

Communication

Long-Term Hydrogen Production from a Methanol–Water Solution Catalyzed by an Iridium Complex

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Abstract: Long-term hydrogen production from a methanol–water solution was achieved by developing a new reaction system employing a homogeneous iridium catalyst bearing a bipyridonate-type functional ligand. By optimizing the methanol:water ratio of the reaction solution, the efficiency of hydrogen production was greatly improved in relation to that reported in our previous studies. Additionally, the effect of the scale of reaction was investigated. It was found that a small-scale reaction led to a longer lifetime of the iridium catalyst, accomplishing long-term continuous hydrogen production at a constant rate for over 500 h. Furthermore, procedures for catalyst reuse were studied. After hydrogen production for 400 h, all volatiles in the reaction system were removed under vacuum. This simple procedure is highly effective for the reactivation and reuse of the catalyst. Finally, hydrogen production (13.7 L, 562 mmol) from methanol (12.3 mL, 303 mmol) and water (5.46 mL, 303 mmol), in a continuous reaction for 800 h, was achieved.

Keywords: hydrogen production; homogeneous catalyst; iridium catalyst; methanol; water



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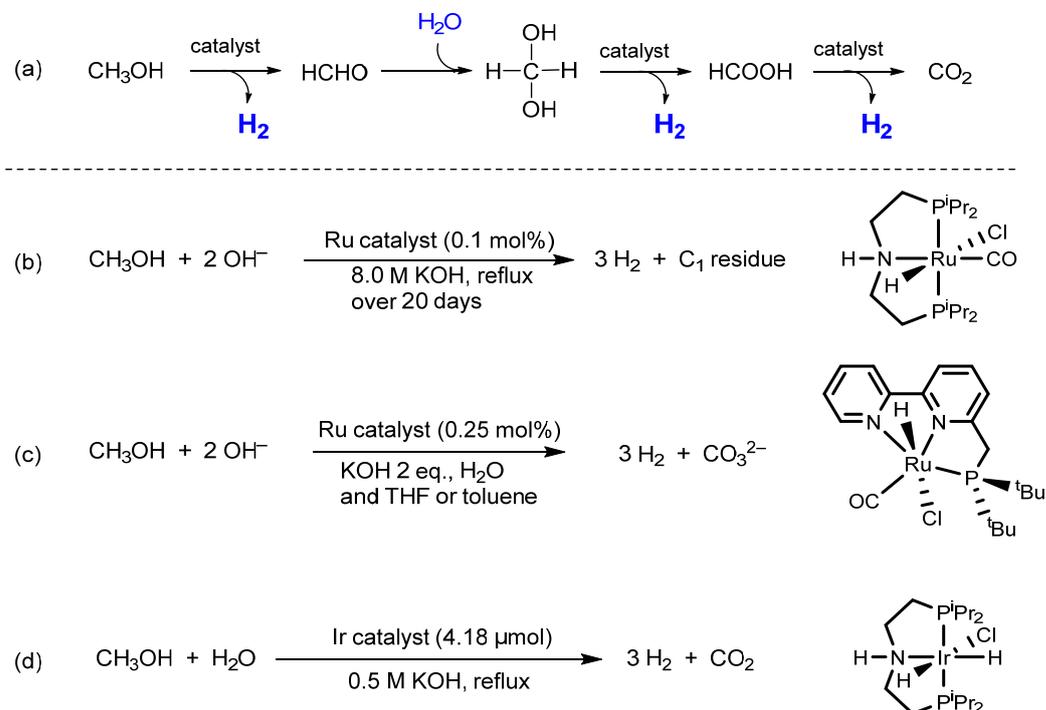
1. Introduction

For the past few decades, hydrogen has been evaluated as a suitable alternative to fossil fuel energy sources for driving the sustainable development of society [1–9]. Some of the many advantages of hydrogen include: (1) it having the highest mass-energy density among all fuels, (2) its easy conversion to electrical or mechanical energy, and (3) the fact that it only generates water during energy conversion.

Several hydrogen production methods, including the heterogeneously catalyzed steam reforming of methanol to produce hydrogen and carbon dioxide, have been explored and investigated by various researchers [10–20]. Heterogeneous catalysts can be recovered and reused in some cases; thus, they are effective systems for hydrogen production. However, such a process commonly requires temperatures of 200 °C or above, leads to the formation of carbon monoxide as a byproduct and to catalyst degradation, and presents operational energy challenges.

In 2013, Beller et al. developed a Ru complex with a PNP pincer-type ligand and applied it as a homogeneous catalyst for the dehydrogenation reaction of a methanol–water solution [21]. This catalytic reaction proceeds through three steps: (1) the dehydrogenation of methanol to form formaldehyde, (2) the hydration of formaldehyde and formation of formic acid, and (3) the dehydrogenation of formic acid to form carbon dioxide (Scheme 1a). Several hydrogen production systems from methanol, at reaction temperatures below 100 °C and using homogeneous catalysts, have been reported [22–28]. However, these methods require the addition of a large amount of a strong base (Scheme 1b) [29] or an organic solvent, such as tetrahydrofuran (THF) or toluene (Scheme 1c) [30]. For further practical applications, low concentrations of a base would be desirable and the use of organic solvents should be avoided. In 2017, Beller et al. developed an iridium complex

with a PNP pincer-type ligand and applied it as a catalyst for hydrogen production from a methanol–water solution (Scheme 1d) [31].



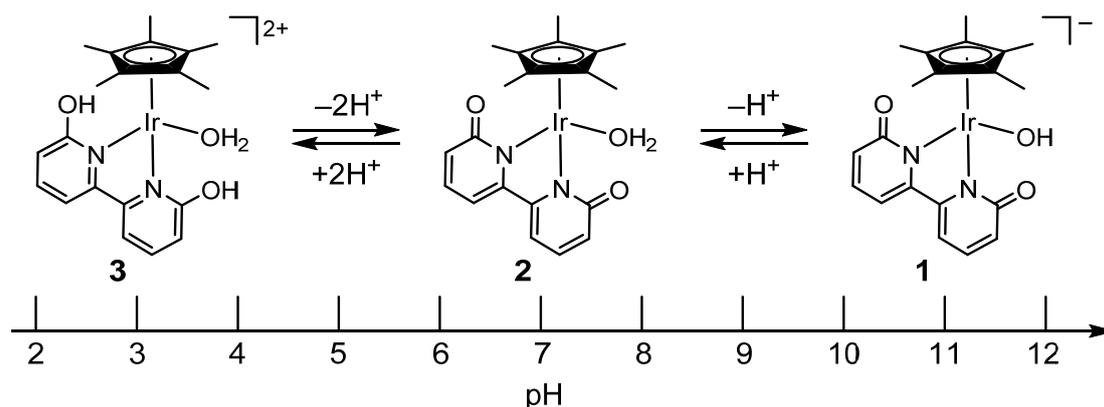
Scheme 1. Hydrogen production from a methanol–water solution catalyzed by homogeneous metal complexes. (a) Possible reaction pathway for hydrogen production from a methanol–water solution. (b) Catalytic system shown in [29]. (c) Catalytic system shown in [30]. (d) Catalytic system shown in [31].

Although this reaction has high catalytic activity, even under weakly basic conditions, only short reaction times were reported. Long-term hydrogen production was achieved with the development of durable homogeneous catalysts. In 2017, Beller et al. reported continuous hydrogen production for over 800 h using Mn catalysts [32]. To the best of our knowledge, this is the longest period of hydrogen production ever reported. However, this reaction required the addition of high concentrations of bases, large quantities of ligands, and organic solvents. In 2021, continuous hydrogen production from a methanol–water solution for over 600 h was achieved by Milstein et al [33]. This reaction is highly favorable because it does not require the use of bases or organic solvents.

We have previously reported the dehydrogenative oxidation of alcohols catalyzed by iridium complexes with functional bipyridine and bipyridonate ligands [34–38].

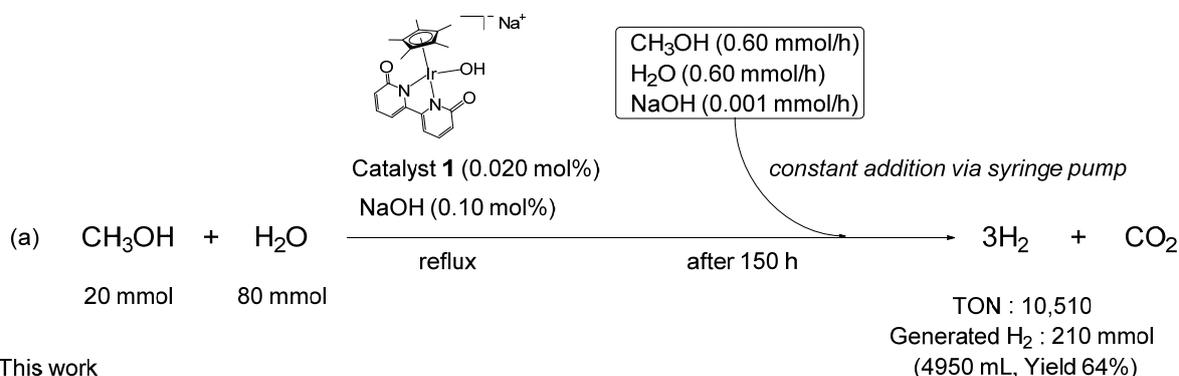
We also reported on hydrogen production reactions from natural compounds such as saccharides and cellulose, which are environmentally sustainable sources of materials for a sustainable society [39,40]. Similarly, we have been studying the dehydrogenative oxidation from methanol as an important source of hydrogen.

We have also reported a hydrogen production method involving the dehydrogenation of methanol using a water-soluble anionic iridium complex, such as catalyst **1** [41]. Anionic catalyst **1** is reversibly interconverted to neutral catalyst **2** and dicationic catalyst **3** by changing the pH of the aqueous solution, as shown in Scheme 2. The catalyst **1** efficiently catalyzed the hydrogen production from a methanol–water solution below 100 °C without the addition of organic solvents. Furthermore, continuous hydrogen production from a methanol–water solution for 150 h, catalyzed by **1**, was also achieved by a procedure including the addition of a solution composed of methanol, water, and NaOH to the system through a syringe pump (Scheme 3a). In this case, the yield of hydrogen was 64% and the turnover number (TON) of the catalyst was 10,510.

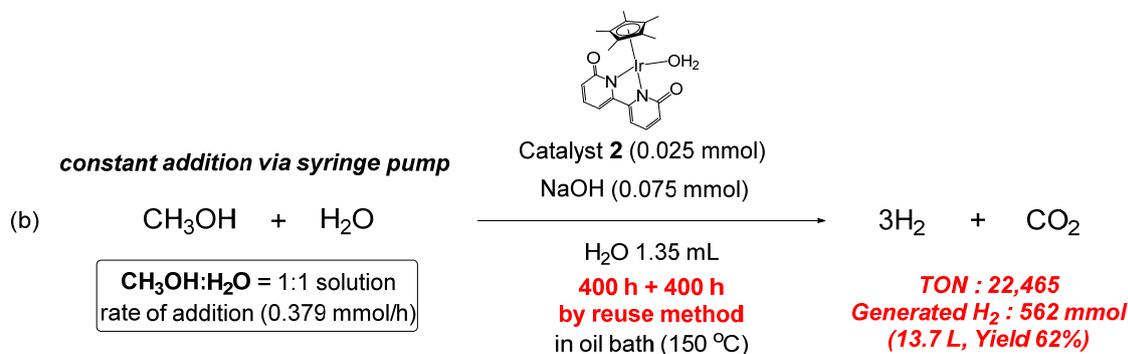


Scheme 2. Reversible interconversion between 1, 2, and 3 upon changing the pH of an aqueous solution.

Our earlier research



This work



Scheme 3. Long-term hydrogen production from a methanol–water solution catalyzed by iridium complexes 1 and 2. (a) Our previous research. (b) This work.

However, various challenges to the practical application of this method, such as the reduction in catalytic activity and the precipitation of carbonates owing to the continuous addition of a base, have been encountered. Strongly basic conditions and base accumulation must be avoided to achieve much longer-term hydrogen production. Furthermore, the development of a reaction system that enables catalyst reuse is highly desirable.

In this study, we developed a simple method using the iridium catalyst that allows continuous hydrogen production over a long period. Specifically, by adding catalyst 2, a base, and water to a flask, followed by the continuous addition of a methanol:water (1:1) mixed solution as the feedstock, at a rate of 0.379 mmol/h using a syringe pump, continuous hydrogen production for over 500 h in a single run was achieved. Furthermore, by removing accumulated (not consumed) methanol and water after 400 h of reaction, the catalytic system was reactivated, and continuous hydrogen production was accomplished

for a total of 800 h (Scheme 3b). This new system can be considered relatively safe, owing to the presence of a large amount of water, which is nonflammable.

2. Results and Discussion

2.1. Effect of Methanol Concentration on the Efficiency of Hydrogen Production

Initially, we investigated the effect of the ratio of methanol-to-water on the amount of generated hydrogen (Table 1, see also Figure 1). The volume of gas generated during the catalytic reaction was measured using the equipment shown in Figure S1. The gas collected in a gas burette was analyzed by gas chromatography (GC); the results confirmed the presence of hydrogen and carbon dioxide in a ratio of 3:1 (Figure S3). Increasing the proportion of methanol decreased the TON of the catalyst and hydrogen yield; this result is explained as follows. Firstly, when water is present in excess relative to methanol, the boiling point of the solution is higher, which accelerates the reaction. Secondly, an excessively high concentration of methanol can reduce the activity of the catalyst. The boiling point of the mixtures, shown as entries 1, 2, and 3 in Table 1, were 97 °C, 75 °C, and 70 °C, respectively.

Table 1. Effect of the ratio of methanol to water on hydrogen production catalyzed by 2.

Entry	X [mmol]	Y [mmol]	Ratio [X:Y]	Generated H ₂ [mL]	TON
1	25	125	1:5	1358	556
2	75	75	1:1	278	116
3	125	25	5:1	240	99

Volume was measured using a gas burette.

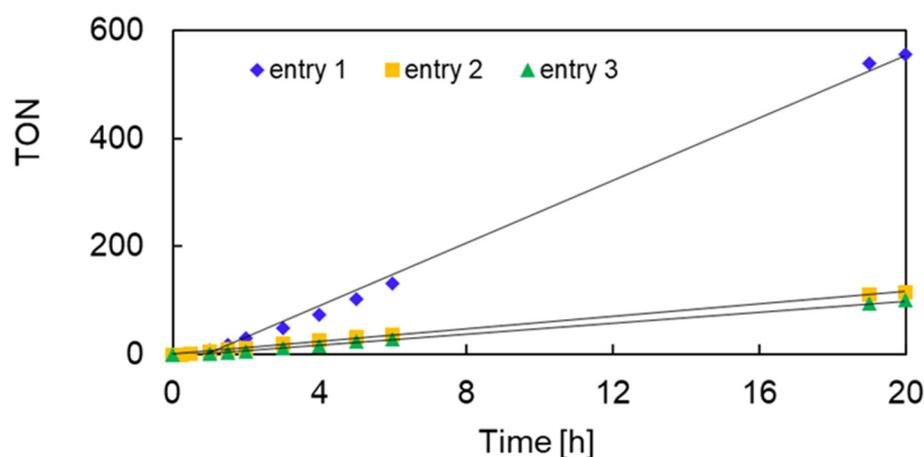


Figure 1. Effect of the ratio of methanol to water on hydrogen production catalyzed by 2. Time-dependent reaction profiles of entries 1–3 in Table 1.

2.2. Stability of the Catalyst at High Temperature for a Long Period of Time

We then investigated the stability of the catalyst over long-term reactions. After heating catalyst 2 in water in an oil bath at 150 °C for 400 h, ¹H NMR analysis was performed (in CD₃OD). The result is shown in Figure S4a. The catalyst 2 was only slightly damaged,

despite exposure to high temperature conditions for a long period of time. The stability of the catalyst 2 in the presence of a base was also investigated. In a 0.067 M NaOH aqueous solution of the catalyst 2, the catalyst 2 was rapidly converted to the anionic catalyst 1. Then, the solution was heated in an oil bath at 150 °C for 400 h and ¹H NMR analysis was performed (in D₂O). The results in Figure S4b indicate that catalyst 1 was maintained at near purity. This confirms that the catalyst 2, which is used as a catalytic precursor, and the catalyst 1, which is a catalytically active species for the production of hydrogen from a methanol–water solution, are stable for a long time under high temperature conditions.

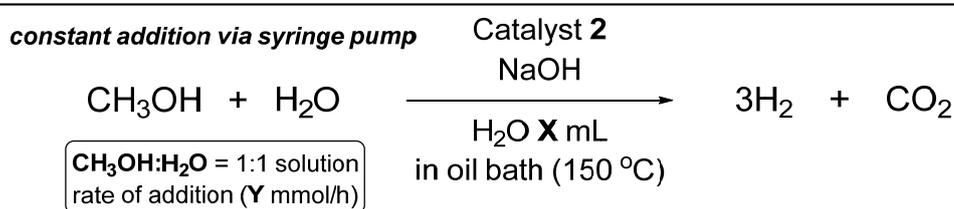
2.3. Optimization of Reaction Conditions for Long-Term Hydrogen Production

Based on the preliminary investigations above, we performed an experiment in which a 1:1 mixture of methanol and water was added, at a constant rate using a syringe pump, to maintain the conditions with a low concentration of methanol. As shown in Figure S2, the volume of gas generated was measured using a milli-gas counter connected to the reaction vessel via a bubbler. The milli-gas counter was connected to a computer, which automatically recorded the cumulative gas production volume and gas production rate for each experiment.

Firstly, the catalyst 2 (0.1 mmol), water (2.7 mL), and NaOH (0.3 mmol) were placed in a round-bottom flask. A methanol–water solution (methanol:water = 1:1) was then added via the syringe pump (1.51 mmol/h) in an oil bath at 150 °C, and gas (hydrogen and carbon dioxide) was generated at a constant rate without deactivation of the catalyst for 350 h (Table 2, entry 1; see also Figure 2). Next, we conducted a similar catalytic reaction in a half-scale compared to entry 1. By changing the scale of the reaction to be smaller, the time for which hydrogen can be produced at a constant rate was extended to 450 h (Table 2, entry 2; see also Figure 2). Furthermore, we conducted a quarter-scale experiment compared to entry 1. However, refluxing could not be successfully performed because the solvent volume was too small for the flask size (Table 2, entry 3). Therefore, the experiment was conducted by doubling the amount of water placed in the flask at the beginning of the reaction. In this case, fortunately, hydrogen production continued at an almost constant rate for over 500 h (Table 2, entry 4; see also Figure 2). The TON of this reaction, shown as entry 4 after 500 h, was 15,001. When the water volume was further increased to 2.0 mL, the rate of hydrogen production dropped after approximately 100 h (entry 5). Therefore, the conditions shown in entry 4 were determined to be the optimal reaction conditions for long-term hydrogen production. The time-dependent reaction profiles of entries 1, 2, and 4 in Table 2 are shown in Figure 2.

Table 2. Optimization of the conditions for long-term hydrogen production from methanol–water solution using iridium catalyst 2.

Entry	constant addition via syringe pump		Catalyst 2		Time [h]	TON
	Cat. [mmol]	NaOH [mmol]	X [mL]	Y [mmol/h]		
1	0.1	0.3	2.7	1.51	350	11,104
2	0.05	0.15	1.35	0.761	450	14,951
3	0.025	0.075	0.68	0.379	-	-
4	0.025	0.075	1.35	0.379	>500	>15,001
5	0.025	0.075	2.0	0.379	100	3228



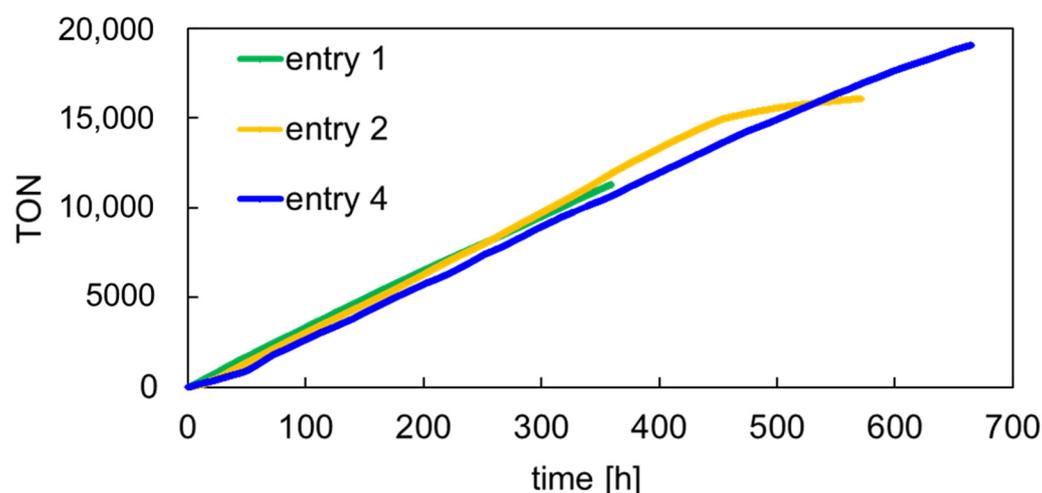


Figure 2. Time-dependent reaction profiles of long-term hydrogen production from methanol–water solutions catalyzed by 2, shown in entries 1, 2, and 4 in Table 2.

2.4. Procedure for the Reactivation and Reuse of the Catalyst

As shown above, we developed a new system for hydrogen production at a constant rate over 500 h. However, we paid attention to the fact that long-term reactions caused the accumulation of unreacted methanol in the flask, because the methanol consumption under the optimal conditions was 66%. Therefore, we started to search for a new procedure for the reactivation and reuse of the catalyst to achieve continuous hydrogen production over a much longer time. We attempted to remove the excess methanol–water solution and restore the initial conditions to allow the reuse of the catalyst without losing its catalytic activity.

The experiment was conducted as follows. As shown in Figure 3, the hydrogen production reaction at a constant rate was intentionally terminated after 400 h. The accumulated methanol–water solution was then removed under vacuum, and the catalyst and base remained as a residue in the flask. Subsequently, water (1.35 mL) was added to the flask, and the addition of the methanol–water (1:1) solution using the syringe pump was restarted. Hydrogen production was continued for an additional 400 h, and the reaction rate was almost equal to the initial rate (Figure 4). This procedure for catalyst reactivation resulted in constant-rate hydrogen production from the methanol–water solution for over 800 h. Furthermore, the TON of the catalyst was increased to 22,465. The volume of generated hydrogen after 800 h was 13.7 L (562 mmol), which was produced from 12.3 mL (303 mmol) of methanol and 5.46 mL (303 mmol) of water. The catalytic mechanism for the dehydrogenation of methanol probably follows the same pathway that we have previously reported (Scheme S1).

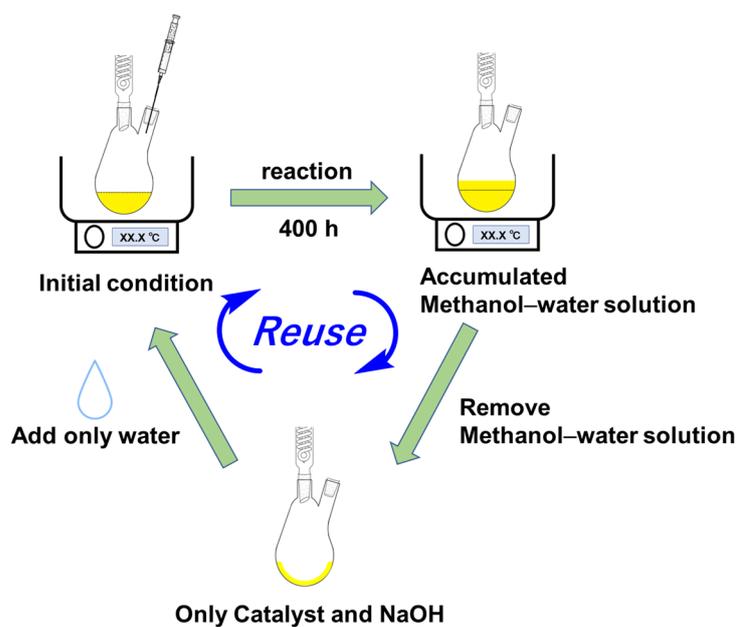


Figure 3. Catalyst reuse method for continuous hydrogen production from a methanol–water solution catalyzed by 2.

constant addition via syringe pump

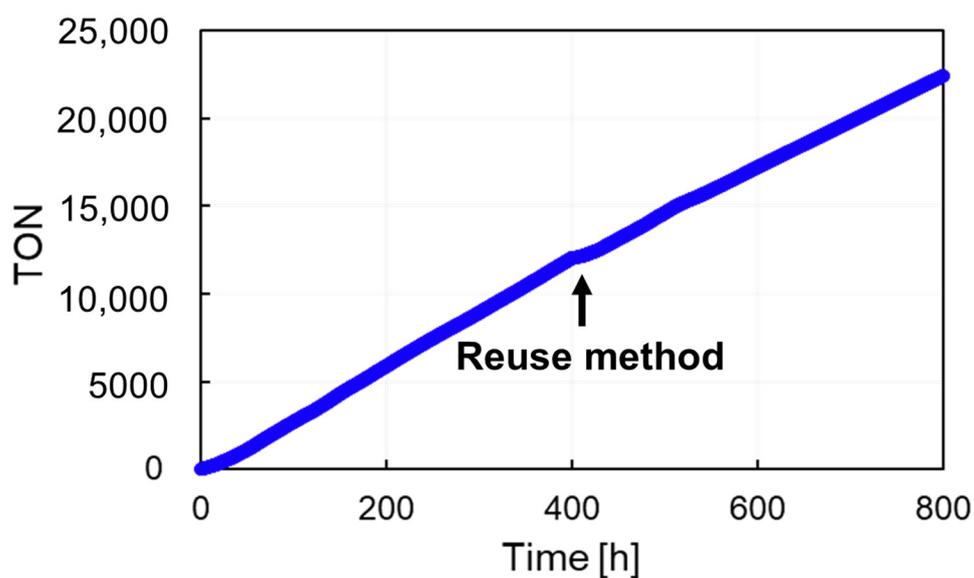
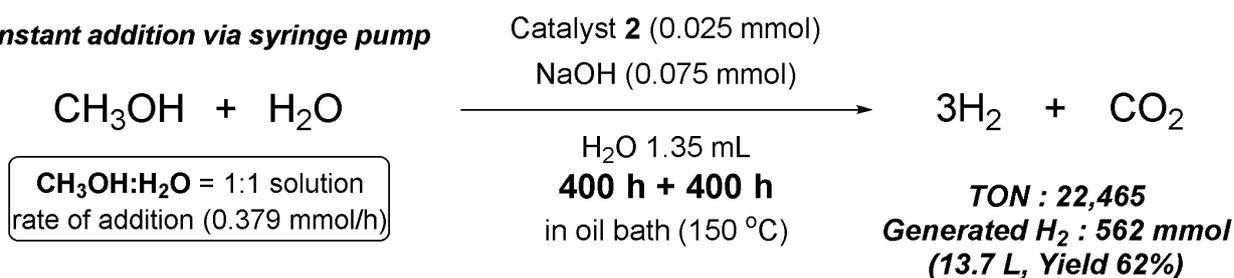


Figure 4. Long-term continuous hydrogen production from a methanol–water solution catalyzed by 2 using the reuse method.

3. Materials and Methods

3.1. General

All reactions and manipulations were performed under argon atmosphere using standard Schlenk techniques. ^1H NMR spectra were recorded on JEOL ECX-500 spectrometers. Gas chromatograph analyses of hydrogen and CO_2 were performed on a GL-Sciences GC390 gas chromatograph with packed columns (Molecular Sieve 5A and Gaskuropack 54). Model MGC-1, from Japan Flow Controls Co., Ltd., (Tokyo, Japan) was used as the milli-gas counter for automatic hydrogen measurement, and REGAMO was used as the software for automatic volume measurement (<https://download.cnet.com/developer/Rega%20Software%20LLC/i-10257150/>, accessed on 14 June 2023). Reagents were commercially available and were used as received.

3.2. Dehydrogenation from Methanol and Water (Measured by the Gas Burette)

The reaction setup is shown in Figure S1. In a 30 mL round-bottom flask, iridium complex **2** (53.1 mg, 0.10 mmol), absolute methanol (25–125 mmol), distilled water (25–125 mmol), and NaOH (0.3 mmol) were placed. The mixture was stirred under reflux at 150 °C (oil bath temp.). The volume of evolved gas was measured by a gas burette. The evolved gas was confirmed to be 3:1 mixture of hydrogen and carbon dioxide by GC analysis. The molar amount of hydrogen was calculated using the ideal gas law.

3.3. Procedure for the Stability Test of the Catalyst **2** in Water

In a 30 mL round-bottom flask, the iridium complex **2** (26.6 mg, 0.05 mmol) and distilled water (125 mmol) were placed. The mixture was stirred for 400 h under reflux at 150 °C (oil bath temp.).

3.4. Procedure for the Stability Test of the Catalyst **2** in 0.067 M NaOH Aq

In a 30 mL round-bottom flask, the iridium complex **2** (26.6 mg, 0.05 mmol), distilled water (125 mmol), and NaOH (0.15 mmol) were placed. The mixture was stirred for 400 h under reflux at 150 °C (oil bath temp.).

3.5. Dehydrogenation from Methanol and Water (Measured by the Milli-Gas Counter)

The reaction setup is shown in Figure S2. In a 30 mL round-bottom flask, iridium complex **2** (13.3–53.1 mg, 0.025–0.10 mmol), distilled water (37.5–111 mmol), and NaOH (0.075–0.30 mmol) were placed. The mixture was stirred under reflux at 150 °C (oil bath temp.). During the reaction, a solution composed of methanol (200 mmol) and water (200 mmol) was added via a syringe pump with rates of 0.379–1.51 mmol/h for methanol and 0.379–1.51 mmol/h for water. The volume of evolved gas was measured by a milli-gas counter.

3.6. Procedure for Long-Term Continuous Hydrogen Production by the Reuse Method

The reaction setup is shown in Figure S2. In a 30 mL round-bottom flask, iridium complex **2** (13.3 mg, 0.025 mmol), distilled water (75 mmol), and NaOH (0.075 mmol) were placed. The mixture was stirred under for 400 h reflux at 150 °C (oil bath temp.). During the reaction, a solution composed of methanol (200 mmol) and water (200 mmol) was added via a syringe pump, with rates of 0.379 mmol/h for methanol and 0.379 mmol/h for water. The volume of evolved gas was measured by a milli-gas counter. After the mixture cooled down for 30 minutes, the mixture was removed by vacuum drying. And, the distilled water (75 mmol) was added in the flask. The mixture was stirred for 400 h under reflux at 150 °C (oil bath temp.) again. During the reaction, a solution composed of methanol (200 mmol) and water (200 mmol) was added via a syringe pump, with rates of 0.379 mmol/h for methanol and 0.379 mmol/h for water. The volume of evolved gas was measured by a milli-gas counter again.

4. Conclusions

Long-term hydrogen production from a methanol–water solution has been achieved by developing a new reaction system employing a homogeneous iridium catalyst using a simple catalyst reactivation and reuse method. The advantages of catalyst **2**, which has important characteristics, including high stability in water, were key to the success of this reaction. Our hydrogen production system is efficient and safe, because the reaction is performed without using organic solvents under low concentrations of basic conditions, unlike the hydrogen production methods developed by other researchers.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13061027/s1>, Figure S1: The reaction setup for the experiments performed in Table 1.; Figure S2: The reaction setup for the experiments performed in Table 2 and Figure 4.; Figure S3: GC analysis of the evolved gas by the reaction of methanol and water under optimal conditions (a) The chromatogram of the evolved gas by the reaction catalyzed by the catalyst **2**. (b) The chromatogram of the standard hydrogen and carbon dioxide mixed gas (H₂:CO₂ = 3:1).; Figure S4: Results of the catalyst stability test at high temperature for a long period of time (a) 1H NMR spectrum of catalyst **2** (measured in CD₃OD) after refluxing for 400 h at 150 °C in a water solvent [36]. (b) 1H NMR spectrum of catalyst **1** (measured in D₂O) after refluxing for 400 h at 150 °C in a 0.067 M NaOH aqueous solution [41]; Scheme S1: Possible mechanism for the hydrogen production from a methanol-water solution [41].

Author Contributions: S.F. performed the experiments, analyzed the results, and wrote the draft of the manuscript. K.K., H.W., H.G. and S.K. performed the experiments. K.-i.F. guided the research, designed the experiments, and wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Rostrup-Nielsen, J.R. Production of Synthesis Gas. *Catal. Today* **1993**, *18*, 305–324. [[CrossRef](#)]
2. Besenbacher, F.; Chorkendorff, I.; Clausen, B.S.; Hammer, B.; Molenbroek, A.M.; Nørskov, J.K.; Stensgaard, I. Design of a Surface Alloy Catalyst for Steam Reforming. *Science* **1998**, *279*, 1913–1915. [[CrossRef](#)]
3. Trimm, D.L. Catalysts for the Control of Coking during Steam Reforming. *Catal. Today* **1999**, *49*, 3–10. [[CrossRef](#)]
4. Osaki, T.; Mori, T. Role of Potassium in Carbon-Free CO₂ Reforming of Methane on K-Promoted Ni/Al₂O₃ Catalysts. *J. Catal.* **2001**, *204*, 89–97. [[CrossRef](#)]
5. Shimura, K.; Kato, S.; Yoshida, T.; Itoh, H.; Hattori, T.; Yoshida, H. Photocatalytic Steam Reforming of Methane over Sodium Tantalate. *J. Phys. Chem. C* **2010**, *114*, 3493–3503. [[CrossRef](#)]
6. Duarte, R.B.; Krumeich, F.; Van Bokhoven, J.A. Structure, Activity, and Stability of Atomically Dispersed Rh in Methane Steam Reforming. *ACS Catal.* **2014**, *4*, 1279–1286. [[CrossRef](#)]
7. Mondal, T.; Pant, K.K.; Dalai, A.K. Mechanistic Kinetic Modeling of Oxidative Steam Reforming of Bioethanol for Hydrogen Production over Rh–Ni/CeO₂–ZrO₂ Catalyst. *Ind. Eng. Chem. Res.* **2016**, *55*, 86–98. [[CrossRef](#)]
8. Che, F.; Gray, J.T.; Ha, S.; McEwen, J.S. Improving Ni Catalysts Using Electric Fields: A DFT and Experimental Study of the Methane Steam Reforming Reaction. *ACS Catal.* **2017**, *7*, 551–562. [[CrossRef](#)]
9. Rostrup-Nielsen, T. Manufacture of Hydrogen. *Catal. Today* **2005**, *106*, 293–296. [[CrossRef](#)]
10. Murcia-Mascarós, S.; Navarro, R.M.; Gómez-Sainero, L.; Costantino, U.; Nocchetti, M.; Fierro, J.L.G. Regular Article. *J. Catal.* **2001**, *2*, 338–347. [[CrossRef](#)]
11. Reitz, T.L.; Lee, P.L.; Lang, J.C.; Lang, J.C.; Kung, H.H. Time-Resolved XANES Investigation of CuO/ZnO in the Oxidative Methanol Reforming Reaction. *J. Catal.* **2001**, *199*, 193–201. [[CrossRef](#)]
12. Palo, D.R.; Dagle, R.A.; Holladay, J.D. Methanol Steam Reforming for Hydrogen Production. *Chem. Rev.* **2007**, *107*, 3992–4021. [[CrossRef](#)] [[PubMed](#)]
13. Wu, H.S.; Chung, S.C. Kinetics of Hydrogen Production of Methanol Reforming Using Cu/ZnO/Al₂O₃ Catalyst. *J. Comb. Chem.* **2007**, *9*, 990–997. [[CrossRef](#)]

14. Halevi, B.; Lin, S.; Roy, A.; Zhang, H.; Jerero, E.; Vohs, J.; Wang, Y.; Guo, H.; Datye, A.K. High CO₂ Selectivity of ZnO Powder Catalysts for Methanol Steam Reforming. *J. Phys. Chem. C* **2013**, *117*, 6493–6503. [[CrossRef](#)]
15. Oar-Arteta, L.; Remiro, A.; Epron, F.; Bion, N.; Aguayo, A.T.; Bilbao, J.; Gayubo, A.G. Comparison of Noble Metal- and Copper-Based Catalysts for the Step of Methanol Steam Reforming in the Dimethyl Ether Steam Reforming Process. *Ind. Eng. Chem. Res.* **2016**, *55*, 3546–3555. [[CrossRef](#)]
16. Mayr, L.; Köpfle, N.; Klötzer, B.; Götsch, T.; Bernardi, J.; Schwarz, S.; Keilhauer, T.; Armbrüster, M.; Penner, S. Microstructural and Chemical Evolution and Analysis of a Self-Activating CO₂-Selective Cu-Zr Bimetallic Methanol Steam Reforming Catalyst. *J. Phys. Chem. C* **2016**, *120*, 25395–25404. [[CrossRef](#)]
17. Lin, L.; Zhou, W.; Gao, R.; Yao, S.; Zhang, X.; Xu, W.; Zheng, S.; Jiang, Z.; Yu, Q.; Li, Y.W.; et al. Low-Temperature Hydrogen Production from Water and Methanol Using Pt/ α -MoC Catalysts. *Nature* **2017**, *544*, 80–83. [[CrossRef](#)] [[PubMed](#)]
18. Cai, F.; Ibrahim, J.J.; Fu, Y.; Kong, W.; Zhang, J.; Sun, Y. Low-Temperature Hydrogen Production from Methanol Steam Reforming on Zn-Modified Pt/MoC Catalysts. *Appl. Catal. B* **2019**, *264*, 118500. [[CrossRef](#)]
19. Sun, Z.; Sun, Z.-Q. Hydrogen Generation from Methanol Reforming for Fuel Cell Applications: A Review. *J. Cent. South Univ.* **2020**, *27*, 1074–1103. [[CrossRef](#)]
20. Lin, L.; Yu, Q.; Peng, M.; Li, A.; Yao, S.; Tian, S.; Liu, X.; Li, A.; Jiang, Z.; Gao, R.; et al. Atomically Dispersed Ni/ α -MoC Catalyst for Hydrogen Production from Methanol/Water. *J. Am. Chem. Soc.* **2021**, *143*, 309–317. [[CrossRef](#)]
21. Nielsen, M.; Alberico, E.; Baumann, W.; Drexler, H.J.; Junge, H.; Gladiali, S.; Beller, M. Low-Temperature Aqueous-Phase Methanol Dehydrogenation to Hydrogen and Carbon Dioxide. *Nature* **2013**, *495*, 85–89. [[CrossRef](#)]
22. Boucher, M.B.; Marcinkowski, M.D.; Liriano, M.L.; Murphy, C.J.; Lewis, E.A.; Jewell, A.D.; Mattera, M.F.G.; Kyriakou, G.; Flytzani-Stephanopoulos, M.; Sykes, E.C.H. Molecular-Scale Perspective of Water-Catalyzed Methanol Dehydrogenation to Formaldehyde. *ACS Nano* **2013**, *7*, 6181–6187. [[CrossRef](#)] [[PubMed](#)]
23. Rodríguez-Lugo, R.E.; Trincado, M.; Vogt, M.; Tewes, F.; Santiso-Quinones, G.; Grützmacher, H. A Homogeneous Transition Metal Complex for Clean Hydrogen Production from Methanol–Water Mixtures. *Nat. Chem.* **2013**, *5*, 342–347. [[CrossRef](#)] [[PubMed](#)]
24. Bielinski, E.A.; Förster, M.; Zhang, Y.; Bernskoetter, W.H.; Hazari, N.; Holthausen, M.C. Base-Free Methanol Dehydrogenation Using a Pincer-Supported Iron Compound and Lewis Acid Co-Catalyst. *ACS Catal.* **2015**, *5*, 2404–2415. [[CrossRef](#)]
25. Campos, J.; Sharninghausen, L.S.; Manas, M.G.; Crabtree, R.H. Methanol Dehydrogenation by Iridium N-Heterocyclic Carbene Complexes. *Inorg. Chem.* **2015**, *54*, 5079–5084. [[CrossRef](#)] [[PubMed](#)]
26. Quan, L.N.; Yuan, M.; Comin, R.; Voznyy, O.; Beauregard, E.M.; Hoogland, S.; Buin, A.; Kirmani, A.R.; Zhao, K.; Amassian, A.; et al. Ligand-Stabilized Reduced-Dimensionality Perovskites. *J. Am. Chem. Soc.* **2016**, *138*, 2649–2655. [[CrossRef](#)]
27. Wang, Q.; Lan, J.; Liang, R.; Xia, Y.; Qin, L.; Chung, L.W.; Zheng, Z. New Tricks for an Old Dog: Grubbs Catalysts Enable Efficient Hydrogen Production from Aqueous-Phase Methanol Reforming. *ACS Catal.* **2022**, *12*, 2212–2222. [[CrossRef](#)]
28. Chen, Z.; Xia, Y.; Ma, C.; Wang, Q.; Qin, L.; Zhu, X.; Zheng, Z. Hydrogen Production via the Aqueous-Phase Reforming of Methanol Catalyzed by Ru(II) Complexes of PNNP Ligands. *Inorg. Chem. Front.* **2023**, *10*, 756–767. [[CrossRef](#)]
29. Alberico, E.; Sponholz, P.; Cordes, C.; Nielsen, M.; Drexler, H.J.; Baumann, W.; Junge, H.; Beller, M. Selective Hydrogen Production from Methanol with a Defined Iron Pincer Catalyst under Mild Conditions. *Angew. Chem. Int. Ed.* **2013**, *52*, 14162–14166. [[CrossRef](#)]
30. Hu, P.; Diskin-Posner, Y.; Ben-David, Y.; Milstein, D. Reusable Homogeneous Catalytic System for Hydrogen Production from Methanol and Water. *ACS Catal.* **2014**, *4*, 2649–2652. [[CrossRef](#)]
31. Prichatz, C.; Alberico, E.; Baumann, W.; Junge, H.; Beller, M. Iridium–PNP Pincer Complexes for Methanol Dehydrogenation at Low Base Concentration. *ChemCatChem* **2017**, *9*, 1891–1896. [[CrossRef](#)]
32. Andérez-Fernández, M.; Vogt, L.K.; Fischer, S.; Zhou, W.; Jiao, H.; Garbe, M.; Elangovan, S.; Junge, K.; Junge, H.; Ludwig, R.; et al. A Stable Manganese Pincer Catalyst for the Selective Dehydrogenation of Methanol. *Angew. Chem. Int. Ed.* **2017**, *56*, 559–562. [[CrossRef](#)]
33. Luo, J.; Kar, S.; Rauch, M.; Montag, M.; Ben-David, Y.; Milstein, D. Efficient Base-Free Aqueous Reforming of Methanol Homogeneously Catalyzed by Ruthenium Exhibiting a Remarkable Acceleration by Added Catalytic Thiol. *J. Am. Chem. Soc.* **2021**, *143*, 17284–17291. [[CrossRef](#)]
34. Fujita, K.; Tanino, N.; Yamaguchi, R. Ligand-Promoted Dehydrogenation of Alcohols Catalyzed by Cp*Ir Complexes. A New Catalytic System for Oxidant-Free Oxidation of Alcohols. *Org. Lett.* **2007**, *9*, 109–111. [[CrossRef](#)]
35. Fujita, K.; Yoshida, T.; Imori, Y.; Yamaguchi, R. Dehydrogenative Oxidation of Primary and Secondary Alcohols Catalyzed by a Cp*Ir Complex Having a Functional C,N-Chelate Ligand. *Org. Lett.* **2011**, *13*, 2278–2281. [[CrossRef](#)]
36. Kawahara, R.; Fujita, K.; Yamaguchi, R. Cooperative Catalysis by Iridium Complexes with a Bipyridonate Ligand: Versatile Dehydrogenative Oxidation of Alcohols and Reversible Dehydrogenation–Hydrogenation between 2-Propanol and Acetone. *Angew. Chem. Int. Ed.* **2012**, *51*, 12790–12794. [[CrossRef](#)]
37. Kawahara, R.; Fujita, K.; Yamaguchi, R. Dehydrogenative Oxidation of Alcohols in Aqueous Media Using Water-Soluble and Reusable Cp*Ir Catalysts Bearing a Functional Bipyridine Ligand. *J. Am. Chem. Soc.* **2012**, *134*, 3643–3646. [[CrossRef](#)]
38. Zeng, G.; Sakaki, S.; Fujita, K.; Sano, H.; Yamaguchi, R. Efficient Catalyst for Acceptorless Alcohol Dehydrogenation: Interplay of Theoretical and Experimental Studies. *ACS Catal.* **2014**, *4*, 1010–1020. [[CrossRef](#)]
39. Fujita, K.; Inoue, T.; Tanaka, T.; Jeong, J.; Furukawa, S.; Yamaguchi, R. Iridium Complex Catalyzed Hydrogen Production from Glucose and Various Monosaccharides. *Catalysts* **2021**, *11*, 891. [[CrossRef](#)]

40. Toyooka, G.; Tanaka, T.; Kitayama, K.; Kobayashi, N.; Watanabe, T.; Fujita, K. Hydrogen Production from Cellulose Catalyzed by an Iridium Complex in Ionic Liquid under Mild Conditions. *Catal. Sci. Technol.* **2021**, *11*, 2273–2279. [[CrossRef](#)]
41. Fujita, K.; Kawahara, R.; Aikawa, T.; Yamaguchi, R. Hydrogen Production from a Methanol–Water Solution Catalyzed by an Anionic Iridium Complex Bearing a Functional Bipyridonate Ligand under Weakly Basic Conditions. *Angew. Chem. Int. Ed.* **2015**, *54*, 9057–9060. [[CrossRef](#)] [[PubMed](#)]

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