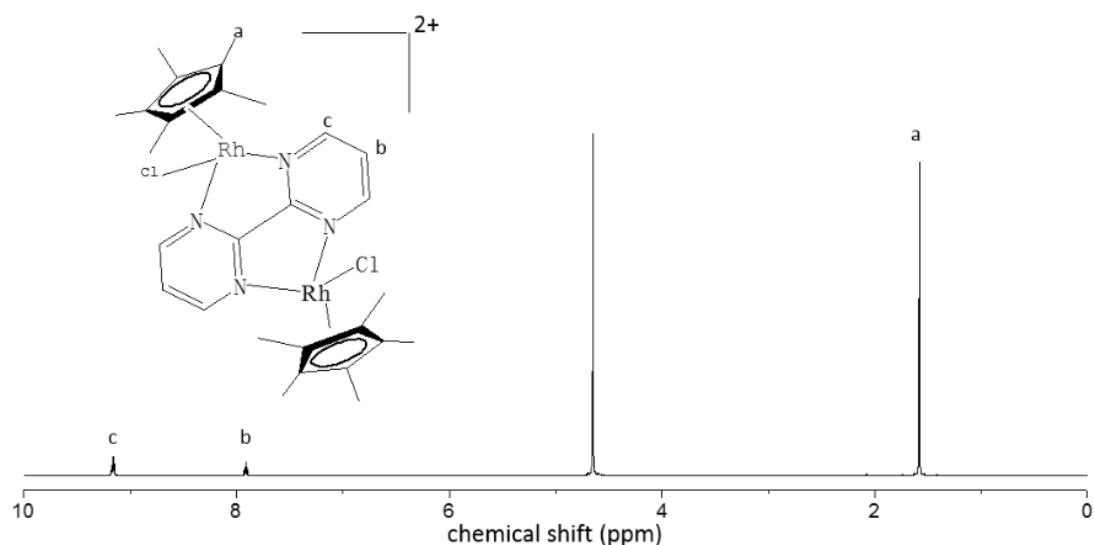


Figure S1. ^1H -NMR spectra of the $[\text{Cp}^*\text{RhCl}_2]_2\text{bpym}$ in D_2O . ^1H NMR (D_2O , 400 MHz) δ_{H} : 1.65 (30H, s), 7.88 (2H, m), 9.16 (4H, dd).

Synthesis of $\text{Ru}(\text{p-cymene})(\text{NH}_3)\text{Cl}_2$. 200 mg $[\text{RuCl}_2(\text{p-cymene})]_2$ in 15 mL water was stirred at room temperature, forming a light brown suspension. Then 200 μL ammonia was dropped into the suspension slowly. Keep stirring at room temperature for 8 hours, the solid would dissolve and turn into pale yellow solution. Then dark brown product would be gained by evaporating solution under reduced pressure.^{52,54} Detail characterization for the catalyst could refer to our previous work.³ (Yield: 84% based on $[\text{Ru}(\text{p-cymene})\text{Cl}_2]_2$).

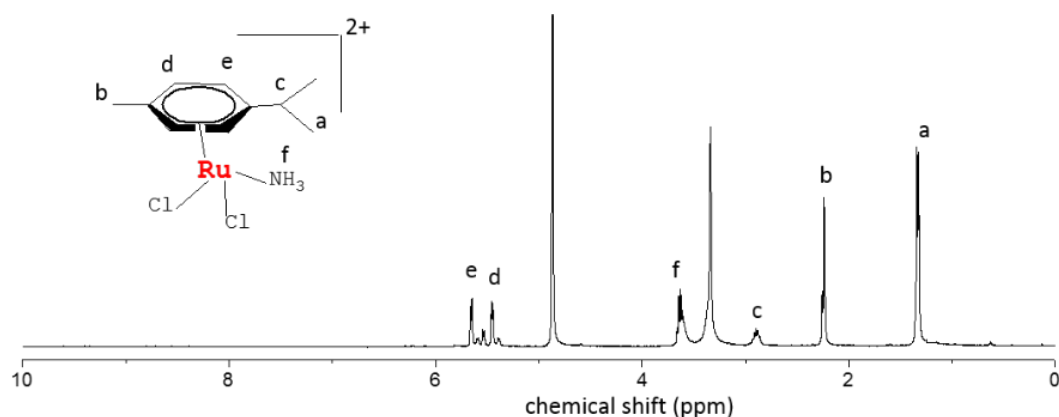


Figure S2. ^1H -NMR spectrums of the $\text{Ru}(\text{p-cymene})(\text{NH}_3)\text{Cl}_2$ in CD_3OD . ^1H NMR (CD_3OD , 400 MHz) δ_{H} : 1.23 (6H, d), 2.15 (3H, d) 2.81 (1H, s), 3.54 (3H, m), 5.45(2H, d), 5.6 (2H, d).

Synthesis of $\text{Ru}(\text{p-cymene})\text{Cl}_2\text{bpym}$. 100 mg $[\text{RuCl}_2(\text{p-cymene})]_2$ ethanol solution was treated with 52 mg 2,2'-bipyrimidyl (bpym) in a 25 mL round-bottomed flask. The mixture solution was stirred and heated under reflux for 8 hours. The insoluble $[\text{RuCl}_2(\text{p-cymene})]_2$ would dissolve and the solution turned pale red during the reflux. Red product would be gained after removing the ethanol by rotary distillation under reduced pressure.³⁻⁴ (Yield: 85% based on $[\text{Ru}(\text{p-cymene})\text{Cl}_2]_2$)

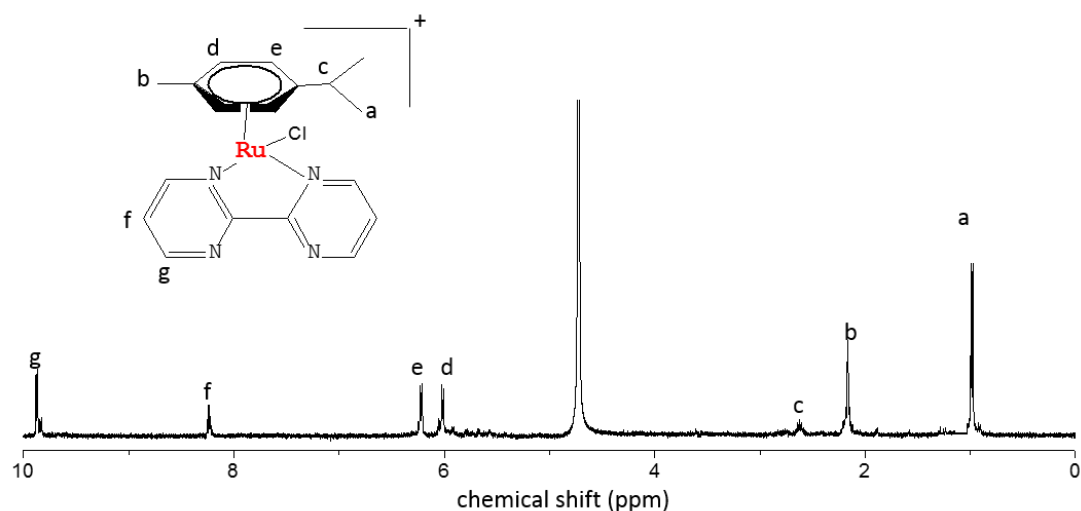


Figure S3. ^1H -NMR spectrums of the $\text{Ru}(\text{p-cymene})\text{Cl}_2\text{bpym}$ in D_2O . ^1H NMR (D_2O , 400 MHz) δ_{H} : 1.02 (6H, d), 2.17 (3H, d) 2.62 (1H, s), 6.02 (2H, d), 6.23(2H, d), 8.24

(2H, d), 9.85 (4H, dd).

Synthesis of Ru(p-cymene)Cl₂phen. Stirring 100 mg [RuCl₂(p-cymene)]₂ in methanol with 60 mg 1,10-phenanthroline (phen) for 1 hour at room temperature, an orange-yellow solution formed, accompanied by the dissolution of [RuCl₂(p-cymene)]₂ during the reaction. Then the orange-yellow powder would be gained after evaporated to dryness under reduced pressure.^{3, 5-6} (Yield: 86% based on [Ru(p-cymene)Cl₂])

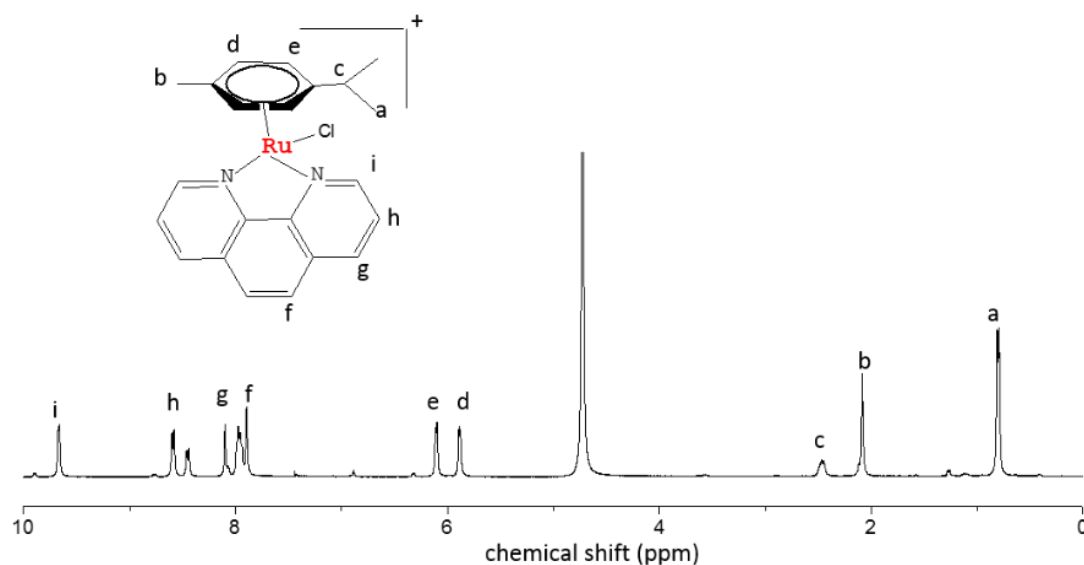


Figure S4. ¹H-NMR spectrums of the Ru(p-cymene)Cl₂phen. ¹H NMR (D₂O, 400 MHz) δH: 0.87 (6H, s), 2.16 (3H, s), 2.52 (1H, s), 5.93 (2H, s), 6.17 (2H, s), 8.03 (4H, d), 8.66 (2H, s), 9.74 (2H, s).

Synthesis of Ru(p-cymene)Cl₂BimH₂. 44 mg 2,2'-biimidazole (H₂Bim) was added into 30 mL ethanol solution containing 100 mg [RuCl₂(p-cymene)]₂, the suspension was stirred and heated under reflux for 4 hours. The solution turned yellow accompanied with [RuCl₂(p-cymene)]₂ dissolving during 4 hours. After reduced pressure distillation, washed with diethyl ether and dried under vacuum, yellow product would be collected.⁷ (Yield: 82% based on [Ru(p-cymene)Cl₂]).

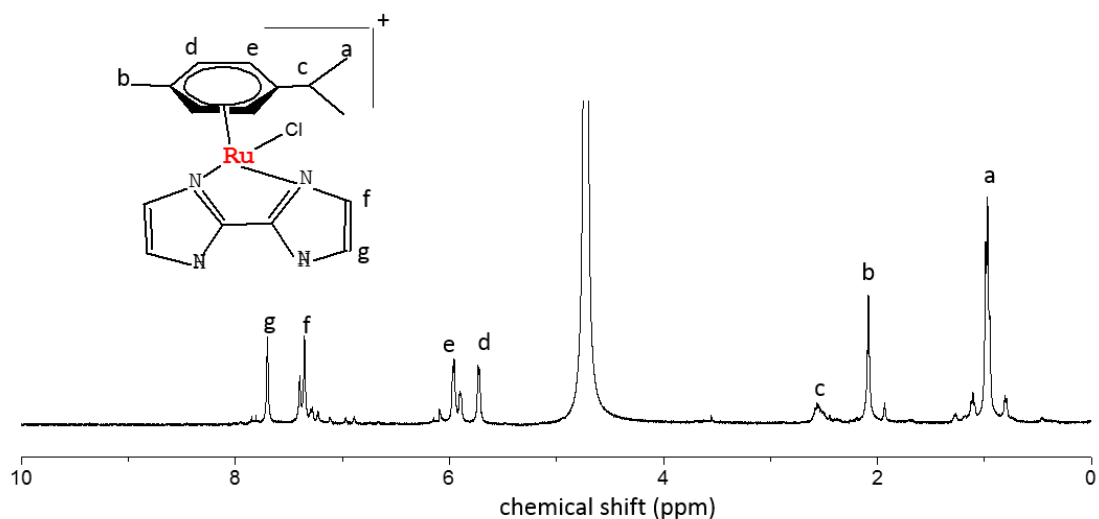


Figure S5. ^1H -NMR spectrums of the $\text{Ru}(\text{p-cymene})\text{Cl}_2\text{BiimH}_2$. ^1H NMR (D_2O , 400 MHz) δH : 0.98 (6H, s), 2.08 (3H, s), 2.56 (1H, s), 5.73 (2H, s), 5.96 (2H, s), 7.35 (2H, d), 7.70 (2H, d).

Synthesis of $\text{Ru}(\text{p-cymene})\text{Cl}_2\text{bpy}$. 100 mg amount of $[\text{RuCl}_2(\text{p-cymene})]_2$ was reacted with 51 mg 2,2'-bipyridine (bpy) in 30 mL ethanol for 4 hours under reflux. Yellow powder would be gained after reduced pressure distillation.⁸ (Yield: 87% based on $[\text{Ru}(\text{p-cymene})\text{Cl}_2]_2$)

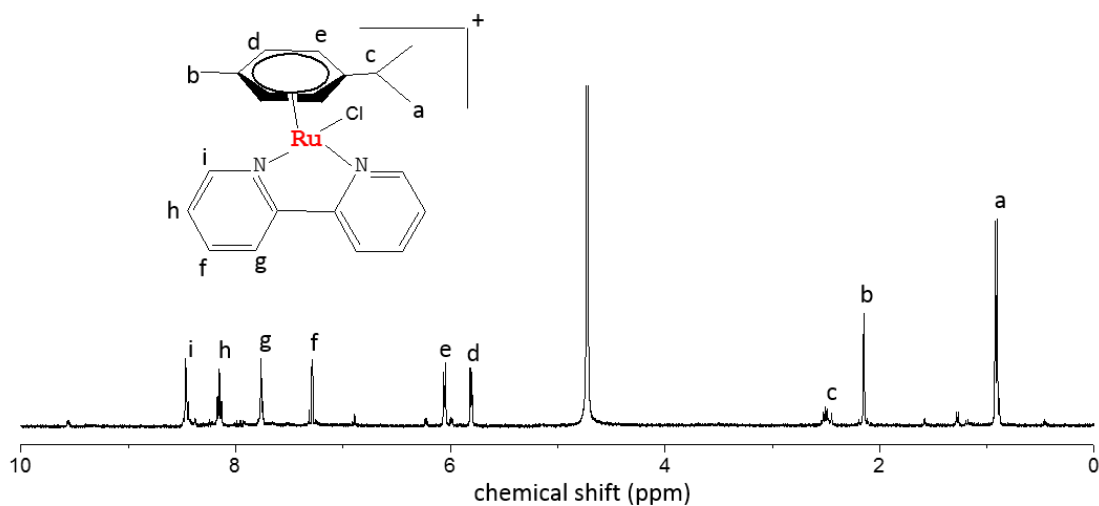


Figure S6. ^1H -NMR spectrums of the $\text{Ru}(\text{p-cymene})\text{Cl}_2\text{bpy}$. ^1H NMR (D_2O , 400 MHz) δH : 0.93 (6H, s), 2.14 (3H, s), 2.50 (1H, s), 5.79 (2H, s), 6.05 (2H, s), 7.29 (2H, d), 7.78 (2H, d), 8.15 (2H, d), 8.47 (2H, d).

Synthesis of Ru(p-cymene)(H₂O)₃SO₄. A round-bottom flask was charged with 300 mg [RuCl₂(p-cymene)]₂ and 20 mL water, the suspension was stirred and heated to 50 °C. Then 306 mg Ag₂SO₄ was added. During the reaction, the [RuCl₂(p-cymene)]₂ dissolved gradually, and white precipitate formed. After 4 hours' reaction, light yellow solution would be obtained after filtering. The product was obtained by evaporating filtrate under reduced pressure, dried in vacuo yielding Ru(p-cymene)(H₂O)₃SO₄.⁹⁻¹¹ (Yield: 83% based on [Ru(p-cymene)Cl₂]₂). The H₂O group in the catalyst is easy to exchange with CD₃OD, so the ¹H-NMR spectrums of the Ru(p-cymene)(H₂O)₃SO₄ couldn't show the full ¹H NMR signal of H₂O.

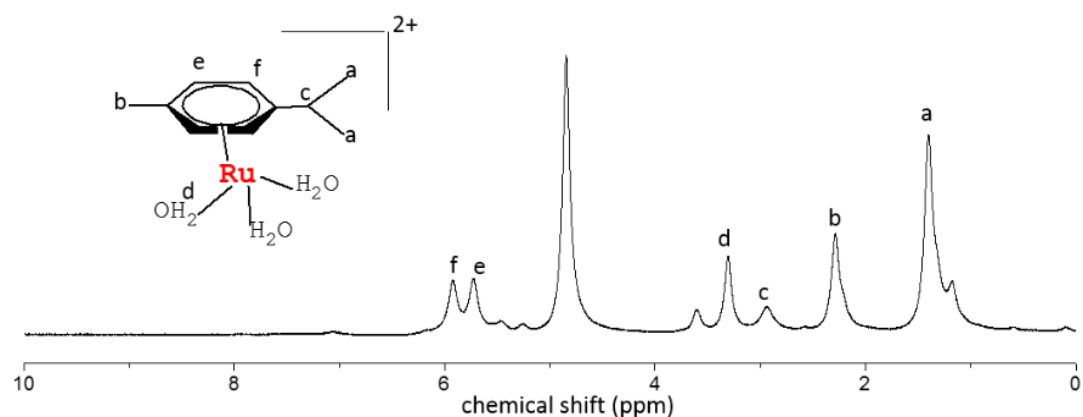


Figure S7. ¹H-NMR spectrums of the Ru(p-cymene)(H₂O)₃SO₄ in CD₃OD. ¹H NMR (CD₃OD, 400 MHz) δH: 1.38 (6H, s), 2.28 (3H, s), 2.94 (1H, s), 3.31 (2H, s), 5.73 (2H, s), 5.93 (2H, s).

SI-4 Formaldehyde decomposition under acidic or basic condition

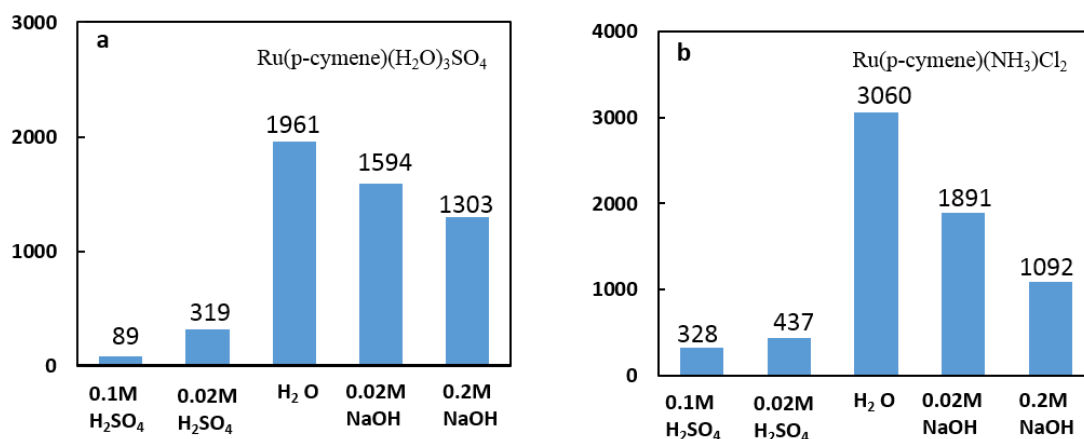


Figure S8. TOF of formaldehyde decomposition vs acidic or basic condition. (a) TOF of formaldehyde decomposition catalyzed by Ru(p-cymene)(H₂O)₃SO₄ (b) TOF of formaldehyde decomposition catalyzed by Ru(p-cymene)(NH₃)Cl₂.

Figure S8 exhibited the TOF of formaldehyde decomposition under acidic or basic condition with different catalysts at 80°C. The catalysts both have a better performance in basic or H₂O condition.

SI-5 Formic acid dehydrogenation

Some literatures have reported the organo ruthenium complex have a good activity for formic acid (FA) dehydrogenation.¹²⁻¹³ As the FA dehydrogenation is last step for gas generation from s-trioxane and water, studying FA dehydrogenation with the catalysts is necessary.

Figure S9 give the relationship between TOF and FA concentration at 80°C. When the FA concentration is low, both the catalysts show a low catalytic activity for FA dehydrogenation.

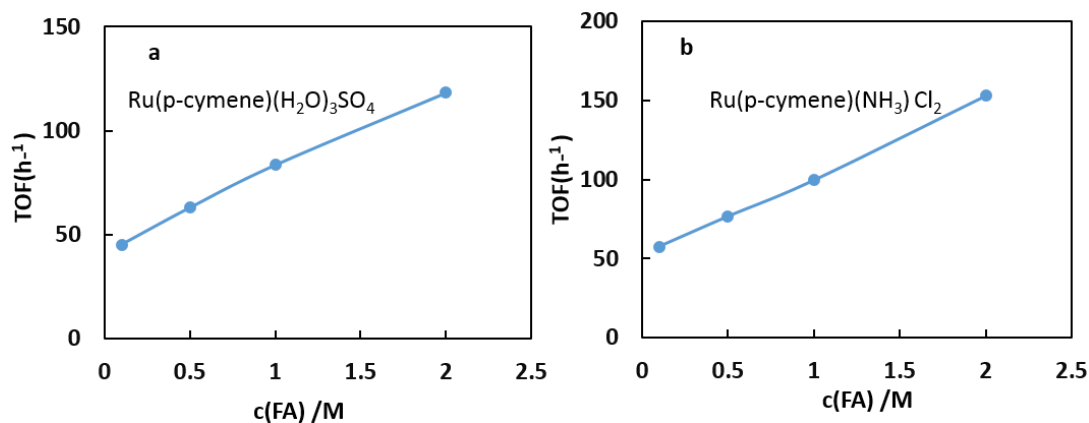


Figure S9. TOF of formic acid (FA) decomposition vs different FA concentration. (a) TOF of FA decomposition catalyzed by Ru(p-cymene)(H₂O)₃SO₄. (b) TOF of FA decomposition catalyzed by Ru(p-cymene)(NH₃)Cl₂.

SI-3 Gas chromatogram

The gas generated from formaldehyde or s-trioxane was analyzed by GC-G5 (Beijing Persee General Instrument CO., Ltd), the gas chromatography assembled with molecular sieve 5A, FID, TCD and methane conversion reactor, N₂ as carrier gas. The detection limit of CO was below 1 ppm by the aids of a methaniser. The H₂ was detected by TCD of the GC. **Figure S10** give the H₂ peak of generating gas from formaldehyde-water reforming reaction catalyzed by different catalysts.

The **Figure S10a** and **b** both give the strong peak for H₂, little CO₂ detected during initial 3 minutes of the total reaction, indicating that the formaldehyde convert into hydrogen and formic acid through aldehyde–water shift reaction in initial period.



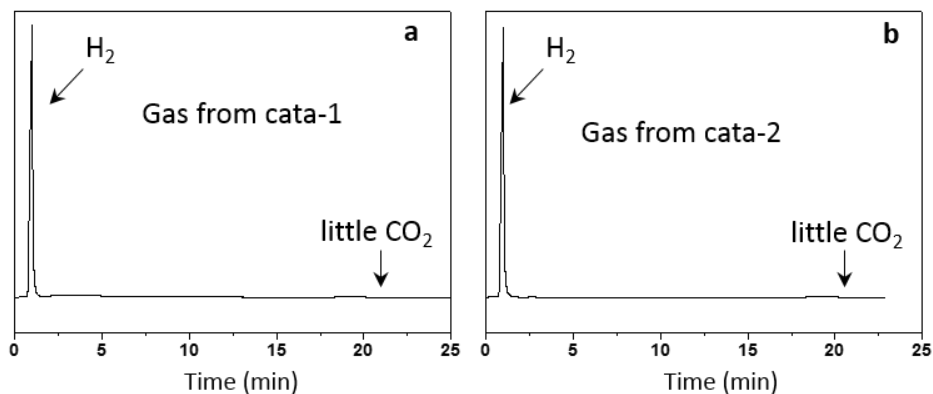


Figure S10. Gas chromatogram of generating gas from formaldehyde-water reforming reaction during initial 3 minutes. (a) The evolved gas from catalyzed by Ru(p-cymene)(H₂O)₃SO₄ (Catalyst-1). (b) The evolved gas from catalyzed by Ru(p-cymene)(NH₃)Cl₂ (Catalyst-2).

Figure S11 give the H₂ peak of generating gas from s-trioxane water reforming reaction catalyzed by different catalysts. As exhibited in the **Figure S11**, the initial generating gas showed no CO₂, prove that the reaction pathway could divided into three steps. As the first step is s-trioxane hydrolysis, then the generating formaldehyde or methanediol convert into hydrogen and formic acid catalyzed by catalysts. So, the period generating little CO₂.

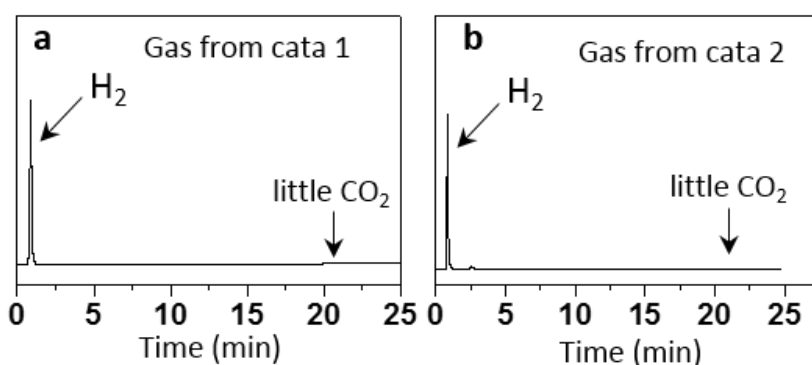


Figure S11. Gas chromatogram of generating gas from s-trioxane and water reforming reaction during initial 3 minutes. (a) The evolved gas catalyzed by Ru(p-cymene)(H₂O)₃SO₄ (Catalyst-1). (b) The evolved gas catalyzed Ru(p-cymene)(NH₃)Cl₂ (Catalyst-2).

SI-7 Equipment for gas generation

The reaction mechanism is exhibited in the **Scheme 3**, two ruthenium hydride intermediates, A and B could be formed during the AWS reaction and formic acid decomposition. We have gained the intermediates by NMR. The chemical shift of H atom on metal hydride complex is negative value on ^1H -NMR spectrum¹⁴. So we could gain two negative chemical shift signal, -7.29 and -8.28 was showed in **Figure S12**. The NMR signal is weak because of the high activity of the intermediates.

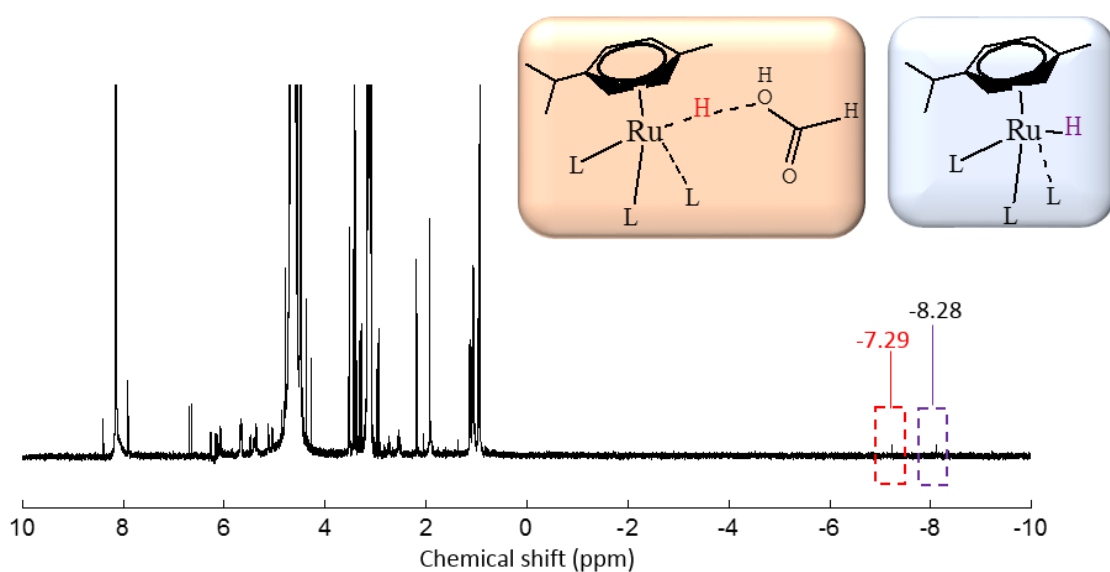


Figure S12. ^1H -NMR spectrums of the ruthenium hydride intermediates in D_2O during s-trioxane dehydrogenation.

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