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Production of Bio Hydrofined Diesel, Jet Fuel, and Carbon Monoxide from Fatty Acids Using a Silicon Nanowire Array-Supported Rhodium Nanoparticle Catalyst under Microwave Conditions

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ABSTRACT Biodiesel was efficiently produced from biomass fatty acids using renewable gas H₂ and a reusable heterogeneous catalyst under low-energy-consumption microwave conditions. As the decarboxylation of fatty acids to

alkanes is an important transformation in the production of bio hydrofined diesel (BHD) and jet fuel, we herein report the development of a highly active and reusable Rh nanoparticle catalyst supported by a silicon nanowire array (SiNA-Rh) and its application in the decarboxylation of fatty acids to alkanes under mild conditions. More specifically, SiNA-Rh (500 mol ppm) selectively promoted the hydrogenative decarboxylation reaction at 200 °C under microwave irradiation (~40 W) in a H₂ atmosphere (10 bar) to afford the corresponding alkanes in high yields selectively. The only co-product observed was carbon monoxide, an important and essential staple for the chemical industry. Importantly, carbon dioxide formation was not observed. Moreover, the aldehydes were efficiently converted to alkanes by SiNA-Rh, and this



catalyst was reused 20 times without any loss in catalytic activity. Finally, to investigate the effects of microwave irradiation on the enhancement of this chemical transformation based on the Si nanorod structures present in the SiNA-Rh catalyst, the effect of the microwave electric field and magnetic field in the microwave to the reaction was experimentally investigated, and the spatial distribution of the electric field intensity around the surface of the Si nanostructure was simulated using the Finite Element Method.

INTRODUCTION

The decarboxylation of fatty acids to yield alkanes is an important reaction not only in organic synthesis but also in the production of biodiesel fuel (BDF).1-4 Indeed, the use of free fatty acids is particularly desirable, because they are readily available through the decomposition of vegetable oils by enzymes. For example, following the harvest of palm fruit from palm trees, the palm oil present in the fruit was decomposed over several hours to form free fatty acids.⁵ The efficient conversion of free fatty acids to high quality BDF under mild conditions is therefore desirable. In terms of the composition of BDF itself, it can be categorized into first-generation biodiesel fuel, i.e., fatty acid methyl esters (FAME), and second-generation biodiesel fuel, i.e., bio hydrofined diesel (BHD, hydrocarbons). To date, FAME has been synthesized by a variety of basic (and sometimes acid) catalysts, including our polymeric acid catalyst.⁶⁻¹¹ However,

since the stability and combustibility of FAME are poorer than that of BHD, the development of suitable catalysts for the efficient production of BHD is of particular importance in the context of renewable energy sources. In this context, a number of homogeneous¹² and heterogeneous catalysts have been reported.^{13–21} For example, Vardon et al.²² reported that the decarboxylation of stearic acid using a Pt-Re/C catalyst resulted in the highly selective formation of C₁₇ alkanes, while Kaneda et al.²³ and Zhang et al.²⁴ reported the decarboxylation of fatty acids using Ru-CeO₂ and Ru-HAP catalysts, respectively, to yield BHD. However, the development of highly active, reusable, and selective supported catalysts for BHD production remains a challenge.

In this context, we previously reported the development of a silicon nanowire array-stabilized Pd nanoparticle catalyst for organic transformations such as cross-coupling reactions, where the nanospace within the support worked efficiently as a nano reaction field.²⁵ We expected that this nanospace structure composed of a silicon nanowire array (i.e., silicon nanowire array-stabilized Rh nanoparticle catalyst (SiNA-Rh)) would provide a highly efficient and reusable catalyst for the production of BHD via the hydrogenative decarboxylation of fatty acids (i.e. carboxylic acids).

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Moreover, we believed that the use of microwave irradiation for activation of the heterogeneous catalyst should be key to lowering the electric power consumption of this chemical catalytic process, as previously reported by coauthor Wada.²⁶ As microwaves improve the efficiency of industrial processes and have been recognized as a novel heating source in industry, Wang et al. investigated the effect of microwave drving on the behavior of biomass pyrolysis on a bench scale. They concluded that microwave drying is a technically and economically feasible pretreatment method for biomass fast pyrolysis when compared to conventional heating at 105 °C.27 In addition, Vongpradubchaihi et al. established a continuous microwave applicator technology and reported several advantages, including shortening of the processing time and a greater energy efficiency over various the product scales. ²⁸ Indeed, it has been reported that microwaves can reduce the energy cost of the drying process by 35% and reduce the defective rate by 50%.^{29,30} Furthermore, when Scuracchio et al. employed microwave heating in the preparation of pulverized rubber, they reported shorter process times at low temperature, and concluded that the glass transition temperature was lowered by microwave heating.³¹ Moreover, Sombatsompop et al. experimentally monitored the physical and mechanical properties of vulcanized natural rubber/carbon black/recycled rubber formulations,³² where they compared microwave heating with conventional heating in the vulcanization process. They found that the chemical structure of the two obtained rubber products differed. More specifically, with microwave heating, the vulcanization process was more efficient, and as a result, numerous practical applications and patents have been established.³³ In terms of sustainable development goals set by the United Nations, industrial heterogeneous catalytic processes based on microwave irradiation should be applied to not only biomass and polymer chemistry but also to chemical and catalytic reactions. As such, microwave received significant attention irradiation has in heterogeneously-catalyzed organic processes, although its industrial application is still under development.34



Scheme 1. Selective bio hydrofined diesel formation accompanied by the production of carbon monoxide from abundant biomass fatty acids and renewable hydrogen gas, catalyzed by a low loading of a reusable heterogeneous catalyst under microwave irradiation.

Thus, we herein developed a novel reusable supported nanospace catalyst, namely a silicon nanowire arraystabilized Rh nanoparticle catalyst (SiNA-Rh), which efficiently produced biodiesel fuel from biomass fatty acids using renewable H₂ gas under low energy consumption microwave conditions. Indeed, we found that the use of SiNA-Rh containing 0.05 mol% Rh (i.e., 500 mol ppm Rh) promoted the decarboxylation of a variety of carboxylic acids at 200 °C under microwave irradiation (~40 W) and a hydrogen pressure of 10 bar to give the corresponding alkanes, including BHD, in high yields. In this transformation, a one-carbon degraded alkane (A) was selectively produced without the formation of hydrocarbons such as **B1** and **B2** (Scheme 1). In addition, although carbon monoxide and carbon dioxide are possible co-products in this process, only carbon monoxide was obtained, which could be employed as an important and essential staple for the chemical industry. In addition, the developed SiNA-Rh catalyst was reused 20 times without any loss in catalytic activity (i.e., consecutive turnover number = 35000). SiNA-Rh was also applied in the decarbonylation of aldehydes in an Ar atmosphere to give the corresponding alkanes (including BHD) and carbon monoxide in high yields. Moreover, based on numerical calculations, the electric field distribution of the small area (nano order) of the catalyst surface was estimated to determine the effects of microwave irradiation on the functional groups of the SiNA-Rh catalyst.

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Figure 1. a) Photographic image of SiNA-Rh. b) SEM image of SiNA-Rh. c) Schematic representation of SiNA-Rh. d) and e) TEM images of the Rh nanoparticles on SiNA-Rh (scale bars = 20 and 5 nm, respectively). f) Particle size distribution of the Rh nanoparticles in SiNA-Rh ($\phi = 4.29 \pm 1.14$ nm). g) STEM image of SiNA-Rh. h) EDX image of the Rh nanoparticles in SiNA-Rh. i) Rh K-edge XANES spectra of Rh foil, Rh₂O₃, and SiNA-Rh. j) Fourier transform of the EXAFS of SiNA-Rh and the corresponding best fit.

RESULTS AND DISCUSSION

The silicon nanowire array was previously developed for silicon-based optoelectronics, fuel cells, solar cells, and photoelectrodes, and was prepared by metal-assisted catalytic etching to silicon wafers.³⁵ The silicon nanowire

array-stabilized rhodium nanoparticle catalyst was then readily prepared as follows. Initially, a silicon nanowire array (SiNA)³⁶⁻³⁸ (2" wafer) was treated with hydrofluoric acid to form a Si-H surface, which was dipped in an aqueous acetone solution of rhodium chloride to afford SiNA-Rh as a black plate (Figure 1(a)). Analysis of a cross-section of SiNA-Rh by scanning electron microscopy (SEM) showed the presence of a 'nano-forest' measuring <360 nm in width by 9 µm in height although we were not able to control the size (Figures 1(b) and 1(c)). In addition, transmission electron microscopy (TEM) observations showed that the Rh nanoparticles on the silicon array had a mean diameter of 4.29±1.14 nm (Figures 1(d)-1(f)). Furthermore, analysis by combined energy-dispersive X-ray spectrscopy and scanning transmission electron microscopy (EDX/STEM) indicated that the Rh species was well dispersed on the silicon nanowire array (Figures 1(g)-1(h)). In addition, Rh Kedge X-ray absorption near edge structure (XANES) analysis of SiNA-Rh was employed to investigate formation of the metallic Rh nanoparticles (Figure 1(i)). Indeed, the spectrum of Rh₂O₃ showed guite different features from those of Rh foil and SiNA-Rh. More specifically, the broader peaks of SiNA-Rh compared with those of Rh foil were attributed to the nanoparticle size. The best fit for extended X-ray absorption fine structure (EXAFS) analysis of SiNA-Rh was then obtained for the Rh-Rh first coordination shell (Figure 1(j)), and the fitted parameters were as follows: R factor: 0.001, coordination number: 7.3, Rh-Rh distance: 2.68 Å, and σ^2 : 0.006 Å². Since the ideal coordination number of the first coordination shell of bulk metallic Rh is 12, the lower coordination number in SiNA-Rh also indicated the formation of Rh nanoparticles. These observations thereby suggest that the desired silicon nanowire array-supported rhodium nanoparticle catalyst was successfully prepared.

With SiNA-Rh in hand, the hydrogenative decarboxylation of stearic acid (1a) was investigated using the nanoparticle catalysts, and the results are presented in Table 1. More specifically, the reaction of **1a** was carried out in the presence of 500 mol ppm Rh of SiNA-Rh in a hydrogen atmosphere (10 bar) at 200 °C (confirmed by a fiberoptic thermometer) with microwave irradiation (~40 W power to maintain a temperature of 200 °C) over 6 h. The decarboxylated BHD product heptadecane (2a) was selectively obtained in 47% yield (entry 1), but deoxygenated products such as octadecane (3a) and octadecanol were not detected. In addition, carbon monoxide, an important and essential staple for the chemical industry, was selectively obtained as a co-product without the formation of the undesired carbon dioxide. The formation of CO/CO₂ was checked with GC/PDHID. Since water was not detectable with GC/PDHID, we cannot check the mass balance of the formation of CO but the ratio of CO/CO₂. The recovered SiNA-Rh was then reused without any loss in catalytic activity, giving 2a in 41% and 57% yields after the 2nd and 3rd uses, respectively. In contrast, the reaction with SiNA-Pd was performed under similar conditions to give 2a in 32% yield (entry 2), while a

significantly lower yield was obtained in the second cycle following catalyst recovery (i.e., 12% 2a). Several other silicon nanowire array-stabilized metal nanoparticles were prepared for testing, and these were based on Pt (SiNA-Pt), bimetallic Pd and Pt (SiNA-PdPt), bimetallic PdRh (SiNA-PdRh), and bimetallic Pd and Ir (SiNA-PdIr) (entries 3-7). The reaction with SiNA-Pt was carried out under similar conditions to give 2a in a 38% yield (Entry 3). Although SiNA-PdPt gave 2a in a 49% yield, its reusability was extremely poor (i.e., 15% 2a on the 2nd use, entry 4). Moreover, the yields obtained using SiNA-PdRh and SiNA-PdIr were relatively poor, i.e. 37 and 36%, respectively (entries 6 and 7), and no reaction was observed when the SiNA catalyst without metal deposition was employed (entry 8). Other rhodium catalysts were also investigated for this transformation (entries 9-12); however, no reaction took place in the presence of Rh/Si (entry 9). This result suggests that the silicon nanostructure of the prepared SiNA is key to the catalytic process. Moreover, the general heterogeneous catalysts Rh/C, Rh/Al₂O₃, and the homogeneous RhCl₃•3H₂O catalyst gave 2a in low yields (22, 0, and 0%, respectively) (entries 10-12), and reused Rh/C gave a <1% yield of 2a, indicating that the heterogeneous SiNA-Rh catalyst exhibited a higher catalytic activity than its homogeneous RhCl₃ counterpart and common heterogeneous catalysts. In addition, to indicate the importance of hydrogen gas and microwave heating in this reaction, a number of control experiments were conducted. More specifically, the reaction under N_2 without the use of H_2 did not proceed (Entry 13). Surprisingly, when the reactions were performed at 200 and 300 °C under traditional thermal heating conditions (oil bath at 200 °C, sand bath at 300°C), no decarboxylative products were obtained (0% yield) (entries 14 and 15). Rhodium particles on an original p-type silicon wafer (Rh/Flat Si) were also prepared for investigating significance of silicon nanowire array in the reaction. Reactivity and reusability of Rh/Flat Si was lower than those of SiNA-Rh (Entry 16).

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Table 1. Catalytic screening for the hydrogenative decarboxylation of 1a using SiNA-metal nanoparticles (MNPs)^a

С ₁₇ Н ₃₅ -СО ₂ Н - 1а		catalyst	► C ₁₇ H ₃₅ −H +	+ C ₁₇ H ₃₅ -CH ₃ + CO + (
		H ₂ (10 bar) 200 °C, 6 h microwave irradiation	BHD product 2a	by-product 3a	Fischer- Tropsch substrate
Entry	Catalyst (mol ppm)		2a yield (%) 1st, 2nd, 3 rd use of catalysts	3a yield (%) 1st, 2nd, 3 rd use of catalysts	CO:CO ₂
1	SiNA-Rh	(500)	47, 41, 57	0, 0, 0.2	100:0
2	SiNA-Pd	(670)	32, 12, -	0, 0, -	100:0
3	SiNA-Pt (690)	38, 22, -	0, 3, -	100:0
4	SiNA-Pd ₀	.65Pt _{0.35} (660)	49, 15, -	0, 0, -	100:0
5	SiNA-Pd ₀ (410)	_{.81} Rh _{0.19}	37, 33, 33	0, 0, 0	100:0
6	SiNA-Pd ₀	_{.92} Ru _{0.08}	36, 25, 0	0, 0, 0	100:0

	(300)			
7	SiNA-Pd _{0.98} Ir _{0.02} (680)	24, -, -	0, -, -	100:0
8	SiNA (no metal)	0, -, -	0, -, -	-
9	Rh/Si (6500)	0, -, -	0, -, -	-
10	Rh/C (500)	22, <1, -	1, 0, -	100:0
11	Rh/Al ₂ O ₃ (500)	0, -, -	0, -, -	-
12	RhCl ₃ •3H ₂ O (560)	0, -, -	0, -, -	-
13 ^b	SiNA-Rh (500) (no H ₂)	0, -, -	0, -, -	-
14 ^c	SiNA-Rh (500) (oil bath at 200°C)	0, -, -	0, -, -	-
15 ^d	SiNA-Rh (500) (sand bath at 300 °C)	0, -, -	0, -, -	-
16	Rh/Flat Si (500)	34, 12, 2	7, 19, 0	(not checked)

^a **1a** (1 mmol equiv), 200 °C, 6 h, H₂ (10 bar), microwave irradiation (~40 W; using a CEM microwave reactor) in a glass vial, ^b under N₂ without H₂ gas, ^c thermal heating at 200 °C, and ^d thermal heating at 300 °C.

Since the catalytic activity of SiNA-Rh was superior to those of the other catalysts, it was selected for application in the hydrogenative decarboxylation of various carboxylic acids (1). Thus, when the reaction of 1a was carried out over 24 h under the above conditions, complete conversion was achieved to afford 2a in 94% yield without by-product formation being observed (Table 2, entry 1). In this reaction, only carbon monoxide was produced, with no carbon dioxide being detected. Arachidic acid (1b) and heptadecanoic acid (1c) were also converted to nonadecane (2b) and hexadecane (2c) in yields of 93% and 95%, respectively (entries 2 and 3). In addition, palmitic acid (1d), pentadecanoic acid (1e), and myristic acid (1f), which are the most common fatty acids in animals and plants, were quantitatively converted to the corresponding BHDs, pentadecane (2d), tetradecane (2e), and dodecane (2f) without the formation of by-products (entries 4-6). Furthermore, oleic acid (1g) and linoleic acid (1h), the most abundant unsaturated fatty acids, were decarboxylated to yield BHD 2a in 98% and 92% yields, respectively (entries 7 and 8). Moreover, the reaction of a dicarboxylic acid, namely octadecanedioic acid (1i), also proceeded effectively to give the desired hexadecane in 92% yield (entry 9), while the carboxylic ester methyl stearate (1j) was selectively converted to heptadecane (2a) in the presence of water (79% yield, entry 10). These results indicate that the preparation of jet and rocket fuel (kerosene = $C_{10}-C_{15}$) can be readily prepared using this system. It was also found that a secondary carboxylic acid 1k was applicable as a substrate to afford 2d in 78% yield (entry 11). Importantly, it should be noted that carbon monoxide was the only by-product detected in the reactions listed in Table 2.

Table 2. Hydrogenative decarboxylation of carboxylic acids (1) using SiNA-Rh^a

R-CC	$ \begin{array}{c} \text{SiNA-Rh} \\ (500 \text{ mol ppm Rh}) & \qquad $	H + R-C uct by-pro 3	H ₃ + (oduct	CO + CO ₂
Entry	Substrate 1 (R)	2 yield (%)	3 yield (%)	CO:CO ₂
1	1a C ₁₇ H ₃₅	94	0 (<1)	100:0
2	1b C ₁₉ H ₃₉	93	2	100:0
3	1c C ₁₆ H ₃₃	95	2	100:0
4	1d C ₁₅ H ₃₁	94	0.2	100:0
5	1e C ₁₄ H ₂₉	90	3	100:0
6	1f C ₁₃ H ₂₇	95	2	100:0
7	1g (<i>Z</i>)-CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇	98 (R = C ₁₇ H ₃₅)	0.3	100:0
8	1h (9- <i>Z</i> , 12- <i>Z</i>) CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇	92 (R = C ₁₇ H ₃₅)	0.4	100:0
9	1i HOOC(CH ₂) ₁₆	92 (R = C ₁₆ H ₃₃)	0	100:0
10 ^b	$\mathbf{1j} = CH_3(CH_2)_{16}\text{-}COOCH_3$	79	1	100:0
11	1k CH ₃ (CH ₂) ₇ CH(CO ₂ H)(CH ₂) ₅ CH ₃	78	0	100:0

^{*a*} **1** (0.5 mmol equiv), SiNA-Rh (0.05 mol%), 200 °C, 24 h, H₂ (10 bar), microwave irradiation (~40 W; using a CEM microwave reactor) in a glass vial. ^{*b*} Methyl stearate (**1**j) (0.5 mmol equiv), H₂O (58.9 mg), 200 °C, 48 h, H₂ (10 bar), microwave irradiation (~40 W).

Following confirmation of the acceptable catalytic activity and substrate scope, the reusability of SiNA-Rh was investigated for the reaction of stearic acid (Figure 2) under the conditions outlined in Table 1. Surprisingly, SiNA-Rh was suitable for reuse 20 times without any loss in catalytic activity: 2a was obtained in yields of 89, 85, 84, 86, and 82% following the 2nd, 3rd, 10th, 15th, and 20th uses, respectively. To the best of our knowledge, this is the first successful example of a high catalyst reusability in the hydrogenative decarboxylation reaction. This result indicates that BHD can be readily and sustainably produced by the reusable SiNA-Rh catalyst under mild conditions while lowering the power consumption required for this transformation. Leaching tests were then conducted on the reaction mixture, where only 0.019 ppm Rh was detected by ICP-MS (for further details, see SI section 4). This indicates that only 0.0066% of the Rh present in SiNA-Rh was leached out. Hot filtration tests were also performed, and the filtrate was not observed to promote the reaction (see SI section 4). Moreover, although the interval between 6th use and 7th use of the catalytic reusability investigation was eight months (SiNA-Rh was left under atmospheric conditions during 8 months.), the reusability of SiNA-Rh was fine to give 2a in 83% (6th use) and 88% (7th use) yield.



Figure 2. Reusability of the SiNA-Rh catalyst in the hydrogenative decarboxylation of **1a**. Reaction conditions: 0.5 mmol stearic acid, H_2 (10 bar), 200 °C, 24 h, microwave irradiation (~40 W) in a glass vial.

As shown in Entries 1, 13, and 14 in Table 1, we were surprised to find that microwave heating promoted the reaction while traditional thermal heating did not. The effect of microwave irradiation was therefore investigated by altering the electric power of the microwave irradiation at 200 °C (Scheme 2). As shown in Table 1, entry 1, the reaction using 40 W of microwave irradiation gave **2a** in a 57% yield when a glass vial was employed. As quartz is known to absorb very little microwave irradiation, the use of a quartz vial was also examined. In this case, it was necessary to irradiate with 100 W of microwave irradiation to maintain the reaction temperature at 200 °C; however, the reaction proceeded to afford **2a** in 73% yield. These results suggest the non-thermal effect of microwave and/or selective heating to SiNA-Rh in this catalytic transformation.

	catalyst	HH
1a	H ₂ (10 bar) 200 °C, 6 h microwave irradiation	2a
thermal heating i 40 W (microwave 100 W (microwave	in a glass vial e in a glass vial) ve in a guartz vial)	0% yield 57% yield 73% yield

Scheme 2. Decarboxylation of **1a** by thermal heating, microwave irradiation at 40 W (in a glass vial), and at 100 W (in a quartz vial) (using a CEM microwave reactor).

Since microwaves are a type of electromagnetic wave composed of an electric field and a magnetic field, an electric- and magnetic-field separable microwave reactor was used for the purpose of this study (Scheme 3). In general, an electric field supplies energy to molecular polarization, while a magnetic field supplies energy to spins and free electrons. Therefore, if an electric field and a magnetic field are separated and heated, we can study which energy path is effective for reaction acceleration. By employing cavity resonator, it was possible to irradiate the sample with either a pure electrical or pure magnetic field.

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When such reactions under electric- and magnetic-field irradiation conditions (employing *E*-max in TM₀₁₀ mode and *H*-max in TM₁₁₀ mode,³⁹ respectively) were carried out at 200 °C for 6 h, 12 and 25 W microwave irradiation were required to produce **2a** in yields of 65 and 46% yield, respectively. These results suggest that the electric field is key to efficient heating (12 W vs. 25 W) and also to promoting the reaction (65% vs. 46% yield). For comparison, when the reaction of **1a** was carried out using a CEM microwave irradiation was required to maintain the temperature at 200 °C and to afford **2a** in a 73% yield.

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46% yield

Scheme 3. Decarboxylation of **1a** using electric and magnetic field microwave irradiation (in 6 h) in a quartz vial under electric- and magnetic-field irradiation conditions (employing *E*-max in TM_{010} mode and *H*-max in TM_{110} mode, respectively), and using a CEM microwave reactor.

magnetic field (25 W)

 Table 3. Complex dielectric constants for the various components at 1.0 GHz^a

Entry	Real part	Imaginary part	Tan δ
Silicon	44.43	9.695	0.2182
Stearic acid (1a)	2.08	0.001	0.0007

^{*a*} Complex dielectric constant measured by cavity perturbation methods (Measured by KEYCOM Corp., Tokyo, Japan).

As outlined in Table 3, the dielectric loss tangents of stearic acid and the silicon substrate are 0.0007 and 0.2182, respectively. Moreover, the microwave heating of stearic acid (1a) and the silicon wafer in a guartz vial at 40W using a CEM microwave reactor gave temperatures of 50 and 145 °C, respectively, as detected by an infrared thermometer. These results indicate that the microwave electric field mainly heats the silicon substrate, and so the presence of hot spots in the solution is unlikely since stearic acid absorbs little microwave energy from the viewpoint of heat transfer theory. The energy concentration structures of the silicon substrate and the stearic acid interface were therefore considered by numerical calculations. It was assumed that some phenomenon responsible for accelerating the reaction exists at the silicon-stearic acid interface.

Indeed, this phenomenon has been discussed in the microwave chemistry community, and it can be explained by considering that the microwave electric field selectively supplies energy to functional groups or rotation levels.^{40,41} To investigate the contribution of this phenomenon on our system, the spatial distribution of the electric field intensity around the surface of the Si nanostructure was simulated using the Finite Element Method. The simulation model contains the tetragonally-aligned Si rods of 50 nm diameter as shown in Figure 3.42 The distance (d) between the rod was varied between 5 and 180 nm, and a microwave electric field with a frequency of 2.45 GHz and an intensity of 1 [V/m] was introduced along the z direction in the model. Although the wavelength of the incident electromagnetic wave (which is ~122.36 [mm] in free space) is significantly larger than the size of the Si rod, the incident microwave generates enhanced electric fields. Similar phenomena are known in the light region.43,44 Numerical calculations therefore indicated that the nanostructure amplifies the intensity of the electric field, and its amplification rate increases with a decreased rod spacing.

The relationship between the amplified electric field and the enhanced chemical reaction rate was then considered in more detail. Thus, the SiNA surface is decorated with Rh nanoparticles, and Si-OH, Si-O, and Rh-Si bonds are present on its surface and these functional groups present have polarities. The microwave electric field is enhanced several times by the structure of the Si rod as calculated in Figure 3, the enhanced microwave field combined with these functional groups and charge transfers were driven at this surface. For the physical image, the motion of the electric _charge is not like direct current, but like rotation as observed in microwave heating of water ⁴⁵. This charge transfer is well known as the primary heating mechanism of microwaves, ⁴⁶ which forms local heating. It is well known that high selectivity of microwave energy creates local heating on the order of nm, 47-49 and since there is thought to be a reaction where a H₂ become into protons and Rh-H on the surface, the local heating accelerates the reaction. In addition, the amplified electric field may also enhance these functional group activities to improve the reaction rate.

As mentioned above, numerical simulations indicate that the enhancement of the electric field becomes larger upon decreasing the distance between the rods (Figure 3). If this reaction is accelerated as a result of enhancement of electrons and protons by an electric field, the reaction rate of our system would be expected to be enhanced by increasing the microwave electric field or decreasing the distance between rods. This increasing of reaction yield is often observed and known as microwave effect ⁵⁰. These results thereby account for the fact that only the silicon nanowire array-stabilized Rh catalyst (SiNA-Rh) efficiently promoted the reactions (entry 1 vs. entries 9–12, Table 1).

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Figure 3. Numerical calculation results for the electric field strength between Si rods (ϕ 50 [nm] × h) in electromagnetic waves (scattered electric field: 1 [V/m], wave vector of the background field: [0,0,-1], rod length h: 10000 [nm]). The shorter the rod spacing, the stronger the microwave electric field.

A plausible catalytic pathway for this decarboxylation process has been proposed, as shown in Figure 4.^{51–53} Two carboxylic acids (**A**) are converted to a single carboxylic anhydride **B**, whose oxidative addition to SiNA-Rh (Rh/Si_{nano}) gives an acyl rhodium carboxylate **C**. The insertion of hydrogen to **C** gives the acyl rhodium hydride **D** in addition to regenerating **A**. Subsequent decarbonylation followed by β -hydride elimination gives **E**, and intramolecular hydrogen transfer in **E** affords the desired alkane (BHD) **F** and carbon monoxide as a co-product, while also regenerating the SiNA-Rh (Rh/Si_{nano}) catalyst.



Figure 4. Plausible catalytic pathway for the decarboxylation reaction using SiNA-Rh.

Since carboxylic anhydride **B** is a possible intermediate for the catalytic pathway, the decarboxylation of **1a** was performed using pivalic anhydride (Piv₂O), which should react with **1a** to form pivalic stearic anhydride. Indeed, the reaction of **1a** with 1.5 mol equiv of Piv₂O in the presence of 500 mol ppm Rh of SiNA-Rh in a hydrogen atmosphere (10 bar) at 200 °C with microwave irradiation (~40 W power to maintain a temperature of 200 °C) gave 2a in 89% yield after 6 h (Scheme 4), indicating that the reactivity of this system was higher than that in the absence of Piv₂O (89%) vs. 47%, Table 1, entry 1). The formation of a carboxylic anhydride therefore appears to be key to this reaction process. In addition, a suitable catalyst reusability was achieved under these reaction conditions, with 2a being obtained in yields of 89, 88, 87, 87, 89, 86, and 86% after the 2nd, 3rd, 4th, 5th, 6th, 8th, and 10th uses, respectively. As in the above reactions, only carbon monoxide was formed as a co-product.



Scheme 4. Decarboxylation of 1a in the presence pivalic anhydride (Piv₂O).

As indicated previously in Figure 2, compound **D** is also a possible intermediate in the proposed catalytic cycle; therefore, we envisioned that the decarbonylation of aldehydes should also proceed to produce BHD and CO.54,55 We therefore attempted the decarbonylation of octadecanal (4a) using 500 mol ppm Rh of SiNA-Rh at 150 °C over 24 h under Ar. This reaction afforded heptadecane (2a) in a 99% yield after the 1st catalyst cycle and 98% after the 2nd use (Scheme 5). In this reaction, microwave heating was not essential to promote the reaction although microwave heating provided higher reactivity (In 6 h: with microwave, 2a 70% yield; with conventional heating, 2a 11% yield. In 24 h: with microwave, 2a 95% yield; with conventional heating, 2a 99% yield)). These results suggest that microwave irradiation contributes especially to the process at some point between compounds **B** and **D** (and between **D** and **C** a little bit). Finally, we note that E could also be an intermediate in the plausible catalytic pathway since heptadecane was detected in the course of the optimization reaction using stearic acid (**1a**).



Scheme 5. SiNA-Rh-catalyzed decarbonylation of aldehyde **4** under Ar.

CONCLUSION

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We herein reported the development of a novel silicon nanowire-stabilized rhodium nanoparticle catalyst (SiNA-Rh), which smoothly and selectively promoted the hydrogenative decarboxylation of fatty acids under mild conditions to yield the corresponding alkanes for producing bio hydrofined diesel (BHD) in high yields with the formation of only carbon monoxide (an important and essential staple for the chemical industry) as a co-product. More specifically, SiNA-Rh (500 mol ppm) selectively promoted the hydrogenative decarboxylation reaction at 200 °C under microwave conditions (~40 W) in a H₂ atmosphere (10 bar) to afford the corresponding alkanes in high yields. We also found that this heterogeneous catalyst could be reused over 20 cycles without any loss in catalytic activity. To the best of our knowledge, this is the first report of such an excellent reusability of a supported catalyst in this reaction. During our investigations into the catalytic activity and mechanism, we found that the decarbonylation of aldehydes also proceeded smoothly. The role of microwave irradiation in this reaction was also examined, and it was found that the microwave electric field influenced the silicon nanowire array to efficiently promote the reaction of interest. Since this catalytic system exhibits a greater efficiency and higher reusability than similar catalysts, we expect that it will be applicable to a range of chemical and industrial processes.

ASSOCIATE CONTENT

Supporting Information Available: Preparation of SiNA-Rh and other catalysts. ICP-MS analysis. General procedure for the decarboxylation and decarbonylation. Catalyst reuse experiments. Characterization of the products (including ¹H and ¹³C NMR charts).

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ACS Paragon Plus Environment

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8	С ₁₇ Н ₃₅ -СО ₂ Н		$\sim C_{17}H_{35}-H +$	$C_{17}H_{35}-CH_{3}$	$+ CO + CO_2$
9		H ₂ (10 bar)		la su	F ielder
10	1a	200 °C, 6 h	BHD product	by-product	Fischer-
11	Tu	microwave	2a	3a	Tropsch
12		irradiation			substrate
12		Induction			
13		-			
14		I	able 1: Scheme		
15		11672	4mm (300 v 303 F		
16		11022	411111 (300 X 303 L	/F1)	
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60		ACS Par	agon Plus Environr	nent	

ACS Catalysis

R-CO ₂ H 1	SiNA-Rh (500 mol ppm Rh) H ₂ (10 bar) 200 °C, 24 h microwave irradiation	$R-H + R-CH_3 + CO + CO_2$ product by-product 2 3
	Table 2:	Scheme
	116x23mm (3	300 x 304 DPI)
	ACS Paragon P	lus Environment





Figure 2: Scheme



ACS Paragon Plus Environment



1	
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7	SiNA-Rh
8	(500 mol ppm Rh)
9	
10	H_{2} (10 bar)
10	
11	1a 200°C, 6 n 24
12	microwave
13	irradiation
14	in a quartz vial
15	
16	
17	CEM microwave reactor 73% yield
18	electric field (12 W) 65% yield
19	magnetic field (25 W) 46% yield
20	
21	Scheme 3
22	
23	112x49mm (301 x 301 DPI)
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59	ACS Daragon Dlug Environment
60	ACS Paragon Plus Environment







Figure 3 77x77mm (179 x 179 DPI)



ACS Catalysis

2a

10th use 86%

Scheme 4

111x63mm (300 x 301 DPI)

2a:

➤ product + by-product + CO + CO₂

3a

1st use 89%, 2nd use 93%, 3rd use 88%

4th use 87%, 5th use 87%, 6th use 89%

7th use 87%, 8th use 86%, 9th use 84%



1			
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7		SiNA-Bh	
8		(500 mol ppm Bh)	
9	C ₁₇ H ₃₅ -CHO		$\sim C_{17}H_{35}-H + CO$
10	17 00	Ar (1 bar)	17 00
11	4	150 °C 24 h	2a
12		100 0, 2111	1st use: 99%
13			2nd use: 98%
14			
15		Scheme 5	
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18		96x25mm (300 x 301 DPI)	
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60		ACS Paragon Plus Environmer	nt

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