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Hydrogen Generation from Catalytic Reforming of Paraformaldehyde and Water by Polymeric Bifunctional Catalysts Comprising Ruthenium and Sulfonic Acid Units

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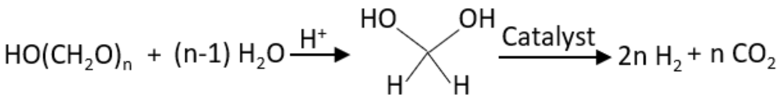
Abstract:

As a clean and sustainable source of energy, hydrogen shows great potential to be the ultimate energy in future. In this research, we employ paraformaldehyde as the hydrogen source. We prepare several bifunctional catalysts for hydrogen generation from paraformaldehyde decomposition. Every bifunctional catalyst contains two catalytic active sites, one is sulfonic acid group for paraformaldehyde catalytic hydrolysis, and the other is organometallic group for hydrogen generation from formaldehyde catalytic reforming. The initial evolved gas contain trace hydrogen when bifunctional iridium catalyst or bifunctional rhodium catalyst is employed for the hydrogen generation from paraformaldehyde. Only the bifunctional ruthenium catalyst shows high activity due to its bifunctional catalytic active sites, more than 98.0% of the initial gaseous production is hydrogen. The initial TOF is up to 685 h^{-1} at 363K when the paraformaldehyde concentration is 20 wt%. We propose the reaction mechanism of hydrogen generation from paraformaldehyde. The formaldehyde and the formic acid are the intermediate products during the total reaction. We also confirm the formic acid decomposition is the rate-determining step in the later stage of the paraformaldehyde decomposition.

1. Introduction

Hydrogen is considered to be the ultimate energy in future due to its high combustion value. While hydrogen storage is one of the major barriers for its commercialization. It remains difficult to store large amount of hydrogen safely. Thus, organic liquid is experiencing increasing popularity for hydrogen storage research. Growing attention is given to hydrogen generation from methanol, formic acid and formaldehyde because of their low costs, alternative sources and high gravimetric hydrogen contents.[1-9] The CO-free hydrogen from organic liquid decomposition has been used in proton exchange membrane fuel cell (PEMFC) successfully.[10-14] Researchers have put great efforts on organic liquid for hydrogen storage, but little attention has been paid to the solid organic polymers despite of their high hydrogen content. It is well known that it is difficult to decompose polymers into hydrogen under mild condition. The paraformaldehyde might be a promising candidate for hydrogen storage and production, and this solid polymer is derived from the formaldehyde polymerization. The paraformaldehyde could be hydrolyzed into formaldehyde under acid condition. In aqueous solution, the major species is methanediol with the hydrogen content of 8.4 wt%. The formaldehyde could decompose into hydrogen and carbon dioxide (**Scheme 1**).



Scheme 1. Reaction Pathway Using Paraformaldehyde and Water for Hydrogen Generation.

As exhibited in **Table 1**, the volumetric hydrogen content of paraformaldehyde is 95.34 g/L, which is slightly lower than 98.75 g/L of methanol. But 1 cm^3 paraformaldehyde could produce 2288 cm^3 hydrogen if it could be completely decomposed into H_2 and CO_2 through formaldehyde-water reforming, 1 cm^3 methanol only produces 1782 cm^3 hydrogen through methanol-water reforming. The paraformaldehyde could produce more hydrogen compared with methanol.

Table 1. Representative Organic Molecules for Hydrogen Production.

Hydrogen carriers	State at r.t.	Density [g/cm^3]	Volumetric Hydrogen Content[g/L]	Gravimetric Hydrogen Content [wt%]	Evolved H_2 volume per cm^3 substrate [cm^3]
HCHO	gas	/	54.36	6.67	1304
CH_3OH	liquid	0.79	98.75	12.5	1778
HCOOH	liquid	1.22	53.04	4.34	636
$(CH_2O)_n$	**solid**	**1.43**	**95.34**	**6.67**	**2288**

[a] Refer to the reactions in **SI-1** for hydrogen production from the representative organic molecules.

Therefore, paraformaldehyde is a promising solid organic hydrogen carrier, the initial TOF for hydrogen generation from paraformaldehyde could be up to 2020 h^{-1} over the homogeneous ruthenium catalyst.[15] However, certain technical problems still exist for hydrogen generation from paraformaldehyde. The paraformaldehyde can’t react with water in solution directly. It should be hydrolyzed into formaldehyde or methanediol in acid solution firstly,[16] then the formaldehyde could react with water and generate hydrogen.[17-22] It seems promising to produce hydrogen from paraformaldehyde through a two-steps reaction under acid condition (**Scheme 1)**. However, the formaldehyde decomposition prefers alkaline or neutral reaction conditions.[20-23] Few researchers report the formaldehyde catalytic decomposition in acid solution. Paraformaldehyde hydrolysis and formaldehyde catalytic decomposition require distinct reaction conditions.

In order to generate hydrogen from paraformaldehyde, for one thing paraformaldehyde hydrolysis should be performed under strong acidic condition, for another new catalysts have to be prepared for the hydrogen generation from formaldehyde. It is worth mentioning that the formaldehyde-water shift reaction is the key step for hydrogen generation from paraformaldehyde. This reaction could be catalyzed by many heterogeneous noble metal nanoparticles and homogeneous organometallics in neutral or alkaline solution.[20-23] The catalytic activities are sensitive to the reaction solution. The acidic condition could reduce the catalytic activity for hydrogen generation from formaldehyde sharply, which is confirmed by our previous study.[24]

The catalytic microenvironment can be designed on the heterogeneous catalysts, making the catalysts possess the solvation ability.[25, 26] Hereby we prepare some heterogeneous bifunctional catalysts based on coordination polymers. The coordination polymers could provide two catalytic active sites, the sulfonic acid and the organometallics. The sulfonic acid group could catalyze the paraformaldehyde hydrolysis, which will not change the solution pH, because the two catalytic active sites are both fixed on the polymer. Therefore, the organometallics on the catalysts could keep the high catalytic activity for hydrogen generation from formaldehyde in neutral solution. Consequently, the paraformaldehyde could produce hydrogen continuously through the synergetic catalysis of the sulfonic acid and the organometallics on the surface of the bifunctional catalysts.

2. Results and Discussion

2.1 Selectivity and Activity of Bifunctional Catalysts for Hydrogen Generation from Paraformaldehyde.

The paraformaldehyde is decomposed into hydrogen and carbon dioxide by the synergetic catalysis of two catalytic active sites on the bifunctional catalysts. The bifunctional catalysts are coordination polymers that contain sulfonic acid and organometallics. We find the pyridine-containing polymer is not suitable for immobilizing the ruthenium complex (**SI-2**). Therefore, we immobilize the ruthenium complex by imino-containing polymers carriers. The polymers are prepared through cross-linking polymerization of diallylamine, sodium p-styrenesulfonate and divinylbenzene. The diallylamine and divinylbenzene are the frequently-used cross-linking agents, making the catalysts own three-dimensional microstructures and insoluble in water.

As exhibited in **Table 2**, the bifunctional catalysts show different catalytic activity and selectivity for hydrogen generation from paraformaldehyde. The bifunctional iridium catalyst and bifunctional rhodium catalyst show low catalytic activity and selectivity for the paraformaldehyde decomposition, and a small amount of gas will be generated when we employ the two catalysts (**SI-4, SI-5**). The main gaseous products are carbon dioxide and trace hydrogen after analyzed by GC-TCD. It implies the formaldehyde disproportionation reactions are carried out when we employ the two catalysts for the paraformaldehyde decomposition.[27] Only the bifunctional ruthenium catalyst shows high activity and selectivity, the main gaseous product is hydrogen. It indicates the formaldehyde-water shift reaction is carried out during paraformaldehyde decomposition. Hence, this research focuses on the bifunctional ruthenium catalyst for the paraformaldehyde and water reforming.

Table 2. The Gas Composition of the Initial Evolved Gas.

Entry	Catalysts	Catalytic Activity	H_2	CO_2	TOF [h^{-1}]
1	Ru	high	98.0%	trace	685
2	Ir	low	trace	91.8%	0.6
3	Rh	low	trace	87.6%	0.2

2.2 Characterization of Bifunctional Ruthenium Catalyst.

The characteristic of bifunctional ruthenium catalyst is exhibited in **Figure 1**. This catalyst has porous structure with the specific surface area of 176.6 m^2/g, and the particle size is mainly distributed from 400 nm to 600 nm. The catalyst does not own any noble metal nanoparticles, which could be proved by SEM and XRD data (**SI-6**). This structure provides large surface for the hydrogen generation from paraformaldehyde and water reforming.

The XPS spectrums show the binding energy of the major elements in bifunctional ruthenium catalyst (**Figure 1**b), indicating the catalyst has the N, O, S and Ru. The binding energy of N 1s is 401.6 eV, indicating the N originates from amine. The amine could coordinate with organometallics. The binding energy of C 1s is 284.6 eV and 291.1 eV, indicating the C originates from benzene ring, polyethylene and Ru(p-Cymene) group (**SI-7**). The binding energy of S 2p and O 1s is 168.3 eV and 531.2 eV respectively, which is consistent with the S 2p and O 1s in benzene sulfonic acid. After analyzing the catalyst by acid-base titration, we confirm the catalyst own 0.00015mol $–SO_3H$ per gram (**SI-8**), hence sulfonic acid could catalyze the paraformaldehyde hydrolysis. The binding energy of Ru 3p in the bifunctional ruthenium catalyst is 463.5 eV and 485.8 eV, and the binding energy of Ru 3p in $[Ru(p\text{-}Cymene)Cl_2]_2$ is 462.3 eV and 484.8 eV (**SI-7**). It reveals the bifunctional ruthenium catalyst have the Ru(p-Cymene) group, although the binding energy of Ru 3p in the bifunctional ruthenium catalyst is slightly different from that in the $[Ru(p\text{-}Cymene)Cl_2]_2$. This difference is mainly caused by the electron states of ruthenium change to some degree after the $[Ru(p\text{-}Cymene)Cl_2]_2$ is immobilized by the N-containing polymer.

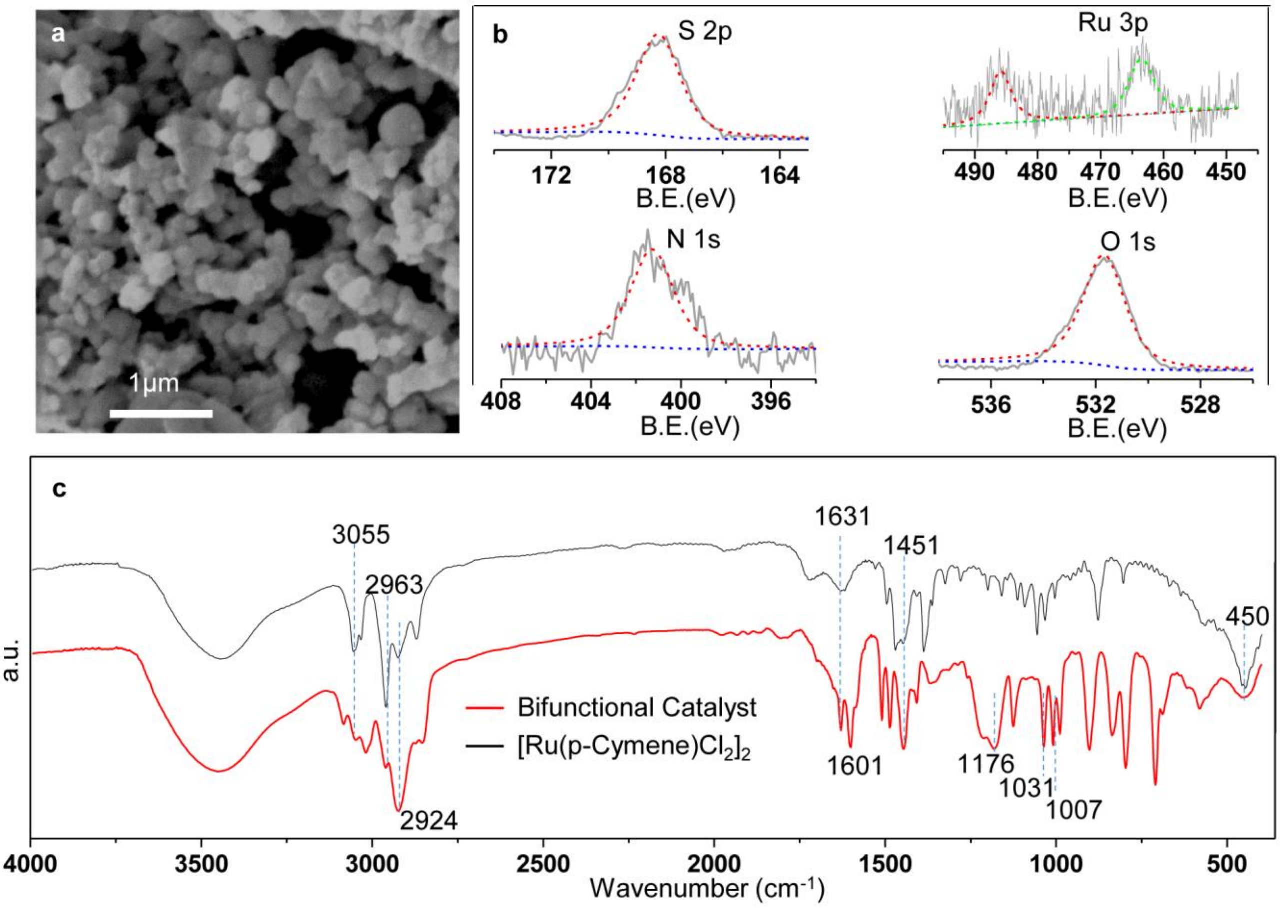


Figure 1. Characterization of Bifunctional Ruthenium Catalyst. (a) SEM image of the catalyst. (b) XPS spectrums of the N, O, S and Ru in the catalyst. (c) FTIR spectrums of the catalysts.

FTIR results show the bifunctional ruthenium catalyst own the characteristic absorption peaks of the sulfonic acid and benzene ring. The 3055 cm^{-1} is the absorption peak of C-H stretching vibration in benzene ring. The 2963 cm^{-1} and 2924 cm^{-1} are the asymmetric stretching vibrations of the $–CH_3$ and $–CH_2–$. The 1631 $cm^{-1}$and 1451 cm^{-1} are the vibration absorption peaks of the benzene ring. The 1176 cm^{-1},1031 cm^{-1} and 1007cm^{-1} are the characteristic absorption peaks of sulfonic acid, the S content is 0.47wt% after analyzed by ICP. 450 cm^{-1} is the characteristic absorption peak of Ru-Cl in the catalyst. All these data confirm the bifunctional ruthenium catalyst owns the $–SO_3H$ and Ru(p-Cymene) group, so it has high catalytic activity for hydrogen generation from paraformaldehyde.

2.3 Catalytic Synergetic Effect and Selectivity of the Bifunctional Ruthenium Catalyst.

Figure 2a shows the gas will be generated from the paraformaldehyde solution catalyzed by different catalytic systems. The brown and grey line indicate the gas generate through the two-steps catalysis process in **Scheme 1**. The paraformaldehyde is hydrolyzed into formaldehyde by hydrochloric acid or acetic acid firstly. These inorganic and organic acid could favor the paraformaldehyde hydrolysis, but they will inhibit the catalytic activity of ruthenium complex for formaldehyde decomposition.[24] Some researchers also find the alkalinity could favor the hydrogen generation from formaldehyde.[20-23] When we employ the bifunctional ruthenium catalyst for paraformaldehyde decomposition, the relatively independent acid active sites and the ruthenium active sites are fixed on the surface of the bifunctional catalyst. The acid active sites will not inhibit the catalytic activity of ruthenium active sites. Consequently, the blue line indicating bifunctional ruthenium catalyst shows higher catalytic efficiency compared with brown and grey line in **Figure 2**a.

We analyze the gas composition of the evolved gas by gas chromatography (GC) during the paraformaldehyde and water catalytic reforming. The gas only contains hydrogen and carbon dioxide (**Figure 2**b). Little carbon monoxide could be detected by the GC-TCD although the GC-TCD has been equipped with methanizer.

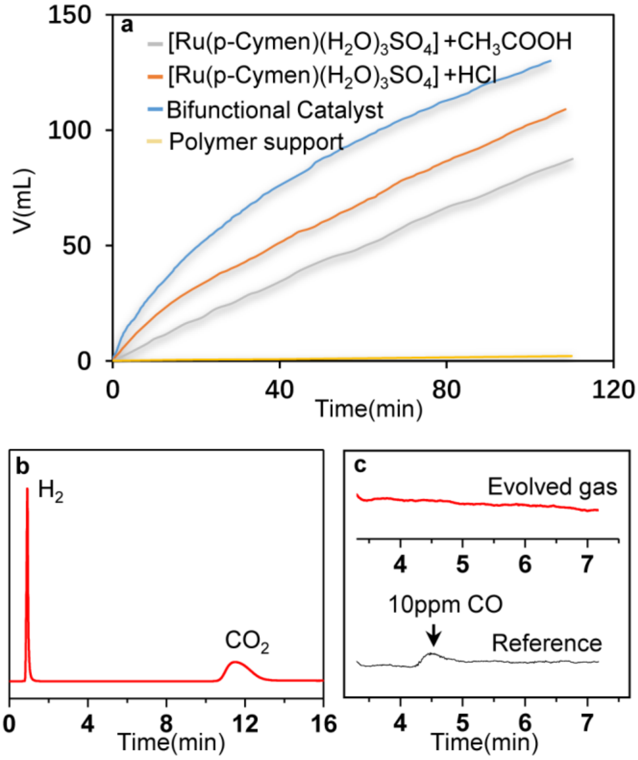


Figure 2. Gas Evolved from Paraformaldehyde and Water Catalytic Reforming. (a) Gas evolved under different conditions at 90°C. Blue, brown, grey and yellow lines indicate the bifunctional ruthenium catalyst, Ru(p-Cymene)(H_2O)$_3$$SO_4$ – CH_3COOH, Ru(p-Cymene)(H_2O)$_3$$SO_4$ – HCl, polymer support respectively. (b) and (c) GC analysis of the evolved gas. Please refer to **SI-9** for more details.

2.4 The Dependence of Paraformaldehyde Concentration and Reaction Temperature on Hydrogen Generation from Paraformaldehyde.

The paraformaldehyde concentration has great influence on hydrogen generation from paraformaldehyde and water catalytic reforming. As exhibited in the **Figure 3**a, the initial TOF is up to 685 h^{-1} when the paraformaldehyde concentration is 20 wt%. Higher or lower concentration could reduce the TOF of the bifunctional ruthenium catalyst. Several reasons could account for this. We consider the paraformaldehyde and water catalytic reforming is a first-order reaction when the paraformaldehyde concentration is low and the water is sufficient. A fraction of water reacts with the paraformaldehyde, while most of water mainly act as solvent, thus the effect of water on the reaction order can be negligible. When the paraformaldehyde concentration is high, the water is not only the solvent for the paraformaldehyde, but also the reactant which should be taken into reaction order. The reaction rate equation can be described as follows.

$$r=k[(CH_2O)_n]^x[H_2O]^y \qquad \textbf{Equation 1}$$

When the paraformaldehyde concentration is below 20%, the reaction order x is 1, and y is 0, which means the water has little influence on the reaction order. If the paraformaldehyde concentration is higher than 20%, the x is 1, and the y is higher than 1, that means the water shows more influences on the reaction order than the paraformaldehyde. When we increase the paraformaldehyde concentration, the water content decreases in the solution, so the reaction rate will also decrease.

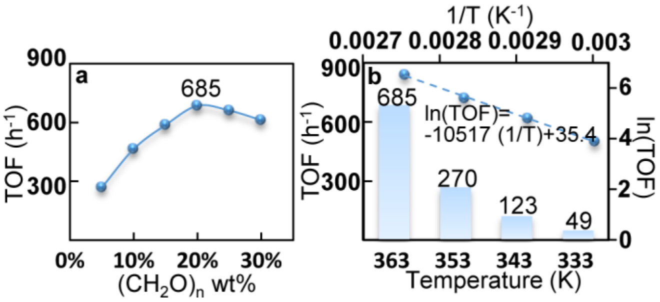


Figure 3. Influence of Reaction Conditions on Catalytic Activity. (a) The concentration dependence of paraformaldehyde on the initial TOF. (b) The TOF values and Arrhenius plot at different temperature.

Figure 3b shows raising temperature could promote the catalytic activity of the hydrogen generation from paraformaldehyde and water catalytic reforming. The TOF could rise from 49 h^{-1} to 685 h^{-1} when the temperature increases from 333 K to 363 K. We could gain the Arrhenius equation from the temperature-dependent TOF, $\ln(TOF)=-10517(1/T) + 35.4$. The reaction activation energy is 87.4 kJ/mol according to the Arrhenius equation.

2.5 Process of the Hydrogen Generation from Paraformaldehyde.

To propose the catalytic process and mechanism of the hydrogen generation from paraformaldehyde decomposition, we analyze the gas and liquid products during the reaction. As showed in **Figure 4**a, trace CO_2 is generated in the initial reaction stage, and more than 98.0% of gaseous production is hydrogen. We could also detect small amounts of formaldehyde in the reaction solution by ^1H NMR, which is from paraformaldehyde catalytic hydrolysis. Then GC could detect both hydrogen and carbon dioxide after several hours' reaction, accompanied with more formaldehyde and formic acid generation. Therefore, we can confirm the formaldehyde-water shift reaction and formic acid decomposition are both carried out after several hours. The former reaction could generate hydrogen and formic acid, and the latter reaction could produce carbon dioxide and hydrogen.

$$HCHO + H_2O = HCOOH + H_2 \qquad \textbf{Reaction 1}$$

$$HCOOH = CO_2 + H_2 \qquad \textbf{Reaction 2}$$

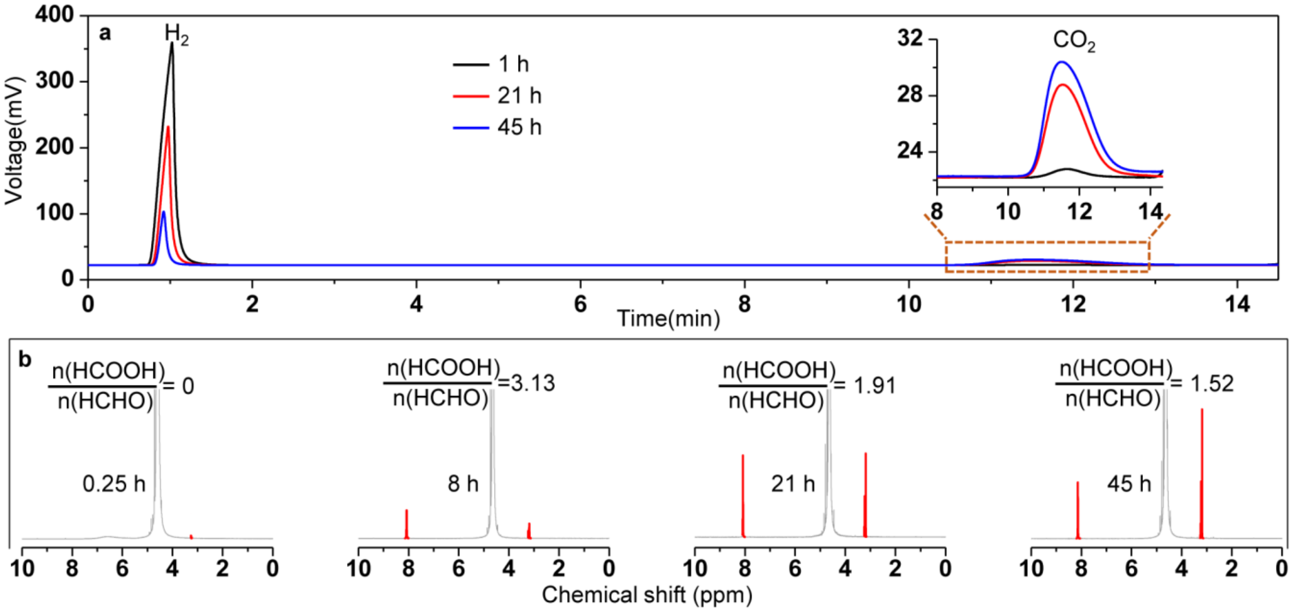


Figure 4. The Process during Paraformaldehyde and Water Catalytic Reforming. (a) The components variation of the evolved gas. (b) The ^{1}H NMR variation of the reaction solution.

We analyze the reaction solution by ^{1}H NMR continuously during the paraformaldehyde catalytic decomposition in **Figure 4**b. No formic acid is detected in the reaction solution in the initial reaction stage, only formaldehyde is generated through paraformaldehyde hydrolysis. Therefore, we could confirm the paraformaldehyde can't be converted into formic acid directly. After several hours' reaction, more formaldehyde is accumulating through paraformaldehyde hydrolysis, and a small amount of formic acid is generated through the formaldehyde-water shift reaction. Meanwhile we find the mole ratio of evolved formic acid to formaldehyde ($\frac{n(HCOOH)}{n(HCHO)}$) drops from 3.13 to 1.52 steadily. We could confirm the formaldehyde can be converted into formic acid quickly attributing to the high activity of bifunctional ruthenium catalyst for the formaldehyde-water shift reaction. The formaldehyde is always accumulating during the entire process, but the formic acid is not. We speculate the bifunctional ruthenium catalyst may prefer formic acid as reaction substrate than the formaldehyde. Therefore, the formic acid could be decomposed continuously while the formaldehyde

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can’t be converted to formic acid effectively.

2.6 The Dependence of Formic Acid on Hydrogen Generation from Paraformaldehyde.

To prove the speculation, we detect the generated gas continuously. We find the hydrogen content of the evolved gas is decreasing steadily, accompanied with the carbon dioxide content increasing. It leads to the mole ratio of hydrogen to carbon dioxide declining continuously (**Figure 5**a). It is noteworthy this ratio could fall below 2 after 21 hours’ reaction. 2 is the theoretical mole ratio of the hydrogen to carbon dioxide during the paraformaldehyde and water catalytic reforming. That means the formic acid could be decomposed into carbon dioxide and hydrogen effectively after 21 hours, but the formaldehyde can’t. In addition, we confirm the hydrogen generation from paraformaldehyde is characterized by stepwise reaction, and each step has its own reaction rate constant.

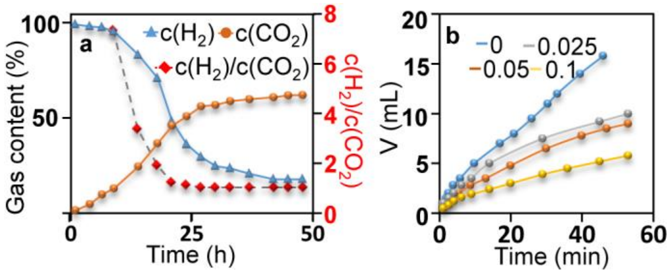

Figure 5. Process of Hydrogen Generation from Paraformaldehyde Decomposition. (a) Components variation of the evolved gas. (b) The effect of formic acid on gas generation from formaldehyde solution. The blue, grey, brown and yellow line indicate the $\frac{n(HCOOH)}{n(HCHO)}$ is 0, 0.025, 0.05 and 0.1 in solution respectively.

We study the effect of formic acid on the gas generation from formaldehyde decomposition. It will help us to confirm the rate-determining step during hydrogen generation from paraformaldehyde. As exhibited in **Figure 5**b, the formic acid has negative effects on the gas generating rate from formaldehyde decomposition. The Ru(Cymene) group may prefer formic acid as its reaction substrate than the formaldehyde, but it has much higher activity for formaldehyde-water shift reaction compared with formic acid decomposition.[24] Consequently, the bifunctional ruthenium catalyst prefer to catalyze the formic acid decomposition in the formic acid and formaldehyde mixed solution. It leads to the $\frac{n(HCOOH)}{n(HCHO)}$ dropping from 3.13 to 1.52 steadily during paraformaldehyde decomposition in **Figure 4**b. It can also explain why the gas generating rate could decrease if the formic acid is added in the reaction solution. The formic acid decomposition will dominate the hydrogen generation after formic acid accumulation in the reaction solution.

We confirm the formic acid will be generated during the paraformaldehyde. We analyze the recycled catalysts by FTIR after they are dried at 105°C for 3 hours. As exhibited in the **Figure 6**, both the recycled homogeneous Ru(p-Cymene)Cl_2 and the recycled immobilized ruthenium catalyst have the absorption peaks at 1933 cm-^{1}, 1723 cm^{-1} and 671 cm^{-1}. 1723 cm^{-1} and 671 cm^{-1} are the characteristic absorptions of the formic acid. It indicates the carboxyl group tend to adsorb on the ruthenium atom of the Ru(p-Cymene)Cl_2, which could lead to the structure change of the ruthenium complexes. The structure change could account for the gas generating rate decrease after the formic acid is generated or added in the solution.

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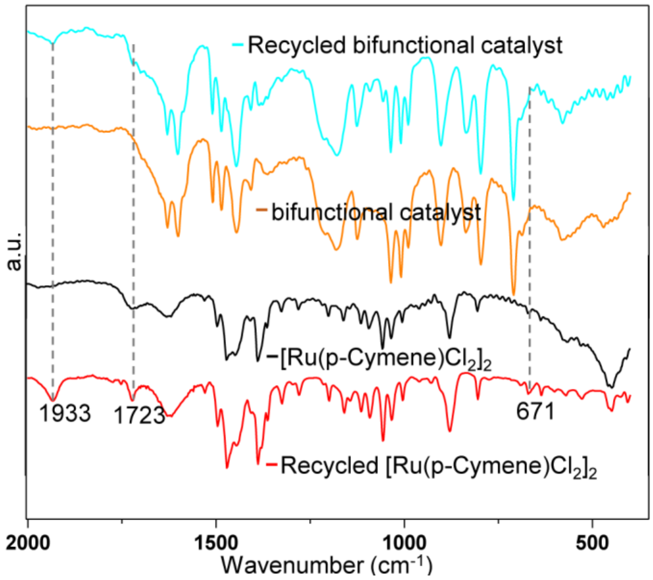
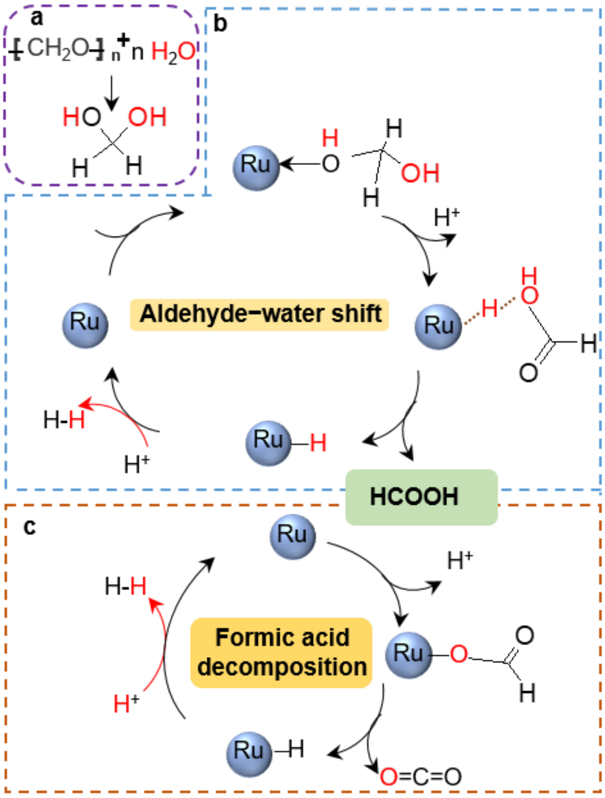


Figure 6. FTIR Spectrums of the Catalysts Before or After the Paraformaldehyde Decomposition.

2.7 Catalytic Mechanism of the Hydrogen Generation from Paraformaldehyde.

We propose the reaction mechanism for the hydrogen generation from the paraformaldehyde based on the above research. The entire reaction process consists of three reaction steps. Firstly, the paraformaldehyde could be hydrolyzed into formaldehyde by the sulfonic acid group of the bifunctional ruthenium catalyst. It’s noteworthy the formaldehyde mainly exists as methanediol in water. The two hydroxyl hydrogen atoms of the methanediol originate from the water.



Scheme 2. Catalytic Cycles for Paraformaldehyde and Water Catalytic Reforming**.** **(a)** Paraformaldehyde hydrolysis**.** **(b)** Formaldehyde-water shift reaction. **(c)** Formic acid decomposition**.** The atoms of H and O from water are marked with red colour.

Secondly, the formaldehyde reacts with the water over the ruthenium complex in the bifunctional ruthenium catalyst. We could gain the Ru(p-cymene) hydride complex after the formic acid released from the catalyst intermediates. The carboxyl-connected hydrogen atoms originate from paraformaldehyde which have been confirmed by the deuterium isotopic labeling (**SI-11**). Then the ruthenium hydride complex will react with H^+ to produce hydrogen in solution. One H atom of hydrogen molecule is from paraformaldehyde, and the other is from water in the solution. This is the complete catalytic process of the formaldehyde-water shift reaction, and the water act as the oxidant in this reaction (**Scheme** 2b).It's a typical aldehyde-water shift reaction, and the catalytic mechanism have been reported in the literatures.[28-30]

At last, the formic acid carries out the β-hydrogen elimination reaction, releasing CO_2 and Ru(p-cymene) hydride complex. The ruthenium hydride complex will react with H^+ to produce hydrogen molecule in the solution (**Scheme 2**c). The ruthenium complex has high selectivity for formic acid decomposition.[31-33]

3. Conclusions

This study proposes a hydrogen generation method based on paraformaldehyde. Several bifunctional catalysts are developed for hydrogen generation from the paraformaldehyde. The catalysts have two catalytic activity sites, the sulfonic acid and organometallics. We find only the bifunctional ruthenium catalyst has high catalytic activity and selectivity for paraformaldehyde and water reforming. The sulfonic acid on the bifunctional ruthenium catalyst could catalyze the paraformaldehyde hydrolysis into formaldehyde efficiently. Then the formaldehyde-water shift reaction is carried out by the ruthenium complex on the bifunctional ruthenium catalyst, generating hydrogen and formic acid. The formic acid could be further decomposed into hydrogen and carbon dioxide. Attributing to the synergistic effect of the sulfonic acid and Ru(p-Cymene) on the bifunctional ruthenium catalyst, the catalyst has high activity for hydrogen generation from paraformaldehyde. The TOF is up to 685 h^{-1} at 363K. We propose the reaction process and mechanism during the hydrogen generation from paraformaldehyde. We find the formaldehyde and formic acid are the intermediate products during the reaction. The carboxyl-connected hydrogen atoms originate from paraformaldehyde which have been confirmed by the deuterium isotopic labeling. This research not only puts forward the new scheme for hydrogen generation from the solid polymer, but also has some potential significance for water-induced conversion of aldehyde to acid by bifunctional catalyst. It proves various types of reactions could be catalyzed by bifunctional catalysts, which makes the catalytic conversion more efficient.

4. Experiments

4.1 Chemicals and Materials

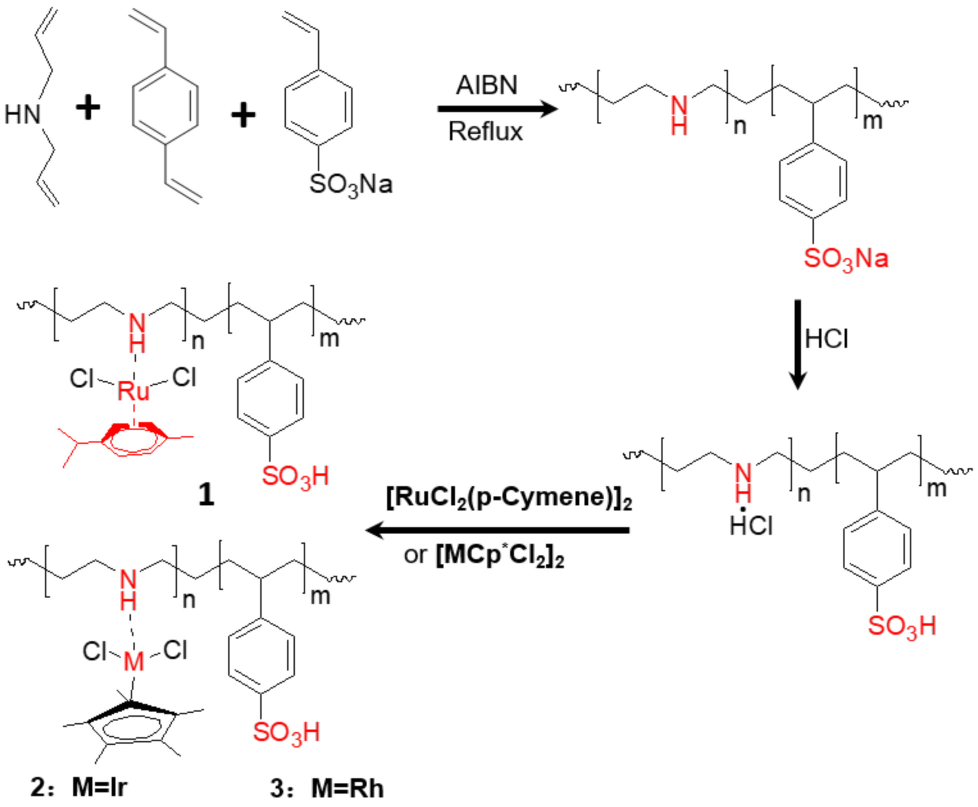
All chemicals were commercial and used without further purification unless otherwise specified. Paraformaldehydede ($(CH_2O)_n$, Shanghai Macklin Biochemical, Co.,Ltd. , 95%), ethanol (C_2H_5OH, Tianjing Baishi Chemical Industry, Co.,Ltd., >99.7%), hydrochloric acid (HCl, Sinopharm Chemical Reagent. Co., Ltd., >37%), formic acid (HCOOH, Sinopharm Chemical Reagent. Co., Ltd., >98%), methanol (CH_3OH, Sinopharm Chemical Reagent, Co., Ltd., >99.7%), azodiisobutyronitrile (AIBN) ($C_8H_{12}N_4$, Shanghai Macklin Biochemical, Co., Ltd., >98%), α-phellandrene ($C_{10}H_{16}$, Jiangxi Gannan natural & perfume oil Co.,Ltd., >98%), diallylamine($C_6H_{11}N$, Shanghai Macklin Biochemical, Co.,Ltd., >98%), chloroiridic acid ($H_2IrCl_6\cdot 6H_2O$, Shanxi Kaida Chemical Engineer Co., Ltd., Ir wt%>35%), rhodium trichloride ($RhCl_3$, Shanxi Kaida Chemical Engineer Co., Ltd., Rh wt%>39.5%), 1,2,3,4,5-pentamethylcyclopentadiene ($C_{10}H_{16}$, Sun Chemical Technology(Shanghai) Co., Ltd., 97%), divinylbenzene ($C_{10}H_{10}$, Shanghai Macklin Biochemical, Co.,Ltd, 80% mixture of isomers), sodium p-styrenesulfonate ($C_8H_7NaO_3S$, Shanghai Macklin Biochemical, Co.,Ltd., 98%), Ruthenium trichloride ($RuCl_3$, Energy-chemical, Co.,Ltd., Ru wt%>48.2%), ultrapure water was prepared by Thermo PureLab Ultra Genetic. The $[Ru(p\text{-}Cymene)Cl_2]_2$, $[Cp^*IrCl_2]_2$ and $[Cp^*RhCl_2]_2$ were synthesized according to literature procedures. [24, 34]

4.2 Characterization and Physical Measurements.

^1H NMR spectra were recorded on Varian Plus 400 MHz. The evolved gas was analyzed by GC-G5 (Beijing Persee General Instrument Co., Ltd.), and the gas chromatography was assembled with FID, TCD and methanizer. With N_2 as carrier gas, the detection limit of CO was below 1 ppm. Powder X-ray diffraction (XRD) patterns of samples were recorded with Bruker D8 X-ray diffractometer using Cu-Kα radiation (λ =1.5406 Å, 40 kV and 40 mA). The XPS measurements were employed via Escalab 250Xi spectrometer. The ruthenium, rhodium and iridium contents of the catalysts were determined by Agilent 720 ICP-OES. SEM images were recorded on Quanta 400 FEG, FEI. The FTIR data were detected by Nicolet iS10 (Nicolet Instrument Co. USA). The pore size distributions and average pore diameter of the catalysts were analyzed by Nano-ZS90 (Malvern), and the surface areas of the bifunctional catalysts were determined by Malvern Instruments Zetasizer Nano ZS90.

4.3 Catalysts Preparation.

The $[Ru(p\text{-}Cymene)Cl_2]_2$ could coordinate with many N-containing ligands, for instance, 2,2'-bipyridine, 2,2'-bipyrimidine, 1,10-phenanthroline, 2,2'-biimidazole. While these ligands will deactivate the ruthenium complex. Only the amino-coordinated ruthenium complex has high catalytic for the formaldehyde.[24] In this research, we immobilize the $[Ru(p\text{-}Cymene)Cl_2]_2$ by the imino group of the polymer.



Scheme 3. Detailed Process to Prepare the Bifunctional Catalysts.

The catalysts preparation is illustrated in **Scheme 3**. 200mg sodium p-styrenesulfonate, 1 mL diallylamine, and 2 mL divinylbenzene were stirring in ethanol-water solution. Then 100mg AIBN were added into the solution, acting as the initiator after the flask was heated to 90 °C. White polymer powder would be formed after 10 hours' reaction. The white polymer powder should be filtered from the solution and washed by the ultrapure water for several times. The polymer powder was ion-exchanged by 1 M HCl (100 mL) for 6 hours, this process was repeated twice. We could gain the –SO_3H and –NH containing polymers which could coordinate with $[Ru(p\text{-cymene})Cl_2]_2$, $[Cp^*IrCl_2]_2$ or $[Cp^*RhCl_2]_2$. At last, 2g polymers were reacted with 100mg organometallics in water at 60°C for 12 hours. After being filtered, washed with water and dried under vacuum, the bifunctional catalysts were prepared. Details are illustrated in **SI-3**

4.4 Hydrogen Generation from Paraformaldehyde and Water Catalytic Reforming.

Typically, 10mL 20 wt% paraformaldehyde water solution was stirred by magnetic bar in 25mL flask. Then, 40mg catalysts were added into the solution after the flask been heated to the preset temperature. The flask was connected to the U-shape tube to measure the volume of the evolved gas during paraformaldehyde decomposition. The gas was analyzed by gas chromatography.

4.5 TOF Calculations.

Little carbon dioxide was detected by GC during the initial 30 minutes of reaction, so we calculated the TOF of the paraformaldehyde and water catalytic reforming based on the following reaction.

$$(CH_2O)_n + n\,H_2O \rightarrow n\,HCOOH + n\,H_2$$

The TOF was calculated by **Equation 2** when the ruthenium catalyst was employed. The water vapor was neglected.

$$\mathrm{TOF}=\frac{V_{H_2}/(t*V_{m,H_2})}{n_{(Ru)}} \qquad \textbf{Equation 2}$$

V_{H2} was the volume of hydrogen that generated during the initial 0.5 hour, t was 0.5 h. n($_{Ru}$) was the molar number of ruthenium. The ruthenium content of the bifunctional ruthenium catalyst was 0.87 wt%. The $V_{m,H2}$ was calculated by van der Waals equation of hydrogen.[35]

$$V_{m,H2}=\frac{RT}{p}+b-\frac{a}{RT}\approx 24\ \mathrm{L/mol}$$

R is 8.3145 m³ Pa mol^{-1} K^{-1}, T is 293.15 K, p is 101325 Pa, b is 26.7x10^{-6} m^3·mol^{-1}, a is 2.49x10^{-10} Pa·m^3·mol^{-2}.

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The TOF was calculated by **Equation 3** when the rhodium or iridium catalyst was employed. The water vapor was neglected.

$$\mathrm{TOF}=\frac{3*V_{CO_2}/(t*V_{m,co_2})}{n} \qquad \textbf{Equation 3}$$

3 was the stoichiometric ratio in **Reaction 3**, V_{CO2} was the volume of carbon dioxide that generated during the initial 0.5 hour, t was 0.5 h. The calculation of $V_{m,CO2}$ was carried out using van der Waals of CO_2 by **Equation 4.** The n was the molar number of rhodium or iridium in the immobilized catalyst. The Ir content of the catalyst is 1.32 wt%, and Rh content of the catalyst is 1.43 wt%.

$$V_{m,CO2} = \frac{RT}{p} + b - \frac{a}{RT} \approx 24\ \mathrm{L/mol} \qquad \textbf{Equation 4}$$

R is 8.3145 m^3Pa mol^{-1} K^{-1}, T is 293.15 K, p is 101325 Pa, b is 42.7 x 10^{-6} m^3 mol^{-1}, a is 36.5 x 10^{-10} Pa m^3 mol^{-2}.

$$3\ (CH_2O)_n + n\ H_2O \rightarrow n\ CO_2 + 2n\ CH_3OH \qquad \textbf{Reaction 3}$$

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Keywords: bifunctional catalysts • catalytic reforming • formaldehyde • hydrogen generation • ruthenium

Author contributions

Y.-B. S. and X.-C. Z. designed and directed the project. Y.-B. S., C.B. and Y.-L. Z. carried out the experiments and prepared the catalysts, F.-D. N performed NMR analysis and analyzed the data. H.-H. W. performed the GC and analyzed the data, G.-J. L test element content of all the catalysts. Y.-B. S. and X.-C. Z. wrote and revised the manuscript.

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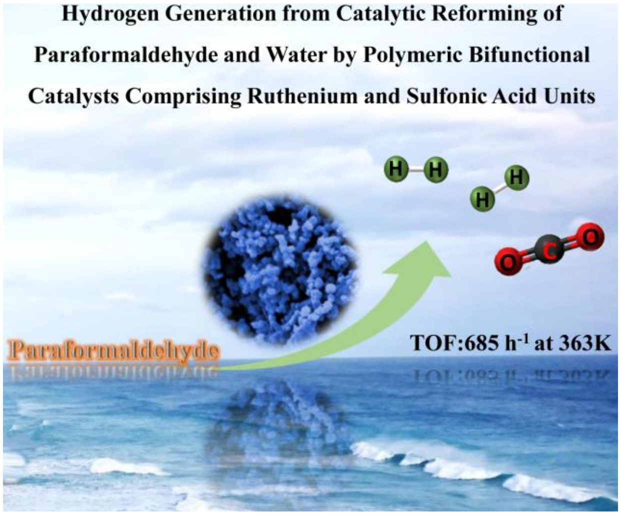

The bifunctional ruthenium catalyst is developed for hydrogen generation from the paraformaldehyde. Attributing to the synergistic effect of the sulfonic acid and Ru(p-Cymene) on the bifunctional ruthenium catalyst, the catalyst has high activity for hydrogen generation from paraformaldehyde. The TOF is up to 685 h^{-1} at 363K. The formaldehyde and formic acid are the intermediate products during the reaction. This research put forward the new scheme for hydrogen generation from the solid polymer.