Article

Microwave-Mediated Continuous Hydrogen Abstraction Reaction from 2-PrOH Catalyzed by Platinum on Carbon Bead

Tomohiro Ichikawa 1, Tomohiro Matsuo 1, Takumu Tachikawa 1, Wataru Teranishi 1, Tsuyoshi Yamada 1*, Yoshinari Sawama 1*, Yasunari Monguchi 2 and Hironao Sajiki 1,*

1 Laboratory of Organic Chemistry, Gifu Pharmaceutical University, 1-25-4 Daigaku-nishi, Gifu 501-1196, Japan
2 Laboratory of Organic Chemistry, Daiichi University of Pharmacy, 22-1, Tamagawa-cho, Minami-ku, Fukuoka 815-8511, Japan
* Correspondence: sajiki@gifu-pu.ac.jp; Tel.: +81-58-230-8109

Received: 27 June 2019; Accepted: 29 July 2019; Published: 31 July 2019

Abstract: We developed a microwave-mediated continuous hydrogen production method from 2-PrOH using platinum on a spherical carbon-bead catalyst. The catalyst cartridge consisted of helical glass part, and straight glass part (helix–straight cartridge) was newly developed for the effective microwave heating of 2-PrOH in the presence of 5% Pt/CB. The microwave resonance was properly adjusted within 2.4–2.5 GHz using the helix–straight cartridge with the glass resonance-adjuster tube. The reaction was conducted by the irradiation of only 10 W of single-frequency microwaves and the catalyst was used continuously for at least 13 h without any loss of catalyst activity.

Keywords: carbon; flow process; heterogeneous catalyst; hydrogen production; microwave chemistry; platinum

1. Introduction

Expanding the use of clean energy sources is essential to mitigating the impending global climate crisis. Although hydrogen is industrially produced by steam reforming, like with methane along with the generation of carbon dioxide [1], the combustion of hydrogen, which does not emit a greenhouse gas, has been proposed as an environmentally friendly energy production method [2–4]. Unlike its high energy density per weight, the energy density of hydrogen per unit volume is low; hence, it is necessary to liquefy the hydrogen for storage and transport, which is an energy-intensive process [5]. Therefore, the storage and transport of hydrogen are important problems to be solved.

Many effective methods for the production, storage, and transport of hydrogen, such as hydrogen absorption in a metal-organic framework [6], hydrogen storage as metal hydrides [7], and the direct production of hydrogen from liquid organic hydrides, have been proposed to overcome previous drawbacks. Liquid organic hydride methods for hydrogen storage have several advantages. For example, the liquid can be handled using an oil infrastructure at ambient temperature and under the pressure, and it can be reused via a hydrogenation-dehydrogenation cycle. The combination of a heterogeneous catalyst and flow reaction system allows for the continuous production of hydrogen gas without a catalyst removal process. Several studies on hydrogen production from methylcyclohexane (MCH) have been conducted using a combination of fixed-bed (flow-type) reactors and heterogeneous catalysts [5,8–18].

2-Propanol (2-PrOH), which is industrially produced by the hydration of propene, is cheap and low in toxicity. In addition, 2-PrOH is a potent hydrogen carrier because 2-PrOH is readily available and reusable via the reduction of acetone, resulting from the dehydrogenation of 2-PrOH [19]. It is crucial...
to maintain recyclability through the hydrogenation-dehydrogenation process for the sustainable use of hydrogen carriers. The dehydrogenation reaction of 2-PrOH catalyzed by a heterogeneous catalyst has been reported to proceed under various conditions [20–36], such as thermal [20–24,27], photocatalytic [28,30,33,34,36], supercritical [29], and electrochemical [31,32].

In 2019, Wada and Tsubaki et al. reported that a molybdenum sulfide supported on Al2O3 (MoS2/Al2O3)-catalyzed hydrogen generation reaction from 2-PrOH using a combination of microwave heating and a fixed-bed flow reactor. This was smoothly enhanced by the microwave-mediated specific local heating effect [35]. However, the reaction efficiencies of these reported methods [20–36] are insufficient for the use of 2-PrOH as a hydrogen carrier, despite the relatively mild endothermic nature of the dehydrogenation of 2-PrOH to acetone compared with the dehydrogenation of MCH. Therefore, the development of more effective methods for hydrogen generation from 2-PrOH is essential.

Since microwave directly heats up reaction systems without heat medium, energetic efficiency during the reaction process is superior to the conventional heating device, such as an oil bath, a heating block, and an air-mediated heater. We recently reported on an activated carbon-supported platinum (Pt) metal-catalyzed effective dehydrogenation method of primary and secondary alcohols in basic aqueous media [37,38], and a method of microwave-enhanced continuous hydrogen production from MCH using a carbon-bead-supported Pt catalyst (Pt/CB) [39]. We also found that the combination of microwave irradiation and a flow system enabled the sufficient progress of the dehydrogenation of MCH. The essential factor was activated carbon adequately heated by microwave irradiation based on its high electron permittivity.

In this paper, we described 5% Pt/CB for continuous-flow hydrogen production from 2-PrOH under low-power microwave irradiation conditions.

2. Results and Discussion

2.1. Microwave Heating Property under Existence of 5% Pt/CB and 2-PrOH

Microwave heating was affected by the electric permittivity of the irradiated components in the reaction field, including the catalyst, the solvent, and even the shape of the reactor. First, the resonant frequency in the range of the 2.4–2.5 GHz ISM band of the catalyst cartridge filled with 2-PrOH and the microwave absorption rate of the catalyst cartridges filled with 2-PrOH were measured under single-mode microwave irradiation conditions (Table 1). We already found that single-mode microwave irradiation intensively and selectively heated 5% Pt/CB in a straight cartridge in the presence of MCH. However, the microwave absorption into the straight cartridge filled with 2-PrOH was never observed even though the resonant frequency was detected at 2.446 GHz (Entry 1). Even when a glass or PTFE resonant frequency adjuster tube was placed around the straight catalyst cartridge, no suitable frequency was detected (Entries 2 and 3). Therefore, it was revealed that the straight catalyst cartridge, which was suitable for the dehydrogenation reaction of MCH, was not suitable for hydrogen generation from 2-PrOH. The structure of the catalyst cartridge significantly affected the resonant frequency (Entries 4–6 vs. 1–3). The catalyst in the helix-straight cartridge exhibited microwave absorbance with the use of a glass adjuster tube (Entry 5). Therefore, we selected the combination of a helix-straight cartridge and a glass adjuster tube.
was conducted using 60% acetone in 2-PrOH as a flow solution to identify the cause of the decrease in the reaction rate (Figure 1b, black line). It took 5 h to transform 60% acetone/2-PrOH (6:4) to 70% acetone, and the total time for the single-pass process was 6.5 h. The dehydrogenation reaction was dominant over the 5% Pt/CB-catalyzed hydrogenation of acetone reaction.

Since the conversion yield of hydrogen gas was insufficient in a single-pass manner, we next examined the dehydrogenation of 2-PrOH by a circulation process to see if this improved the conversion rate. The reaction proceeded smoothly even when the residence time of 2-PrOH in the catalyst cartridge was only 40 s. As 2-PrOH was converted to acetone along with hydrogen generation, the evolved gas was collected in a gas burette (1 L × 2) and was analyzed by GC-TCD to determine the gas component. It was found that 1.10 L (47.1 mmol, 15% yield) of highly pure (99.6%) hydrogen gas evolved, at which time 14% of 2-PrOH was transformed into acetone, as identified by $^1$H NMR analysis. Ultratrace amounts of methane and carbon dioxide were also obtained, although the production pathways for the byproduced gases were not revealed.

2.2. Dehydrogenation of 2-PrOH

In this experiment, 2-PrOH (24.0 mL, 312 mmol) was pumped into the microwave flow system which included 80 mg of 5% Pt/CB (Pt: 20.5 µmol) packed in a cartridge, surrounded with a glass adjuster tube at 0.40 mL/min under 10-W microwave irradiation and 2.0-MPa backpressure in a single-pass manner for 1 h (Scheme 1). The microwave system also monitored the power of the generated microwave and the microwave reflected from the cavity without absorption into the catalyst system. As the power of the reflected microwave was 1.46 W under 10-W microwave irradiation, it is estimated that the catalyst system absorbed 85.4% of the microwave.

The reaction proceeded smoothly even when the residence time of 2-PrOH in the catalyst cartridge was only 40 s. As 2-PrOH was converted to acetone along with hydrogen generation, the evolved gas was collected in a gas burette (1 L × 2) and was analyzed by GC-TCD to determine the gas component. It was found that 1.10 L (47.1 mmol, 15% yield) of highly pure (99.6%) hydrogen gas evolved, at which time 14% of 2-PrOH was transformed into acetone, as identified by $^1$H NMR analysis. Ultratrace amounts of methane and carbon dioxide were also obtained, although the production pathways for the byproduced gases were not revealed.

| Entry | Type of Catalyst Cartridge | Adjuster Tube  | Resonant Frequency (GHz) |
|-------|---------------------------|----------------|--------------------------|
| 1     | Straight                   | None           | 2.446 $^3$               |
| 2     | Straight                   | Glass          | Not detected $^4$        |
| 3     | Straight                   | PTFE           | 2.382                    |
| 4     | Helix–Straight             | None           | 2.566                    |
| 5     | Helix–Straight             | Glass          | 2.412                    |
| 6     | Helix–Straight             | PTFE           | 2.505                    |

$^1$ The resonant frequency of catalyst cartridge filled with 2-PrOH was measured in presence of 5% Pt/CB (80.0 mg).
$^2$ A resonant adjuster tube was placed around catalyst cartridge. $^3$ The microwave was not absorbed into the catalyst cartridge filled with 2-PrOH. $^4$ The resonant frequency was not found around the range of 2.4–2.5 GHz.

Scheme 1. Dehydrogenation of 2-PrOH in a single-pass manner.
70% acetone/2-PrOH, starting with 60% acetone/2-PrOH, although it took only 1.5 h for the same transformation when starting with pure 2-PrOH.

These results strongly indicate that the degradation of the reaction rate was caused by the reduced ratio of 2-PrOH in the flow solution rather than the deactivation of 5% Pt/CB. Thus, the dehydrogenation of 2-PrOH was dominant over the 5% Pt/CB-catalyzed hydrogenation of acetone [40,41] in the early stage of the reaction. The hydrogenation of acetone competed with the dehydrogenation of 2-PrOH as the ratio of 2-PrOH to acetone decreased with the progress of the reaction.

The hydrogen evolution from 2-PrOH proceeded with the generation of a small number of gaseous byproducts, such as methane, carbon dioxide, and carbon monoxide. To reveal the mechanism of the generation of these byproduct gases, we used pure acetone as a substrate and solvent instead of 2-PrOH. Acetone was passed through a 5% Pt/CB-packed cartridge at 0.40 mL/min with 10-W microwave irradiation and 2.0-MPa backpressure in a circulating mode, but no gaseous product was observed.

Next, the long-term hydrogen generation from 2-PrOH under 10-W microwave irradiation was carried out under the conditions: 0.40 mL/min flow rate, 10-W microwave irradiation, and 2.0 MPa backpressure in circulation manner. Theoretical hydrogen evolution amount: 5.86 L.

![Figure 1](image-url)

**Figure 1.** Time course study of the generation of various gases under dehydrogenation conditions of 2-PrOH under a circulation manner [methane (green line with rhombus dots), carbon dioxide (yellow line with trigonal dots), and carbon monoxide (red line with square dots)]. (a) Time-dependent production of each gas. The reaction was carried out under the conditions described in Scheme 2. (b) Time-dependent change of acetone/2-PrOH ratio. The reaction was started with pure 2-PrOH (blue line) or acetone/2-PrOH (6:4, black line). The hydrogen generation using acetone/2-PrOH (6:4) was carried out under the conditions: 0.40 mL/min flow rate, 10-W microwave irradiation, and 2.0 MPa backpressure in circulation manner. Theoretical hydrogen evolution amount: 5.86 L.

### 2.3. Long-Term Experiment

Next, the long-term hydrogen generation from 2-PrOH under 10-W microwave irradiation was investigated. As a result, a total of 9.21 L of hydrogen was continuously produced at 99% purity at
a constant rate for at least 13 h. Notably, 5% Pt/CB catalyzed the dehydrogenation of 2-PrOH over 18,000 times without reducing the catalyst activity (Scheme 3 and Figure 2).

Scheme 3. A long-term experiment of dehydrogenation of 2-PrOH.

Figure 2. Time course study of long-term dehydrogenation of 2-PrOH. The reaction was carried out under the conditions described in Scheme 3.

2.4. Effects of Reaction Conditions

Some reaction conditions influence the reaction efficiency of the dehydrogenation of 2-PrOH (Table 2). When the reaction was conducted at a flow rate of 0.80 mL/min for 1 h (Entry 2), the yield and generation rate of hydrogen gas decreased compared to the flow rate of 0.40-mL/min, indicated in Scheme 1, probably due to the decrement of the residence time of 2-PrOH in 5% Pt/CB-packed cartridge (from ca. 40 s to ca. 20 s). When the reaction was carried out under a 1.0-MPa backpressure, the highest temperature of the reaction solution was 142 °C, which caused a decrease in the yield of hydrogen gas (Entry 3). The reaction efficiency was also slightly affected by the use of both 5 mol% and 20 mol% aqueous 2-PrOH solutions (Entries 4 and 5), resulting in a decrease in the yield of hydrogen gas and the absorptivity of microwave power. The power of the absorbed microwave in the case of those H2O-added conditions (77.1% and 78.4%, respectively) was lower compared to the power under standard conditions (85.4%) (Entries 4 and 5 vs. 1). The decrease of the reaction efficiency would be caused by the competing of hydroxyl groups of 2-PrOH and H2O. On the other hand, microwave absorptivity and the reaction efficiency improved when 60 mg of 5% Pt/CB was used (Entries 6–8). However, the generation rate and the purity of hydrogen gas were degraded to 13.7 mmol/h and 89% in the case using 60 mg of 5% Pt/CB, respectively in comparison with the case using 80 mg of 5% Pt/CB (Entry 6 vs. 1). In contrast, although the hydrogen generation rate was increased by the use of
60 mg of 5% Pt/CB in aqueous 2-PrOH, the amounts of gaseous byproducts, such as methane (CH₄), carbon dioxide (CO₂), or carbon monoxide (CO) increased to result in the decrement of the purity of hydrogen gas (Entries 7 vs. 4 and 8 vs. 5). These results indicate that reaction progress, including the side reactions under microwave irradiation, depend on the microwave absorptivity of the reaction cartridge. Therefore, it is appropriate for the generation of highly pure hydrogen gas at a high yield to operate the hydrogen generation reaction at a flow rate of 0.40 mL/min under 10-W microwave irradiation and 2.0-MPa backpressure without any additives under a circulation manner.

Table 2. Efficiency of the reaction parameter ¹.

| Entry | Deviation from Above | t (h) | T (°C) | H₂ Gas | Other Gases (mmol) |
|-------|----------------------|------|--------|--------|-------------------|
|       |                      |      |        | Total Amount (mmol) | Production Rate (mmol/h) | Yield (%) | Purity (%) |
| 1     | none                 | 5.5  | 176    | 195    | 35.5              | 81        | 96        |
| 2     | 0.8 mL/min           | 1    | 157    | 13.0   | 13.0              | 5         | 98        |
| 3     | 1 MPa                | 6    | 142    | 181    | 30.2              | 75        | 97        |
| 4     | w/H₂O (20 mol %)     | 5.5  | 176    | 166    | 30.2              | 72        | 97        |
| 5     | w/H₂O (5 mol %)      | 5    | 168    | 167    | 33.4              | 71        | 93        |
| 6     | w/H₂O (20 mol %)     | 3.5  | 154    | 220    | 62.9              | 95        | 89        |
| 7     | w/H₂O (5 mol %)      | 4.8  | 150    | 209    | 43.5              | 90        | 87        |
|       | 5% Pt/CB (60 mg)     |      |        |        |                   |           |           |

Each reaction was run up to 6 h or until the gas generation was almost stopped. ¹ The reaction mixture passed through 5% Pt/CB-packed glass cartridge under 10-W microwave irradiation at 0.4 mL/min and 2-MPa backpressure under the circulation manner. The total volume of the path of reaction system was 16.0 mL, and 2.5 mL of reaction mixture was taken in the reservoir. The reaction was completed when the gas generation rate decreased. The composition of the collected gas was analyzed by GC–TCD. ² 7.7 mL (232 mmol) of 2-PrOH was included in the reaction system. Theoretical H₂ generation amount was 5.66 L. ³ Additionally, 18.3 mL (240 mmol) of 2-PrOH was included in the reaction system. Theoretical H₂ generation amount was 5.85 L. ⁴ 5.40 mL (70.2 mmol) of 2-PrOH was included in the reaction system. Theoretical H₂ generation amount was 1.71 L.

3. Materials and Methods

3.1. General

All reagents were obtained from commercial sources and used without further purification. The 5% Pt/CB was supplied from N.E. Chemcat Co. (Minato-ku, Tokyo, Japan). The microwave flow reactor [microwave controller unit: MOC-33, the MW generator unit: MA-41 (maximum 50 W), pump unit: YA-20] was developed by SAIDA FDS, Inc. (Yaidzu, Shizuoka, Japan). The glass cartridges and adjuster tubes were also obtained from SAIDA FDS, Inc. Gas chromatography (GC) analyses were performed on a GL Science GC-3200 equipped with a thermal conductivity detector (TCD), an MS5A-packed column (GL science), and a CP-PoraPLOT Q column (Agilent Technology). ¹H NMR spectra were recorded on JEOL ECA-500 (500 MHz for ¹H NMR) and JEOL ECZ-400 (400 MHz for ¹H
NMR) spectrometers. CDCl$_3$ was used as a solvent for NMR measurement. Chemical shifts ($\delta$) are expressed in parts per million using tetramethylsilane (0.00 ppm) for $^1$H NMR.

3.2. Experimentals

3.2.1. Reaction System

The reaction system is shown in Figure 3. When the catalyst-packed cartridge equipped with a thermocouple was set in the microwave cavity, the catalyst was located on the horizontal center line in the microwave cavity [39]. This device uses a solid-state oscillator and can change the frequency of the irradiated microwave based on the shift in the resonant frequency in 1-W increments between 1–50 W, and the resonant frequency was always monitored during microwave irradiation. In addition, this device monitors the power of reflected microwaves that were not absorbed into the catalyst cartridge in a cavity.

The pump unit was equipped with a plunger pump, two pressure gauges upstream and downstream of the catalyst cartridge, the inline filter, and the backpressure regulator. Then, 2-PrOH was passed through the line in the following order: (1) reservoir, (2) plunger pump, (3) pressure gauge, (4) catalyst cartridge, (5) inline filter, (6) pressure gauge, (7) backpressure regulator, and (8) receiver. Two gas burettes (1 L) were connected to a reservoir at the end through the water-filled gas washing bottle. The generated gas flowed to the receiver and was collected through the gas line in the order that follows: (8) receiver, (9) water-filled gas washing bottle, (10) three-way stopcock for switching tracks toward each gas burette, and (11) three-way stopcock for changing lines toward a gas burette or a gas-sampling bag (1 L).

![Conceptual reaction system](image)

**Figure 3.** Conceptual reaction system. (1) Reservoir. (2) Pump. (3) Pressure gauge at an entrance. (4) 5% Pt/CB-packed catalyst cartridge. (5) Inline filter. (6) Pressure gauge at an exit. (7) Backpressure regulator. (8) Receiver. (9) Water-filled gas washing bottle. (10 and 11) Three-way stopcock.

3.2.2. Preparation of Catalyst Cartridge

Two types of quartz glass tubes (a straight glass tube and a helix-straight glass tube) were used as catalyst cartridges (Figure 4). The straight glass tube consists of a partially bulging part with an internal diameter of 10 mm and a narrow part with an internal diameter of 3.6 mm, and the glass filter is attached to the partially bulging part (Figure 4a). The helix-straight tube is composed of a helical part...
with an internal diameter of 2.0 mm and a straight part with an internal diameter of 3.6 mm (Figure 4b). The glass filter is placed in the straight part.

**Straight cartridge.** The 5% Pt/CB (80 mg, Pt: 20.5 μmol)-packed cartridge was prepared according to the procedure demonstrated in our recently reported literature [39]. Glass beads (0.991–1.397-mm diameter, 2.01 g) were packed on the glass filter, which reached the narrow part over the partially bulging part of the straight glass tube, and then a small amount of glass wool was packed on the glass beads. 5% Pt/CB was tightly filled on the glass wool by tapping the tube (the catalyst layer reached about 1.4 cm in height), and another glass wool was then packed on the catalyst to prevent disorder of the 5% Pt/CB layer (Figure 4c).

**Helix-straight cartridge.** A total of 5% Pt/CB (80 mg) was packed on the glass filter, and glass wool was then packed on the catalyst to prevent disorder of the 5% Pt/CB layer (Figure 4d). Both catalyst cartridges were arranged so that 5% Pt/CB was located at almost the same position from the top of the cartridge.

![Image showing different types of quartz-glass cartridges for hydrogen generation from 2-PrOH](image)

**Figure 4.** Two different types of quartz-glass cartridges for hydrogen generation from 2-PrOH. (a) Straight cartridge. (b) Helix-straight cartridge. (c) 5% Pt/CB (80 mg) and glass bead-packed straight tube. (d) 5% Pt/CB (80 mg)-packed helix-straight tube.

### 3.2.3. Hydrogen Generation from 2-PrOH

**Single-Pass Method.** The entire flow path was filled with 2-PrOH. The exit line penetrating through the rubber septum was attached to a rubber-septum-capped receiver connected to the gas-flowing line via a needle. Afterwards, 2-PrOH (total usage: 24.0 mL, 18.7 g, 312 mmol) was passed through the 5% Pt/CB (80 mg)-packed cartridge equipped with a glass adjuster tube at 0.4 mL/min under 10-W microwave irradiation and 2.0-MPa backpressure conditions in a single-pass manner for 1 h. The generated gas was collected in two gas burettes. After one gas burette was almost filled with hydrogen gas (ca. 900 mL), the stopcock (10, Figure 1) was turned to allow the gas to collect in the other burette. The yield and purity of the hydrogen in the collected gas were determined by gas chromatography equipped with a thermal conductivity detector (GC-TCD). The reaction conversion was determined by $^1$H NMR. 7.6 L (312 mmol) of hydrogen gas which can be theoretically generated after the full conversion of 2-PrOH [24.0 mL (18.7 g, 312 mmol)] to acetone.
Circulation Manner. The entire flow path was filled with 2-PrOH. The suction line and exit line were penetrated through the rubber septum and attached to the rubber-septum-capped reservoir connected to the gas-flowing line via a needle. The 2-PrOH was passed through the 5% Pt/CB-packed cartridge with a glass adjuster tube at 0.4 mL/min under 10-W microwave irradiation and 2.0-MPa backpressure conditions in a circulating manner. The operation was stopped when the rate of gas generation decreased. The generated gas was collected in two gas burettes. After one gas burette was almost filled with hydrogen gas (ca. 900 mL), the three-way stopcock (10, Figure 3) was turned to allow the gas to collect in the other burette. The yield and purity of hydrogen in the collected gas were determined by GC-TCD. The reaction conversion was determined by $^1$H NMR.

4. Conclusions

An efficient method for hydrogen generation from 2-PrOH and the novel catalyst cartridge for effective heating of 2-PrOH in the presence of 5% Pt/CB were developed. This method requires only 10 W of microwave irradiation and 80 mg of 10% Pt/CB to achieve a high conversion of 2-PrOH and highly pure hydrogen generation. Since the space-time yields of the present system are 183 (mol/L\textsubscript{cat}/h) and 324 (mol/kg\textsubscript{cat}/h), this can be considered efficient in comparison with the reported K–Pt/Al\textsubscript{2}O\textsubscript{3}-catalyzed hydrogen generation method using MCH as a liquid organic chemical hydride [46.3 (mol/L\textsubscript{cat}/h)] [42], which is currently being considered for practical use by a demonstration plant. This system was applied for 13 h of continuous operation without loss of catalyst activity. The present method is an energy-efficient hydrogen extraction system as only 10-W of the microwave was used for sufficient heating and the system has significant practical value.

Author Contributions: Writing and original draft preparation, T.I.; designating the research, T.I., Y.S., T.Y., Y.M., and H.S.; investigation, T.I., T.M., T.T., and W.T.; project administration, supervision, and polishing the manuscript, H.S.

Acknowledgments: This work was partially supported by JSPS KAKENHI grants (16K15100 and 18J14100), the Sasagawa Scientific Research Grant from the Japan Science Society, and the Nagai Memorial Research Scholarship from the Pharmaceutical Society of Japan. We sincerely appreciate N.E. Chemcat Co., which kindly provided 5% Pt/CB. We would like to thank Editage (www.editage.com) for English language editing.

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

References

1. Sá, S.; Silva, H.; Brandão, L.; Sousa, J.M.; Mendes, A. Catalysts for methanol steam reforming: A review. Appl. Catal. B 2010, 99, 43–57. [CrossRef]
2. Teichmann, D.; Arlt, W.; Wasserscheid, P. Liquid Organic Hydrogen Carriers as an efficient vector for the transport and storage of renewable energy. Int. J. Hydrogen Energy 2012, 37, 18118–18132. [CrossRef]
3. Dalebrook, A.F.; Gan, W.; Grasemann, M.; Moret, S.; Laurenczy, G. Hydrogen storage: beyond conventional methods. Chem. Commun. 2013, 49, 8735–8751. [CrossRef] [PubMed]
4. Sartbaeva, A.; Kuznetsov, V.L.; Wells, S.A.; Edwards, P.P. Hydrogen nexus in a sustainable energy future. Energy Environ. Sci. 2008, 1, 79–85. [CrossRef]
5. Horikoshi, S.; Kamata, M.; Sumi, T.; Serpone, N. Selective heating of Pd/AC catalyst in heterogeneous systems for the microwave-assisted continuous hydrogen evolution from organic hydrides: Temperature distribution in the fixed-bed reactor. Int. J. Hydrogen Energy 2016, 41, 12029–12037. [CrossRef]
6. Murray, L.J.; Dincă, M.; Long, J.R. Hydrogen storage in metal–organic frameworks. Chem. Soc. Rev. 2009, 38, 1294–1314. [CrossRef] [PubMed]
7. Sakintuna, B.; Lamari-Darkrim, F.; Hirscher, M. Metal hydride materials for solid hydrogen storage: A review. Int. J. Hydrogen Energy 2007, 32, 1121–1140. [CrossRef]
8. Li, J.; Chai, Y.; Liu, B.; Wu, Y.; Li, X.; Tang, Z.; Liu, Y.; Liu, C. The catalytic performance of Ni$_2$P/Al$_2$O$_3$ catalyst in comparison with Ni/Al$_2$O$_3$ catalyst in dehydrogenation of cyclohexane. Appl. Catal. A 2014, 469, 434–441. [CrossRef]
9. Suttisawat, Y.; Sakai, H.; Abe, M.; Rangsunviritchai, P.; Horikoshi, S. Microwave effect in the dehydrogenation of tetralin and decalin with a fixed-bed reactor. Int. J. Hydrogen Energy 2012, 37, 3242–3250. [CrossRef]
10. Li, X.; Luo, Y.; Li, P.; Duan, X.; Jiang, H.; Zhou, X. Effects of carbon support on microwave-assisted catalytic dehydrogenation of decalin. *Carbon* 2014, 67, 775–783. [CrossRef]

11. Lázaro, M.P.; García–Bordejé, E.; Sebastián, D.; Moliner, R. In situ hydrogen generation from cycloalkanes using a Pt/CNF catalyst. *Catal. Today* 2008, 138, 203–209. [CrossRef]

12. Usman, M.R.; Alotaibi, F.M.; Aslam, R. Dehydrogenation—hydrogenation of methylcyclohexane-toluene system on 1.0 wt % Pt/zelite beta catalyst. *Prog. React. Kinet. Mec.* 2015, 40, 353–366. [CrossRef]

13. Kariya, N.; Fukuoka, A.; Ichikawa, M. Efficient evolution of hydrogen from liquid cycloalkanes over Pt-containing catalysts supported on active carbons under “wet–dry multiphase conditions”. *Appl. Catal. A* 2002, 233, 91–102. [CrossRef]

14. Alhumaidan, F.; Tsakiris, D.; Cresswell, D.; Garforth, A. Hydrogen storage in liquid organic hydride: Selectivity of MCH dehydrogenation over monometallic and bimetallic Pt catalysts. *Int. J. Hydrogen Energy* 2013, 38, 14010–14026. [CrossRef]

15. Nakano, A.; Manabe, S.; Higo, T.; Seki, H.; Nagatake, S.; Yabe, T.; Ogo, S.; Nagatsuka, T.; Sugiura, Y.; Iki, H.; et al. Effects of Mn addition on dehydrogenation of methylcyclohexane over Pt/Al2O3 catalyst. *Appl. Catal. A* 2017, 543, 75–81. [CrossRef]

16. Chen, Y.-R.; Tsuru, T.; Kang, D.-Y. Simulation and design of catalytic membrane reactor for hydrogen production via methylcyclohexane dehydrogenation. *Int. J. Hydrogen Energy* 2017, 42, 26296–26307. [CrossRef]

17. Boufaden, N.; Akkari, R.; Fierro, J.L.G.; Said Zina, M.; Ghorbei, A. Dehydrogenation of methylcyclohexane to toluene over partially reduced silica-supported Pt-Mo catalysts. *J. Mol. Catal. A* 2016, 420, 96–106. [CrossRef]

18. Yokular, S. Organic chemical hydride dehydrogenation over nickel catalysts supported with SiO2 for hydrogen recovery. *Energy Sources Part A* 2016, 38, 2031–2034. [CrossRef]

19. Mitsui Chemicals, Inc. Method for Producing Isopropyl Alcohol. JP4321838B2, 12 June 2009.

20. Yamashita, M.; Kawasaki, T.; Suzuki, M.; Saito, Y. Characteristics of suspended Ru/carbon catalyst for 2-propanol dehydrogenation applicable to chemical heat pump. *Bull. Chem. Soc. Jpn.* 1991, 64, 272–278. [CrossRef]

21. Yamashita, M.; Dai, F.-Y.; Suzuki, M.; Saito, Y. Mechanism of 2-ProOH dehydrogenation with suspended Nickel fine-particle catalyst. *Bull. Chem. Soc. Jpn.* 1991, 64, 628–634. [CrossRef]

22. Mooksuwan, W.; Kumar, S. Study on 2-propanol/acetone/hydrogen chemical heat pump: endothermic dehydrogenation of 2-propanol. *Int. J. Energy Res.* 2000, 24, 1109–1122. [CrossRef]

23. Ando, Y.; Yamashita, M.; Saito, Y. Reaction Mechanism of 2-propanol dehydrogenation with a carbon-supported Ru–Pt composite catalyst in the liquid phase. *Bull. Chem. Soc. Jpn.* 2003, 76, 2045–2049. [CrossRef]

24. Ukisu, Y.; Miyadera, T. Dehydrogenation of 2-Propanol with suspended noble metal catalysts: activity enhancement by the addition of sodium hydroxide. *React. Kinet. Catal. Lett.* 2004, 81, 305–311. [CrossRef]

25. Behar, D.; Rabani, J. Kinetics of hydrogen production upon reduction of aqueous TiO2 nanoparticles catalyzed by Pd0, Pt0, or Au0 coatings and an unusual hydrogen abstraction; steady state and pulse radiolysis study. *J. Phys. Chem.* 2006, 110, 8750–8755. [CrossRef] [PubMed]

26. Martinez-Ramirez, Z.; Gonzalez-Calderon, J.A.; Almendarez-Camarillo, A.; Fierro-Gonzalez, J.C. Adsorption and dehydrogenation of 2-propanol on the surface of γ-Al2O3-supported gold. *Surf. Sci.* 2012, 606, 1167–1172. [CrossRef]

27. Sakurai, M.; Honda, H.; Kameyama, H. Fundamental study of a non-steady operation for 2-propanol de-hydrogenation. *Int. J. Hydrogen Energy* 2007, 32, 1303–1308. [CrossRef]

28. Ziełnińska, B.; Sreńcek-Nazzal, J.; Kalerčík, R.J. Photocatalytic hydrogen generation over alkali niobates in the presence of organic compounds. *Pol. J. Chem. Tech.* 2008, 10, 1–3. [CrossRef]

29. Karakus, Y.; Aynaci, F.; Kipcak, E.; Akgun, M. Hydrogen production from 2-propanol over Pt/Al2O3 and Ru/Al2O3 catalysts in supercritical water. *Int. J. Hydrogen Energy* 2013, 38, 7298–7306. [CrossRef]

30. Rodionov, L.A.; Mechtacheva, E.V.; Zvereva, L.A. Photocatalytic Activity of TiO2–MOx Composites in the Reaction of Hydrogen Generation from Aqueous Isopropanol Solution. *Russ. J. Gen. Chem.* 2014, 84, 611–616. [CrossRef]

31. Huang, S.; Wu, X.; Chen, W.; Ma, L.; Liu, S.; He, G. Electrocatalytic dehydrogenation of 2-propanol in electrochemicalhydrogen pump reactor. *Catal. Today* 2016, 276, 128–132. [CrossRef]
32. Huang, S.; Wu, X.; Chen, W.; Wang, T.; Wu, Y.; He, G. A bilateral electrochemical hydrogen pump reactor for 2-propanol dehydrogenation and phenol hydrogenation. *Green Chem.* **2016**, *18*, 2353–2362. [CrossRef]

33. Chai, Z.; Zeng, T.-T.; Li, Q.; Lu, L.-Q.; Xiao, W.-J.; Xu, D. Efficient Visible Light-Driven Splitting of Alcohols into Hydrogen and Corresponding Carbonyl Compounds over a Ni-Modified CdS Photocatalyst. *J. Am. Chem. Soc.* **2016**, *138*, 10128–10131. [CrossRef]

34. López-Tenlladoa, F.J.; Hidalgo-Carrilloa, J.; Montesa, V.; Marinasa, A.; Urbanoa, F.J.; Marinas, J.M.; Ilievab, L.; Tabakovab, T.; Reid, F. A comparative study of hydrogen photocatalytic production fromglycerol and propan-2-ol on M/TiO$_2$ systems (M = Au, Pt, Pd). *Catal. Today* **2017**, *280*, 58–64. [CrossRef]

35. Haneishi, N.; Tsubaki, S.; Abe, E.; Maitani, M.M.; Suzuki1, E.; Fujii, S.; Fukushima, J.; Takizawa, H.; Wada, Y. Reactions under Microwave Irradiation by Local Heating at the Vicinal Contact Points of Catalyst Particles. *Sci. Rep.* **2019**, *9*, 222. [CrossRef] [PubMed]

36. López-Tenllado, F.J.; Hidalgo-Carrillo, J.; Montes-Jiménez, V.; Sánchez-López, E.; Urbano, F.J.; Marinas, A. Photocatalytic production of hydrogen from binary mixtures of C-3 alcohols on Pt/TiO$_2$: Influence of alcohol structure. *Catal. Today* **2019**, *328*, 2–7. [CrossRef]

37. Sawama, Y.; Morita, K.; Asai, S.; Kozawa, M.; Tadokoro, S.; Nakajima, J.; Monguchi, Y.; Sajiki, H. Palladium on Carbon-Catalyzed Aqueous Transformation of Primary Alcohols to Carboxylic Acids Based on Dehydrogenation under Mildly Reduced Pressure. *Adv. Synth. Catal.* **2015**, *357*, 1205–1210. [CrossRef]

38. Sawama, Y.; Morita, K.; Yamada, T.; Nagata, S.; Yabe, Y.; Monguchi, Y.; Sajiki, H. Rhodium-on-carbon catalyzed hydrogen scavenger- and oxidant-free dehydrogenation of alcohols in aqueous media. *Green Chem.* **2014**, *16*, 3439–3443. [CrossRef]

39. Ichikawa, T.; Matsuo, T.; Tachikawa, T.; Yamada, T.; Yoshimura, T.; Yoshimura, M.; Takagi, Y.; Sawama, Y.; Sugiyama, J.; Monguchi, Y.; et al. Microwave-Mediated Site-Selective Heating of Spherical-Carbon-Bead-Supported Platinum for the Continuous, Efficient Catalytic Dehydrogenative Aromatization of Saturated Cyclic Hydrocarbons. *ACS Sustain. Chem. Eng.* **2019**, *7*, 3052–3061. [CrossRef]

40. Ji, Y.; Wu, Y.; Zhao, G.; Wang, D.; Liu, L.; He, W.; Li, Y. Porous bimetallic Pt–Fe nanocatalysts for highly efficient hydrogenation of acetone. *Nano Res.* **2015**, *8*, 2706–2713. [CrossRef]

41. Sen, B.; Vannice, M.A. Metal-support effects on acetone hydrogenation over platinum catalysts. *J. Catal.* **1988**, *113*, 52–71. [CrossRef]

42. Chiyoda Corp. Storage-Transport System of Hydrogen. JP2007-269522, 18 October 2007. © 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).