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Additive-Free Ruthenium-Catalyzed Hydrogen Production from Aqueous Formaldehyde with High Efficiency and Selectivity

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ABSTRACT: An efficient water-soluble ruthenium complex was developed for selective hydrogen production from aqueous formal dehyde under mild conditions with a high yield ($\sim 95\%$). Hydrogen production by this catalytic system proceeds without using any additives or organic solvents, leading to a high turnover frequency (8300 h^{-1}) and a record turnover number of 24000. Additionally, based on mechanistic experiments and density functional theory (DFT) proposed calculations. step-by-step has been mechanism for the catalytic a cycle. **KEYWORDS:** dehydrogenation, formaldehyde, homogeneous catalysis, ruthenium complex, H_2 production

The rapidly dwindling fossil resources and the growing problems of global warming raise the urgent need to find sustainable and renewable energy carriers. Hydrogen is regarded as a promising alternative energy carrier because its combustion leads to no toxic emissions.¹⁻² Moreover, the emerging attractive methods for hydrogen storage are using organic molecules as liquid organic hydrogen carriers (LOHCs), which avoid the difficulties of handling and transport of liquid or gaseous hydrogen. In this respect, methanol and formic acid have been investigated as promising LOHCs in recent years, owing to their various advantages.³⁻⁴

$$HO(CH_{2}O)_{n}H \xrightarrow[HO(CH_{2}O)_{n-1}H]{H_{2}O} H \xrightarrow[H-C]{OH} \xrightarrow[H-C]{H_{2}} HCOOH \xrightarrow[H_{2}]{Catalyst} CO_{2}$$

Scheme 1. Schematic pathway for homogeneously catalyzed dehydrogenation of formaldehyde-water.

More recently, (water-assisted) formaldehyde is emerging as an attractive hydrogen carrier.⁵⁻¹⁰ In this hydrogen storage system, formaldehyde serves as a hydride donor and water serves as a proton donor, leading to a higher hydrogen weight efficiency of 8.4 wt % than that of formic acid (4.4 wt %).⁵ Additionally, using formaldehyde as a CO₂ derivative for methanol production at room temperature with an iridium catalyst can be efficiently achieved.¹¹ It is known that the dehydrogenation of methanol/water is endothermic (ΔH_r = +53.3 kJ mol⁻¹). In contrast, the dehydrogenation reaction of formaldehyde/water (CH₂O+H₂O→2H₂+CO₂) is thermodynamically favorable (ΔH_r = -35.8 kJ mol⁻¹), thus affording a powerful driving force for the dehydrogenation.⁶ The catalytic dehydrogenation reaction can proceed through a one-pot process containing two-step dehydrogenation reactions as shown in Scheme 1: 1) water-assisted dehydrogenation of formaldehyde/paraformaldehyde to formic acid and one equiv. of H_2 ; and 2) dehydrogenation of formic acid to CO_2 and a second equiv. of H_2 .



Scheme 2. Previously reported homogeneous catalysts for hydrogen production from formaldehyde and water.

Currently, there are only few reports available on homogeneously catalyzed H_2 production from formaldehyde/water system (Scheme 2).⁵⁻⁹ Prechtl et al. recently reported the first homogeneous catalytic system for H_2 production from aqueous formaldehyde with a TON of 700 at 95 °C.^{5.7} Later, Suenobu et al. described a catalytic H_2 production system from paraformaldehyde/water using an iridium complex

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acid)(H₂O)]+ [Ir^{III}(Cp^{*})(4-(1*H*-pyrazol-1-yl)benzoic under basic conditions (pH 11) with a TON of 51 at 60 °C.⁸ In the same year, Fujita et al. presented another example using [Ir^{III}(Cp*)(6,6'-dionato-2,2'bipyridine)(OH)]⁻ under basic conditions with a TON of 178 and low reaction rates at reflux temperature.9 Very recently, Grützmacher et al. reported the homogeneously catalyzed dehydrogenation of aqueous formaldehyde to H₂ with a high initial TOF at 60 °C, however, it proceeds only at strongly basic conditions (2.72 mol L⁻¹ KOH). Furthermore, an organic solvent (THF) is required. Although a considerably improved TON of 1787 was achieved after running 6 cycles, the total H₂ yield was only 59%.6 For practical purposes, the efficient dehydrogenation of aqueous formaldehyde without using any additives or organic solvents is highly desirable.

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Chart 1. Screening of water-soluble Ru-catalysts for H_2 production from formaldehyde and water. Conditions: formaldehyde (0.5 mmol), Ru-catalyst (10 µmol), H_2O (5 mL), 50 °C, 7 h, [(C₆M₆)RuCl₂]₂ (5 µmol).

Herein we present a new Ru complex for the dehydrogenation of aqueous formaldehyde under additive- and base-free conditions with excellent H₂ yields and the highest TON yet reported. Initially, several ruthenium complexes were examined as precatalysts for dehydrogenation of aqueous formaldehyde at 50 °C (Chart 1). First, the precatalyst RuCl₃ was tested following the standard conditions in Chart 1, resulting in no observable H₂ production. Moreover, the previously reported precatalyst [(C₆M₆)RuCl₂]₂ for this reaction^{5,7} was also examined here, affording a very low H₂ yield of 2% after 7 hours. Four water-soluble Ru-catalysts were then investigated under the applied conditions. The bipyridine ruthenium complex **1** showed similar activity $(\sim 2\% H_2)$ to that of $[(C_6M_6)RuCl_2]_2$. Interestingly, the ortho-phenylenediamine ruthenium complex 2 obviously enhanced the catalytic activity (10% H₂),

indicating the important role of the ligand on catalytic activity. Following this promising result, other diamine ligands were tested. However, the chiral diamine ruthenium complex 3 showed no improvement in catalytic activity. In the presence of the biphenyldiamine ruthenium complex 4, the activity for H₂ production was greatly improved (42% H₂). Additionally, the chloride analogue 5 instead of an aqua complex decreased the H₂ yield (28% H₂), indicating that the formation of the catalytically active species was inhibited by the strong coordination of chloride to the ruthenium center.¹² Notably, complex **6**, with four methyl substituents in catalyst 4, afforded a much lower yield $(3\% H_2)$ as compared to the diamine catalyst 4. This further suggests the importance of the N-H group in the dehydrogenation of aqueous formaldehyde. Thus, complex 4 was selected as the most promising catalyst for further investigations.

Single crystals of complex **4** suitable for X-ray structure analysis were obtained by recrystallization methanol/ethyl acetate solution.13 from а Crystallographic collection and refinement data are shown in Table S1. An ORTEP drawing of the crystal structure of complex 4 with the numbering scheme used is presented in Figure 1. The molecule consists of a ruthenium ion coordinated to the ligand, 2,2'diaminobiphenyl, through the nitrogen atoms. A coordinated sulfate ion and a hexamethylbenzene ligand complete the sphere. The crystal structure of complex 4 is similar to that of the previously reported [(C₆H₆)Ru(2,2'-diaminobiphenyl)(Cl)][PF₆]•MeOH.¹⁴ Select bonds distance and angles in the two structures are presented in Table S2. The angle between the two phenyl rings of the diaminobiphenyl ligand is 62.0 degrees in and 59.4 in 4 $[(C_6H_6)Ru(diaminobiphenyl)(Cl)][PF_6] \cdot MeOH$. In the crystal structure of **4** all the hydrogen atoms on the two amine groups of the diaminobiphenyl ligand are involved in hydrogen bonds. One of the hydrogen atoms on N(7)forms an intramolecular hydrogen bond to the oxygen atom O(4) of the sulfate ligand while the other hydrogen atom on N(7) forms an intermolecular hydrogen bond to the same O(4) atom that is associated by the symmetry operation. Details of this hydrogen bonding in the crystal structure of 4 are presented in Figure S1 and Table S3.



Figure 1. ORTEP diagram of the crystal structure of complex **4**. Selected bond lengths (Å): Ru(1)-N(7) 2.106(6), Ru(1)-N(9) 2.107(6), N(7)-C(1) 1.441(4), C(12)-N(9)

1.438(4); selected bond angles (deg): N(7)-Ru(1)-N(9) 83.34(11).

We evaluated the rate of aqueous formaldehyde dehydrogenation using catalyst **4** at various low temperatures (below 100 °C, Figure S2). It is clearly seen that the catalytic efficiency for gas production is highly dependent on the temperature. Notably, the best catalytic performance was observed at 95 °C. Additionally, a linear Arrhenius plot was obtained (Figure S3), further indicating the dependency of catalytic activity on temperature in the presence of catalyst **4**.



Figure 2. Reaction progress of aqueous formaldehyde dehydrogenation. (a) Time course of $(CH_2O)_n$ conversion (black), H_2 yield (green), and HCOOH/HCOO⁻ yield (red). (CH₂O)_n conversion and HCOOH/HCOO⁻ yield were determined by HPLC. The H₂ yield was based on the volume of H₂ collected (with respect to $(CH_2O)_n$). (b) The H₂ content in the produced gas mixture for continuous dehydrogenation of aqueous formaldehyde. Reaction conditions: paraformaldehyde (5 mmol), H₂O (5 mL), catalyst **4** (10 µmol), 95 °C (oil bath temperature).

In order to gain further insight into the reaction pathway, the reaction progress of dehydrogenation aqueous formaldehyde was monitored (Figure 2). In aqueous solution, it is known that formaldehyde can be released from paraformaldehyde, which is subsequently hydrated to produce methanediol.^{5,6,8,15} Thus, the methanediol acts as the true starting material for the production of formic acid/formate and H₂. Remarkably, clear changes in the trend of formic acid/formate yield and formaldehyde conversion are observed during the catalytic process (Figure 2a). In the presence of catalyst **4**, a high catalytic rate was observed for the formation of formic acid/formate and H₂ from methanediol. After 1 h,

the yield of formic acid/formate achieved the highest level (49% yield). Then, the produced formic acid/formate was continuously decomposed to H₂ and CO_2 . Thus, a continuous increase in H_2 yield was observed, affording a high yield of 95% after 7 h. The highest yield and selectivity yet reported for H₂ production from aqueous formaldehyde were obtained. Moreover, the released gases were analyzed by gas chromatography (GC) during the entire reaction progress (Figure 2b). The results clearly indicate that the overall process goes through two dehydrogenation steps as shown in Scheme 1: In the initial stage, over 90% of the gas was H₂ (initial 20 min), thus suggesting that the dehydrogenation of methanediol to formic acid/formate and H_2 mainly occurred. In the second stage, the H_2/CO_2 ratio gradually decreased. Furthermore, the expected 1:1 H_2/CO_2 gas composition (gas release from formic acid/formate dehydrogenation) was observed after about 4 h, and remained unchanged until the catalytic progress stopped. In situ analysis of the pH during the entire process of aqueous formaldehyde dehydrogenation indicated a clear change (gradually decreasing from pH 7 to 2, then increasing to an almost neutral condition) as shown in Figure S4, which also demonstrates the proposed two dehydrogenation steps. Additionally, no detrimental CO was detected by GC (< 1 ppm, Figure S5) from the released gas, potentially enabling applications in fuel cells.



Figure 3. Proposed catalytic cycles (A and B) for methanediol dehydrogenation catalyzed by catalyst **4**. The relative free energies are reported in units of kcal/mol.

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A plausible catalytic cycle for the dehydrogenation of aqueous formaldehyde is proposed in Figure 3 (see free energy profiles in Figures S10 and S11 for detailed depiction of the proposed mechanism) based on all the results obtained above and density functional theory (DFT) calculations performed at the Mo6¹⁶ level of theory with SMD aqueous continuum solvation model¹⁷ (see computational methods in the SI for details). The proposed catalytic cycle A begins with coordination of methanediol to catalyst 4 with an aquo ligand (a) generating adduct **b** with a free energy change (ΔG) of 4.0 kcal/mol. Then, in a stepwise process, hydride and proton (both from methanediol) are transferred to the Ru and H₂O, respectively, thus producing a ruthenium hydride species **c** and formate. The optimized transition structure for β-hydride elimination from state methanediol hydrogen bonded to water molecules (see SI for details on the effect of inclusion of explicit water molecules for transition state geometries and energetics) features an activation free energy (ΔG^{\dagger}) of 22.6 kcal/mol followed by proton transfers to aqueous solution releasing formate and forming a ruthenium hydride species with a hydrogen bonded water molecule, \mathbf{c} (ΔG = -11.7 kcal/mol). Next, water-assisted proton transfer from the amino ligand to the ruthenium hydride moiety with ΔG^{\dagger} of 22.8 kcal/mol forms species **d**, and then the first molecule of H₂ is generated by the release of H₂ and coordination of a water molecule to return to species a $(\Delta G = -17.6 \text{ kcal/mol})$, completing the catalytic cycle. Furthermore, the produced formate undergoes a second dehydrogenation process in the presence of 4 (catalytic cycle **B**) through formation of formato complex **e** (ΔG = -7.2 kcal/mol), release of CO_2 by β -hydride elimination to produce the ruthenium hydride complex **f** ($\Delta G^{\dagger} = 16.3$ kcal/mol, $\Delta G = 2.1$ kcal/mol). Finally, the second molecule of H_2 is produced from **f** similar to **c**, completing the catalytic cycle.

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Notably, hydride species can be detected by ¹H NMR spectroscopy under the catalytic conditions (the chemical shift of the **4**-hydride is $\delta = -10.14$ ppm; Figure S6). In addition, we have analyzed the released gas composition from the dehydrogenation of deuterated paraformaldehyde (CD₂O)_{*n*} in H₂O by GC (Figure S7). Remarkably, only HD gas was produced in the initial period, followed by gradually increased H₂ (no detectable amount of D₂). This indicates that H/D exchange¹⁸ is catalyzed by the catalyst **4** between the solvent (H₂O) and the C-H bonds of the methanediol, further suggesting paraformaldehyde serves as a hydride donor and water serves as a proton donor.

Table 1. Kinetic isotope effect in the dehydrogenation of formaldehyde/ H_2O catalyzed by catalyst **4**.^a

Entry	Substrate	Solvent	TOF ^b [h ⁻¹]	KIE ^c
1	$(CH_2O)_n$	H_2O	2020	-
2	$(CH_2O)_n$	D_2O	1720	1.17
3	$(CD_2O)_n$	H_2O	992	2.04
4	$(CD_2O)_n$	D_2O	751	2.69
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 aReaction conditions: substrate (5 mmol), H_2O (5 mL), catalyst 4 (5 $\mu mol), 95 \ ^oC$ (oil bath temperature). bAverage TOF

over initial 5 min. The errors were less than 5%. ^cKIE = TOF(entry 1)/TOF(entry number, 2, 3, and 4).

To gain further mechanistic insight, we carried out a deuterium kinetic isotope effect (KIE) study with catalyst 4. The average TOF over the initial 5 min was used for the KIE studies, and the results are shown in Table 1. The KIE experiments suggest that the deuterated formaldehyde substrate (KIE: 2.04, entry 3) is more influential than the deuterated water (KIE: 1.17, entry 2) on the reaction rate, which indicates that deuterated formaldehyde is involved in the rate-limiting step rather than D₂O. Accordingly, we propose that the formation of [Ru]–H from the species **c** should be rate determining rather than H₂ production from the reaction of [Ru]-H with a proton. Overall, β -hydride elimination from Rumethanediol complex **b** (ΔG^{\dagger} = 22.6 kcal/mol), considering the free energy requirement for the generation of the complex ($\Delta G = 4.0 \text{ kcal/mol}$) in the first place, represents the rate limiting step of the proposed catalytic mechanism. This is further supported by the comparison of the computed deuterium KIEs (Table S4) to experimental results.

To characterize the catalytic performance of catalyst 4 in more detail, we investigated the substrate concentration dependence of aqueous paraformaldehyde dehydrogenation by catalyst 4 (Figure S8 and Table S5). It is known that the undesired disproportionation of formaldehyde easily occurs in the presence of base additives (Cannizzaro reaction), thus the previously reported work usually use low formaldehyde concentration (< 0.5 mol L⁻¹).^{6,8} In order to obtain a high energy density, a relatively high concentration of aqueous formaldehyde is requisite. Notably, under the applied base-free conditions, as the formaldehyde concentration increases from 1 to 10 mol L-1, the initial reaction rate increases markedly (Figure S8). Moreover, from the detailed results summarized in Table S5, excellent H_2 yields (> 93%) were obtained at high formaldehyde concentrations (from 1 to 3 mol L-1). Even at a much higher formaldehyde concentration (10 mol L⁻¹), a good H₂ yield of 79% was obtained; and a high TON of 15800 than ever reported values was also achieved. Additionally, the methanol yields were all lower than 5% (Table S5, entry 1 to entry 5), indicating a high selective hydrogen production system was developed.19



Figure 4. Highly robust hydrogen production from a paraformaldehyde–water solution. Reaction conditions: para-

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formaldehyde (3 mol L⁻¹, 20 mL H₂O), 4 μ mol catalyst **4**, 95 °C (oil bath temperature).

Based on the results observed in Figure S8 and Table S5, a formaldehyde concentration of 3 mol L⁻¹ was selected as the optimal concentration for obtaining high H₂ yield, as well as high TOF and TON. The time course of the TON for hydrogen production under additive-free conditions was carried out (Figure 4). A high TOF of 8300 h⁻¹ (average TOF over initial 5 min) was achieved. Remarkably, catalyst **4** is highly robust under the applied conditions. A maximum TON of 24000 was obtained after 100 h, affording a yield of ~80%.

In conclusion, to the best of our knowledge, the highest TON and selectivity yet reported for H_2 production from aqueous formaldehyde under mild conditions without using any additive or organic solvent were obtained with catalyst **4**. Moreover, mechanistic studies suggest that the formation of ruthenium hydride is the rate determining step for the dehydrogenation of aqueous formaldehyde. Remarkably, the N-H moieties on the coordinated ruthenium complex are crucial to greatly enhance the catalytic activity. The present catalytic system, combined with the detailed mechanistic investigations will provide new opportunities for developing highperformance homogeneous catalysts for effective H_2 production from the liquid organic hydrogen carriers.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>. Experimental section including general methods, supplemental data, and computational details.

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Notes

The authors declare no competing financial interest.

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(19) When a methanol-water solution was heated at 95 °C with catalyst **4**, no gas generation was observed.

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