

## Hydrogen Production

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# Rapid Production of High-Purity Hydrogen Fuel through Microwave-Promoted Deep Catalytic Dehydrogenation of Liquid Alkanes with Abundant Metals

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Dedicated to Professor Roald Hoffmann on the occasion of his 80th birthday

**Abstract:** Hydrogen as an energy carrier promises a sustainable energy revolution. However, one of the greatest challenges for any future hydrogen economy is the necessity for large scale hydrogen production not involving concurrent CO<sub>2</sub> production. The high intrinsic hydrogen content of liquid-range alkane hydrocarbons (including diesel) offers a potential route to CO<sub>2</sub>-free hydrogen production through their catalytic deep dehydrogenation. We report here a means of rapidly liberating high-purity hydrogen by microwave-promoted catalytic dehydrogenation of liquid alkanes using Fe and Ni particles supported on silicon carbide. A H<sub>2</sub> production selectivity from all evolved gases of some 98 %, is achieved with less than a fraction of a percent of adventitious CO and CO<sub>2</sub>. The major co-product is solid, elemental carbon.

Hydrogen offers the prospect of a highly effective fuel for future sustainable energy, not only because of its intensive energy density per unit-mass but also because its combustion produces no environmentally damaging CO<sub>2</sub> at its point-of-use.<sup>[1]</sup> Hydrogen is presently manufactured on an industrial

scale by steam reforming or partial oxidation of methane and to a lesser degree by gasification of coal.<sup>[2]</sup> However, these processes also generate significant quantities of CO<sub>2</sub>, with obvious attendant environmental problems. The utilization of solar energy now yields increasing amounts of hydrogen by the splitting of water, as does the harnessing of other sources of natural energy.<sup>[3]</sup> But even if the photocatalytic or electrolytic breakdown of water could be greatly improved to produce the necessary huge quantities of hydrogen, the resulting challenge of its safe storage and rapid release for immediate use in fuel cells, for example, is problematic.<sup>[4]</sup>

An alternative platform is to utilize the high intrinsic hydrogen content of fossil fuel hydrocarbons but in such a way as to rapidly release only their constituent hydrogen without any CO<sub>2</sub> production. Such CO<sub>2</sub>-free hydrogen production from hydrocarbons has been advanced through pioneering studies on the catalytic thermolysis of methane and petroleum-range hydrocarbons.<sup>[5]</sup> Our recent study has also established that ruthenium metal particles catalytically dehydrogenate solid hydrocarbon wax through microwave promotion.<sup>[6]</sup> Liquid hydrocarbons possess considerable manipulative convenience as compared to their solid or gaseous homologues,<sup>[7]</sup> and here we demonstrate that microwave-promoted deep dehydrogenation of various liquid-range alkanes (from C<sub>9</sub> to C<sub>17</sub>) using the abundant, inexpensive metal catalysts iron or nickel, and alloys of these metals, supported on silicon carbide, provides a highly effective and rapid route to the production of high-purity hydrogen.

The microwave-promoted catalytic dehydrogenation of liquid hydrocarbon was investigated using a purpose-built microwave cavity system embedded within a trickle-column reactor containing the supported metal catalysts. The resulting products were analyzed quantitatively by gas chromatography (GC) (see the Supporting Information for complete experimental details).

Upon exposure to microwaves, all liquid hydrocarbons were rapidly and deeply dehydrogenated to H<sub>2</sub>, solid carbon and minor products (Figure 1). We describe our results in terms of the volume % (or selectivity) of the product composition in the exit gases and we selected hexadecane (C<sub>16</sub>H<sub>34</sub>) as the prototypical alkane for our detailed study, because of its close similarity to hydrocarbon components of

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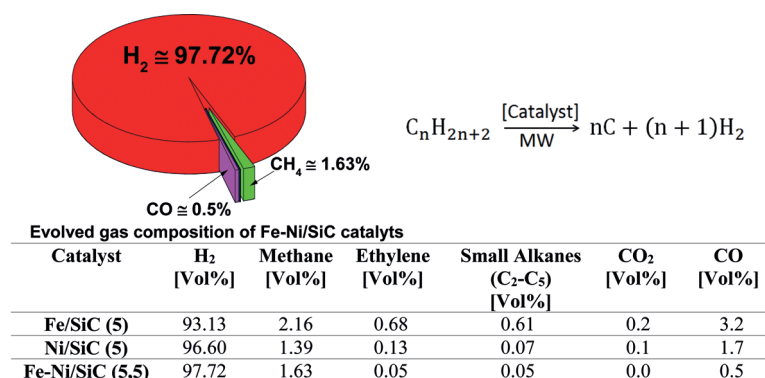
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**Figure 1.** Evolved gas composition of representative catalysts for microwave-promoted dehydrogenation of hexadecane (C<sub>16</sub>H<sub>34</sub>). The results show three catalysts of 5 wt.% Fe/SiC, 5 wt.% Ni/SiC and (5 wt.%-Fe, 5 wt.%-Ni) Fe-Ni/SiC. The catalyst was mixed with 0.5 mL of hexadecane and the sample was subjected to microwave irradiation for 30 minutes.

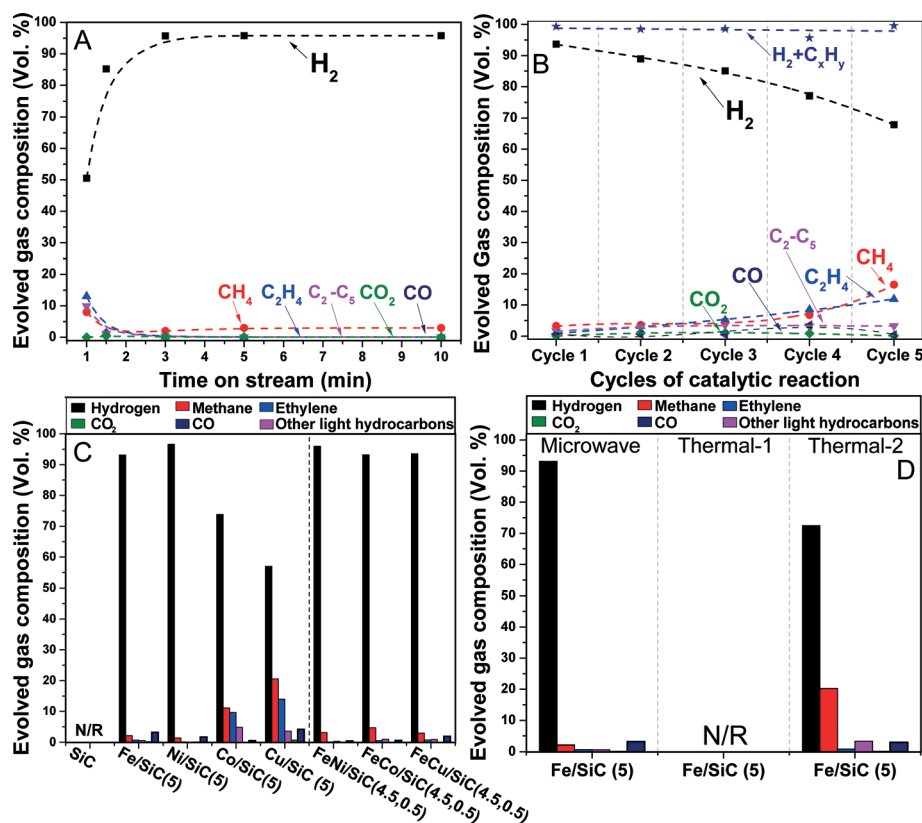
diesel. A high purity H<sub>2</sub> stream was obtained for microwave promoted Fe catalyzed dehydrogenation of hexadecane. Using Ni catalysts or an alloy of Fe and Ni showed even higher H<sub>2</sub> selectivity. The highest H<sub>2</sub> selectivity was observed with a Fe-Ni alloy catalyst reaching levels of ca. 98 vol.%. Low levels of CO<sub>x</sub> were produced (detected by GC at only ca. 0.5 vol.%). Liquid hydrocarbons from C<sub>9</sub> to C<sub>17</sub> were investigated and showed similar results with the H<sub>2</sub> concentration in the exit gas of > 90 vol.% and less than a fraction of a percent of CO<sub>2</sub> (complete data sets are given in Table S1).

The data for a representative “time-on-stream” experiment for Fe/SiC catalyst mixed with hexadecane are illustrated in Figure 2A. High-purity hydrogen was rapidly evolved from the onset of the microwave-promoted catalytic dehydrogenation of hexadecane. The hydrogen concentration rapidly increased over a period of ca. 3 minutes to a yield of 96 vol.%. Such a rapid evolution of hydrogen could help solve the challenge of slow start-up found for on-board steam reforming or partial oxidation of methane, for example, and enable an instant H<sub>2</sub> supply for fuel cell vehicles.

Importantly, the catalyst system can also function efficiently in the deep dehydrogenation of hexadecane for several catalytic cycles through successive additions

of fresh aliquots of substrate to the reactor system; a typical sequence is shown in Figure 2B. Through successive cycles of the catalytic reaction, both the amount of evolved hydrogen and its selectivity gradually decreased, whilst corresponding methane and ethylene concentrations gradually increased. We attribute this to advancing carbon deposition on the metal catalyst active sites, as will be evident in our electron microscopy studies. Importantly, although less hydrogen was produced in the later cycles, the catalyst still remained active through the 5 cycles of substrate additions.

Different metals supported by SiC exhibited various levels of performance under microwave irradiation with somewhat different product distributions. However, elemental hydrogen always remained the dominant product (Figure 2C). Iron or nickel catalysts showed extremely high hydrogen selectivity (ca. 93 vol.% and 96 vol.%, respectively), while other metals (Co, Cu, Pt and Ru) had noticeably reduced values (Table S2). Iron-based bimetallic metal catalysts (Fe-X/SiC, X = Ni, Co, Cu and Ru) were investigated.



**Figure 2.** A) A representative experiment with 0.5 mL hexadecane at 5 wt.% Fe/SiC catalyst for “time-on-stream” evaluation. Each microwave irradiation experiment was carried out for 30 minutes and the gaseous products were collected and analyzed after 1, 1.5, 3, 5 and 10 minutes. B) Recharging catalytic cycles for 0.5 mL hexadecane at 5 wt.% Fe/SiC catalyst. 0.5 mL hexadecane was added for each successive cycle (30 min irradiation). C) Comparison of different metals and binary metals operating under the same conditions of one cycle of substrate and products analyzed after 10 minutes. D) Comparison of microwave and conventional thermal method. For the microwave method, the average and the highest temperature recorded were 462 °C and 617 °C, respectively. For the thermal method, the temperature was set for 550 °C. “N/R” means no reaction was observed under these conditions. The number in parentheses after catalyst shows the metal content, wt. %.

The Fe-Ni/SiC catalyst shows an extremely high hydrogen selectivity of ca. 98 vol. % and CO<sub>2</sub> formation was zero. We found that the presence of nickel improves the dispersion of metal particles on the SiC surface and appears to suppress the formation of iron carbides, implicated in the gradual reduction in catalytic activity.

For comparison with our microwave-promoted experiments, a set of thermal dehydrogenation reactions were investigated through two different procedures (Figure 2D). Labelled Thermal-1, an oil pre-loaded Fe/SiC sample was subjected to a pre-heated furnace (550°C), while in the Thermal-2 procedure, the Fe/SiC catalyst (without fuel) was pre-heated in the furnace to 550°C and the hexadecane was then carefully introduced to the hot catalyst bed by a syringe. The lack of H<sub>2</sub> formation over the oil pre-loaded Fe/SiC catalyst under conventional thermal reaction conditions (Thermal-1), but very high yield of H<sub>2</sub> under microwave irradiation illustrates that the high H<sub>2</sub> selectivity obtained over metal/SiC catalyst is strongly dependent on the use of microwaves. The reactions may be catalyzed by microwaves at the temperature below the (bulk) boiling point of the fuel, while the thermal process necessarily gives rise to fuel vaporization before any dehydrogenation on the catalyst surface. A second hypothesis could be that the rapid heating of microwave energy converts part of the hydrocarbons before losing the liquid by vaporization, suggesting that two main processes are taking place simultaneously: vaporization and chemical reactions. Vaporization predominates in the thermal experiment because of slow heating of the catalyst particle, whilst the microwave-promoted catalysis proceeds rapidly, probably as a consequence of the rapid heating of the particles by microwave radiation. We note that SiC supported catalysts have very low surface areas, typically less than 2.0 m<sup>2</sup> g<sup>-1</sup>. Although, the Fe/SiC catalyst can clearly catalyse the dehydrogenation of hexadecane under pre-heated conditions (Thermal-2), the hydrogen selectivity is noticeably different.

Unlike conventional thermal fluid catalytic cracking (FCC), our results show that the cleavage of C–H bonds is strongly preferred upon microwave irradiation or promotion. Our previous studies suggested that the scission of C–H bonds during dehydrogenation could take place through a consecutive mechanism.<sup>[6]</sup> Dehydrogenation steps occur on the metal catalyst surface to give adsorbed intermediates before the cleavage of C–H. Adsorbed species with metal–C bonds and subsequent cleavage of C–H leads to the formation of H<sub>2</sub> and carbon. Meanwhile, the minor products of small hydrocarbons may be generated through the hydrogenation of developing carbon residues or directly via a cracking process.<sup>[8]</sup> Clearly, further studies are needed to ascertain the precise catalytic processes.

The presence of high-frequency electromagnetic fields makes microwave systems more complex and challenging to understand.<sup>[9,10]</sup> We believe that the extremely high hydrogen selectivity obtained in these studies may be a direct result of the intrinsic response of the metal catalysts under microwave irradiation.

The intrinsic dielectric properties of individual metal particle catalysts are clearly a critical factor affecting its

response to incident microwave irradiation. These properties have been carefully characterized by cavity perturbation measurements under both room temperature and high temperature conditions (Table S3 and Figure S6). Although no simple dependency has been found between the so-called loss tangent ( $\tan\delta$ ) and the product distributions, microwave irradiation clearly gives higher product selectivity as compared to conventional thermal reactions (Figure 2D). However, the dielectric properties of the catalysts are also temperature dependent, which could alter any trend observed at a single temperature. We find that the dielectric property of metal catalysts showed a similar trend with increasing temperature. A higher loss tangent was obtained at higher temperatures, but no clear differences were observed for the dielectric constant ( $\epsilon'$ ). Unlike carbon based catalyst materials which can be highly efficient absorbers of electromagnetic energy, for metal/SiC catalysts, various polarization and dissipation mechanisms clearly contribute to drive the reactions under microwave irradiation which lead to the high hydrogen selectivity.

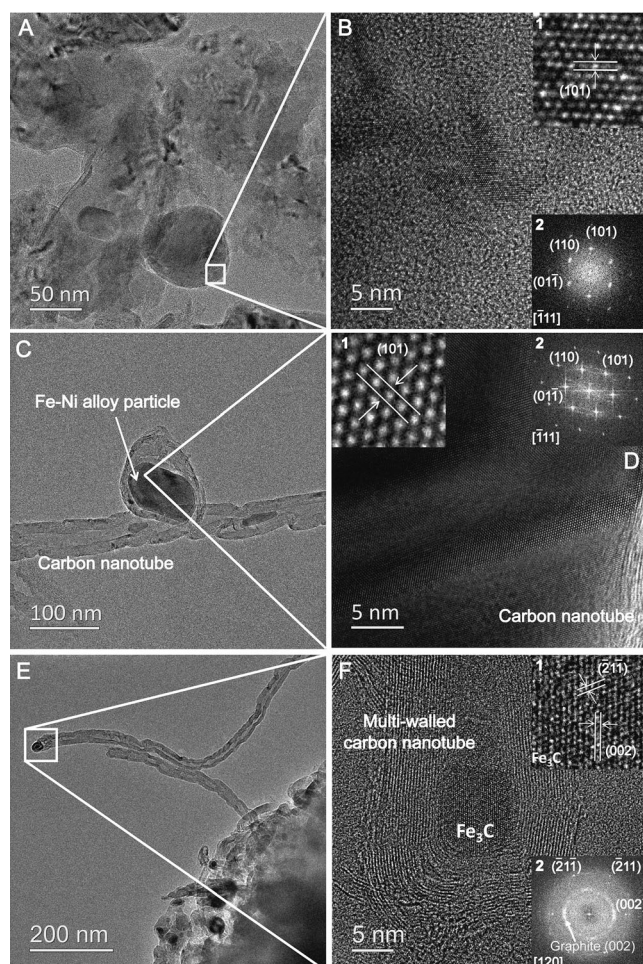
In relation to microwave field effects, the applied microwave electric field causes highly non-uniform field distributions in the catalyst bed, leading to regions of high electric field on the surfaces of metal particles on the SiC, consequently, both an (induced) electron-rich and strong polar medium can be created that could enhance the polarization of, for example, a C–H bond and subsequently the hydrogen formation. The complete cleavage of C–H via two mechanisms of oxidative addition and electrophilic substitution are accelerated by microwave irradiation which leads to the high hydrogen selectivity.<sup>[11]</sup> The high thermal conductivity and mechanical strength of SiC, together with a clearly reduced tendency to yield oxygenated products, are also considered important. These factors contribute by restricting the formation of by-products under microwave irradiation by avoiding any thermal degradation to the support during the reactions and quickly achieving a thermal balance in the system.<sup>[12]</sup>

The catalyst particles were examined by X-ray diffraction and high resolution transmission electron microscopy both before and after microwave treatment. Metallic iron, nickel and iron-nickel alloy particles, having typical particle diameters less than 150 nm, have been identified in fresh samples (Figure 3A and Figure S3).

Following the microwave-promoted catalytic decomposition of hexadecane, multi-walled carbon nanotubes that encapsulate some of the metal nanoparticles were found (Figure 3C and 3E). Iron carbide was observed in spent Fe/SiC catalyst but not in FeNi/SiC catalyst, which suggests—importantly—that the presence of Ni can suppress the formation of iron carbide (Figure 3D and 3F). These results are consistent with data obtained from XRD (Figure S3 and S4).

Thus, the key challenge of rapid production of, and high selectivity towards, H<sub>2</sub> production has been demonstrated using resonant microwave-electric field irradiation applied in a laboratory device, typically achieving >98 % H<sub>2</sub> purity. Such a rapid and selective production of hydrogen from liquid hydrocarbon alkanes reveals a powerful new platform for hydrogen production. We believe these findings represent





**Figure 3.** Representative high resolution transmission electron microscopy (HRTEM) images of 5 wt. %Fe, 1 wt. %Ni FeNi/SiC before (A, B) and after (C, D) microwave-promoted catalytic decomposition of hexadecane. A, C) Low magnification transmission electron microscopy (TEM) images of FeNi/SiC before and after microwave treatment, respectively. B, D) HRTEM images and magnified insets (B1, D1) recorded along  $\langle \bar{1}11 \rangle$  zone axes of  $\alpha$ -(Fe, Ni) alloy particles. The one in (D) is embedded in a carbon nanotube. The power spectra (B2, D2) calculated from (B, D) show characteristic reflections from  $\alpha$ -(Fe,Ni) along  $\langle \bar{1}11 \rangle$  zone axes. E) Low magnification TEM images of 5 wt. % Fe/SiC after microwave treatment. F) The HRTEM images of 5 wt. % Fe/SiC after microwave treatment. Magnified inset (F1) recorded along a  $\langle 120 \rangle$  zone axis of a  $\text{Fe}_3\text{C}$  particle that is encapsulated in a multi-walled carbon nanotube. The power spectrum (F2) calculated from (F) shows characteristic reflections from graphite (002) plane and  $\text{Fe}_3\text{C}$  along  $\langle 120 \rangle$  zone axis.

a new and attractive path towards a decarbonized fossil fuels economy: Thus fluid hydrocarbon fuels are not consumed by aerial combustion as in the conventional use of fossil hydrocarbon fuel with attendant problems of  $\text{CO}_2$  emission. Rather these valuable hydrocarbon resources are utilized through microwave-promoted catalytic deep hydrogenation as an abundant, widespread source for the rapid production of high purity hydrogen for use in fuel cell vehicles. In this approach suitably optimized  $\text{CO}_2$  would never enter the

atmosphere as in a conventional combustion process. The utilization process yields elemental hydrogen and elemental carbon; the latter can then be readily subjected to recycling through a range of established chemical routes.

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### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** decarbonization · iron · hydrogen production · microwave catalysis · nickel

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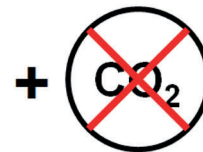
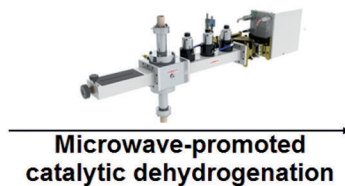
## Communications



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**Stop CO<sub>2</sub>!** Microwave-promoted, catalytic deep dehydrogenation of liquid alkanes using the abundant metals iron and nickel as catalysts produces CO<sub>2</sub>-free hydrogen, signaling a route to the decarbonization of fossil fuels.