Electronic Supplementary Information for

The decarbonisation of petroleum and other fossil hydrocarbon fuels for the facile production and safe storage of hydrogen

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The compositions analysis on the various fossil fuels

Extra-heavy crude oil and crude oil were both from Saudi Arabia and supplied by Saudi Aramco. The extra-heavy crude oil, crude oil, diesel and petrol were all analysed quantitatively by gas chromatography-mass spectrometry (GCMS) and the results are shown in Supplementary Figure 5. The chemical compositions for petrol, extra-heavy crude oil and crude oil are given in Supplementary Table 4, 5 and 6, respectively.

Evaluation of energy efficiency

As a preliminary investigation, we carried out a detailed thermodynamic analysis of the deep dehydrogenation process of diesel to yield hydrogen and carbon, via Eq. S1:

$$\mathrm{C_nH_m} \xrightarrow{catalyst} \mathrm{nC} + \frac{\mathrm{m}}{2}\mathrm{H_2} \qquad \text{(S1)}$$

Petroleum-derived diesel is usually composed of about 75% of saturated hydrocarbons (primarily paraffin, including *n*, *iso*, and cycloparaffin) and 25% aromatic hydrocarbons (including naphthalene and alkyl benzene). However, different content of diesel is found in different literature [1-3]. For simplicity, a specific diesel content was chosen for the calculation as follow:

Normal paraffin (60%): n-pentadecane (n-$C_{15}H_{32}$, 20%), n-hexadecane (n-$C_{16}H_{34}$, 20%) and n-heptadecane (n-$C_{17}H_{36}$, 20%)

Cyclo-paraffin (15%): Decylcyclopentane (c-$C_{15}H_{30}$, 5%), Decylcyclohexane (c-$C_{16}H_{32}$, 5%) and Undecylcyclohexane (c-$C_{17}H_{34}$, 5%)

Alkylbenzeners (15%): 1,3,5-trimethyl benzene (C_9H_{12}, 7%), and Diphenyl ($C_{12}H_{10}$, 8%)

Indane: indane (C_9H_{10}, 5%)

Naphthalenes: Naphthalene ($C_{10}H_8$, 5%)

Here, the *n*-hexadecane is taken as an example to show the calculation of energy request for the cracking process (Supplementary Figure 6). The energy requirement for the deep dehydrogenation of diesel was then calculated separately among different compounds following the various proportions shown above. The results of energy requests as well as the volumes of H_2 gas produced are listed in Supplementary Table 2. The result shows that the energy requirement for the deep dehydrogenation of the diesel described above is 1.40 kJ/g and 1.43 Nm^3 H_2 gas can be obtained per kg diesel. The energy output of this system is then calculated as the enthalpy of combustion of the hydrogen produced. For the 1.43 Nm^3 H_2 gas obtained per kg diesel, the energy out is 18.25 MJ.

The composition of tested diesel is given in Supplementary table 1. Based on its constitution, same thermodynamics analysis was carried out and the energy requirement and the energy output are 2.04 MJ/kg and 20.97 MJ/kg, respectively (Supplementary Table 7).

Comparison of energy balance between microwave and conventional thermal methods

As shown in Figure 2d, the different levels of both catalytic activity and the hydrogen selectivity are found different between the microwave and conventional thermal methods. The energy balance of both methods is also compared based on our laboratory set-up. The results and experimental parameters are given in Supplementary Table 3.

The energy balance of two processes were evaluated by the "Net energy balance" (NEB) ratio which simply gives the ratio of chemical energy derived from the products (energy out) to the energy invested (energy in) in the process[4, 5]. For simplicity, equating the energy out as the enthalpy of combustion of the hydrogen produced, and the energy in as the electricity consumed by microwave reactor and electric furnace, the net energy balance was calculated by the equations shown below:

$$NEB = \frac{Energy\ out}{Energy\ in} = \frac{Enthalpy\ of\ combustion\ of\ produced\ hydrogen}{Electric\ power \times\ reaction\ time} \times 100\%$$

Hydrogen density

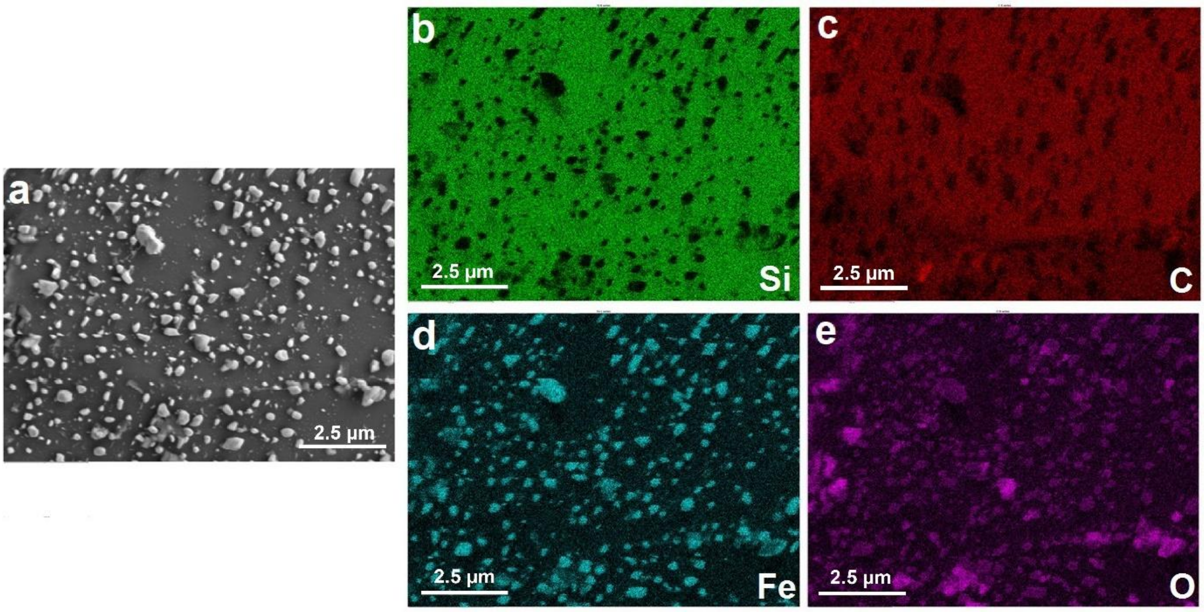
The hydrogen density was calculated as following. Through the microwave-initiated catalytic dehydrogenation of various fossil fuels over Fe catalysts, the fuels were rapidly and deeply decomposed to hydrogen and solid carbon. The experimental hydrogen density of G value and V value was then calculated by the equations showing below:

$$G\ value = \frac{Mass\ of\ H_2\ obtained}{Fuel_{input} - Fuel_{re-collect}} \times 100\%$$

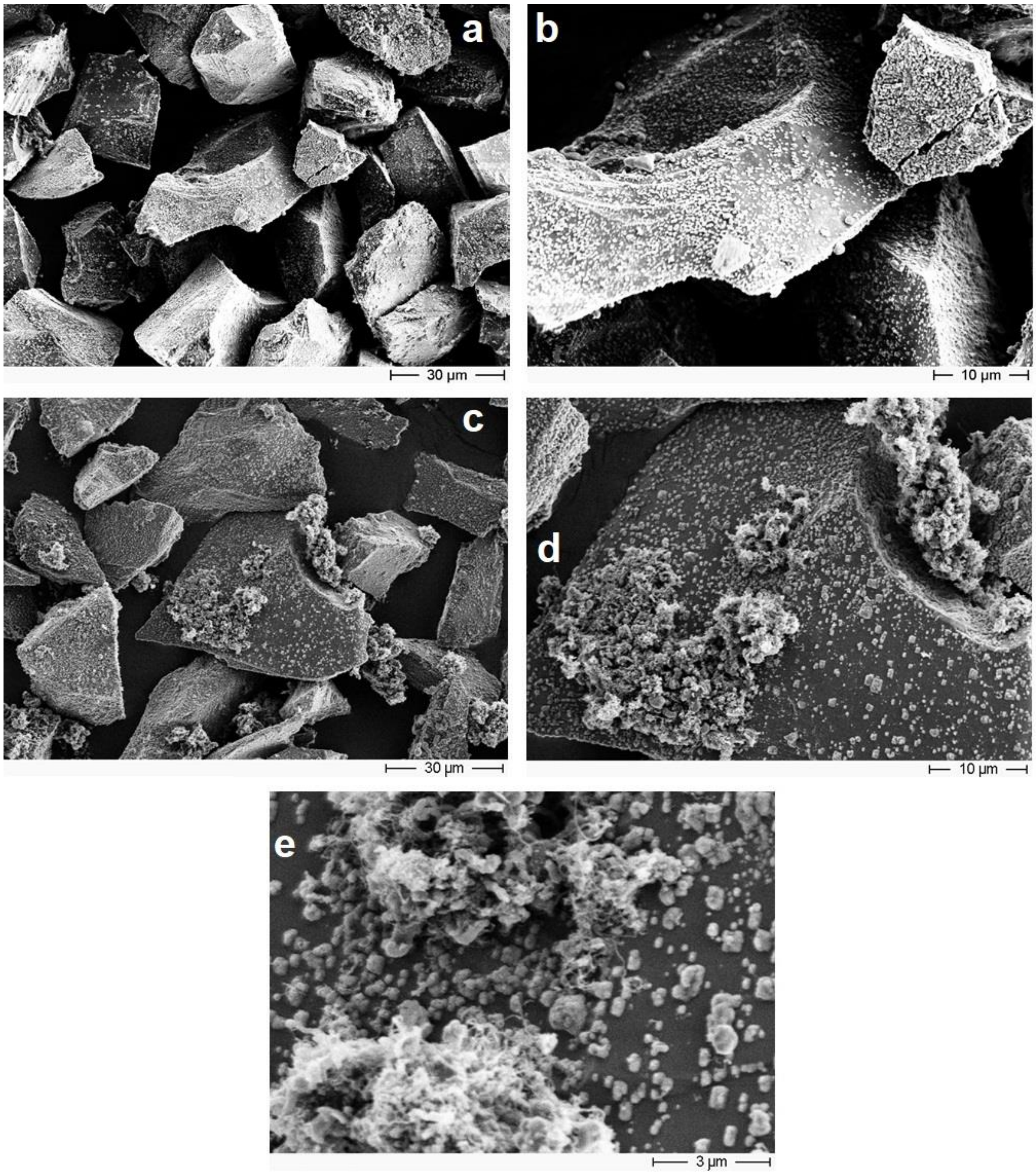
$$V\ value = \frac{Mass\ of\ H_2\ obtained}{(Fuel_{input} - Fuel_{re-collect}) \times D_{fuel}}$$

Here, the mass of H_2 is calculated from the collected gas volume and the H_2 selectivity obtained by GC. D_{fuel} refers to the density of fuel.

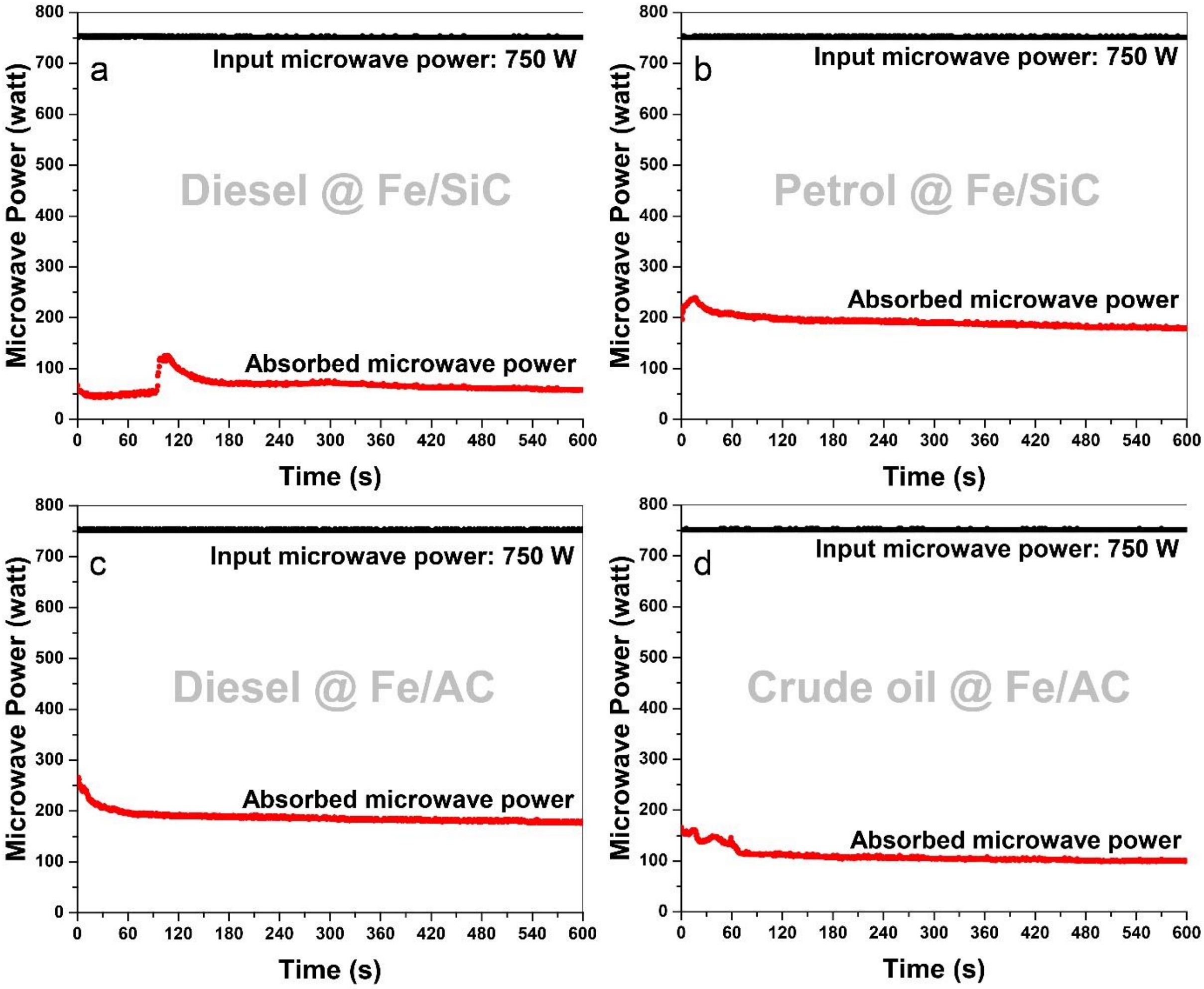
The theoretical hydrogen densities of various hydrogen storage materials are given in Supplementary Table 8 and the experimental hydrogen densities of diesel, petrol and hexadecane obtained over 5 wt.% Fe/SiC catalyst are shown in Supplementary Table 9.



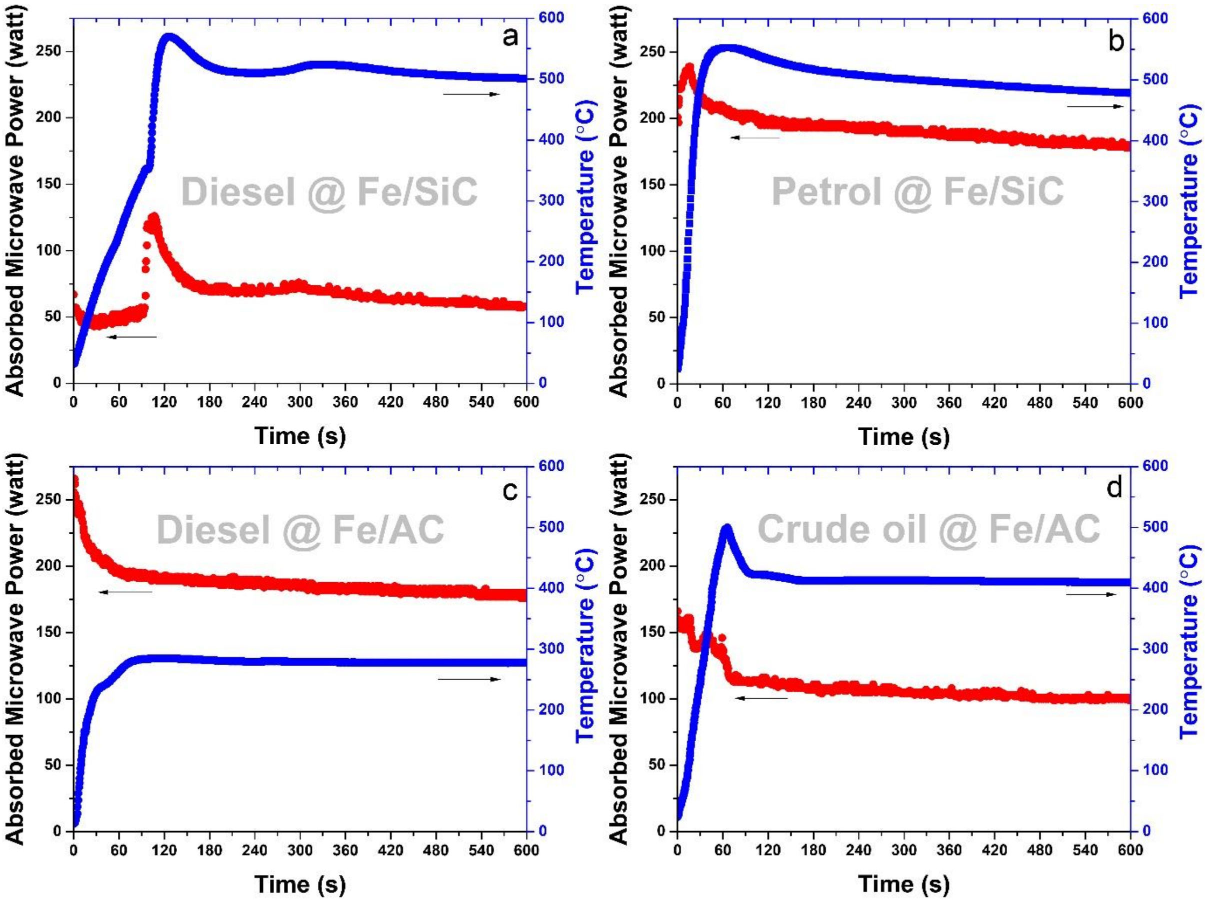
Supplementary Figure 1. Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX) mapping of the elemental species on the surface of 5 wt.% Fe/SiC catalysts before microwave initiation. **(a)** SEM (backscattered electron) morphology, **(b)** Si map, **(c)** C map, **(d)** Fe map, and **(e)** O map.



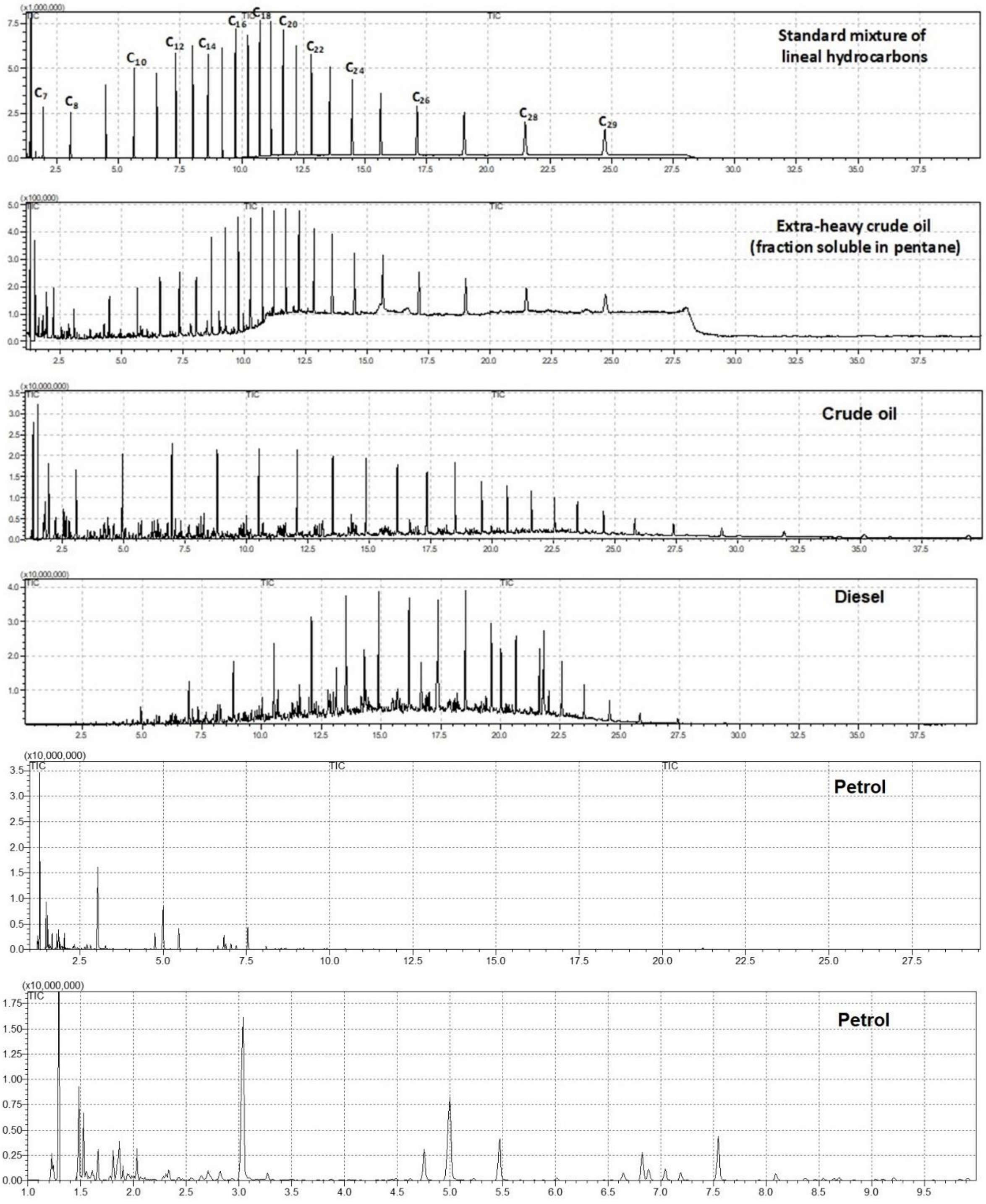
Supplementary Figure 2. The scanning electron microscope (SEM) of Fe/SiC catalyst, **(a), (b)** before and **(c), (d) and (e)** after microwave initiation.



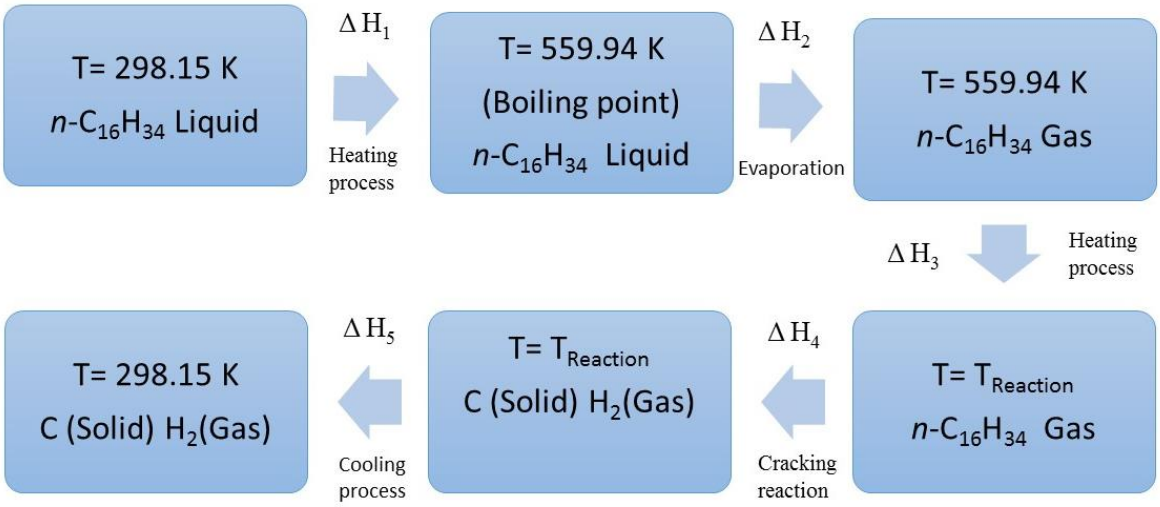
Supplementary Figure 3. Original microwave input power and absorbed power (delivery power) of representative **(a)** Diesel @ Fe/SiC; **(b)** Petrol @ Fe/SiC; **(c)** Diesel @ Fe/AC **(d)** Crude oil @ Fe/AC.



Supplementary Figure 4. Record reaction temperature and absorbed power (delivery power) of representative **(a)** Diesel @ Fe/SiC; **(b)** Petrol @ Fe/SiC; **(c)** Diesel @ Fe/AC **(d)** Crude oil @ Fe/AC.



Supplementary Figure 5. Gas chromatography-mass spectrometry (GCMS) analysis on extra-heavy crude oil, crude oil and diesel.



$$\Delta H = \sum_{i=1}^{5} H_i$$

Supplementary Figure 6. Energy input of *n*-hexadecane cracking in atmospheric pressure.

Supplementary Table 1. The composition of diesel determined by GCMS. (The percentage is the area% obtained from GCMS)

Compounds	**Formula**	**Percentage (%)**
Nonane	C_9H_{20}	0.97
1-Octanol, 2-butyl-	$C_{12}H_{26}O$	1.43
Decane	$C_{10}H_{22}$	2.39
Benzene, 1,2,3-trimethyl-	C_9H_{12}	1.00
Decane, 4-methyl-	$C_{11}H_{24}$	0.82
1-Iodo-2-methylnonane	$C_{10}H_{21}$	1.15
Undecane	$C_{11}H_{24}$	3.48
Octane, 2,3,6,7-tetramethyl-	$C_{12}H_{26}$	1.81
Undecane, 2-methyl-	$C_{12}H_{26}$	0.95
Dodecane	$C_{12}H_{26}$	4.49
Tridecane	$C_{13}H_{28}$	5.92
Tetradecane	$C_{14}H_{30}$	7.22
Hexadecane	$C_{16}H_{34}$	17.56
Octadecane	$C_{18}H_{38}$	13.06
Heptadecane	$C_{17}H_{36}$	6.75
Nonadecane	$C_{19}H_{40}$	5.26
9-Octadecenoic acid, methyl ester, (E)-	$C_{19}H_{36}O_2$	8.01
Octadecanoic acid, methyl ester	$C_{19}H_{38}O_2$	1.84
Heneicosane	$C_{21}H_{44}$	12.30
Eicosane	$C_{20}H_{42}$	2.26

Tetracosane	$C_{24}H_{50}$	1.32
Sum	**(-)**	**100**

Supplementary Table 2. The energy requirement and energy output for the combustion of H_2 produced via the diesel cracking

Compounds	Formula	Percentage (%)	Energy requirement MJ/kg	H_2 product* Nm^3/kg	Energy output MJ/kg
Pentadecane	$C_{15}H_{32}$	20	2.02	1.69	21.53
Hexadecane	$C_{16}H_{34}$	20	2.01	1.68	21.46
Heptadecane	$C_{17}H_{36}$	20	2.00	1.49	19.02
Decylcyclopentane	$C_{15}H_{30}$	5	1.73	1.60	20.38
Decylcyclohexane	$C_{16}H_{32}$	5	1.85	1.60	20.38
Undecylcyclohexane	$C_{17}H_{34}$	5	1.74	1.60	20.38
1,3,5-trimethyl benzene	C_9H_{12}	7	0.51	1.12	14.27
Diphenyl	$C_{12}H_{10}$	8	-0.76	0.73	9.27
Indane	C_9H_{10}	5	-0.09	0.95	12.09
Naphthalene	$C_{10}H_8$	5	-0.76	0.70	8.92
Sum	**(-)**	**100**	**1.40**	**1.43**	**18.25**

Supplementary Table 3. Comparison of the energy balance of microwave and conventional thermal methods.

	Microwave method*	**Thermal method**
Input power (W)	750 (126)	1200
Pre-heating (min)**	0	52.5
Experimental time (min)	10	10
Energy In (J)	450000 (75600)	4500000
Produced H_2 (mL)	182	90
Energy Out (J)***	2323	1149
Net Energy Balance (NEB)	0.516 (3.072)	0.026

* The number in parentheses shows the absorbed microwave power with corresponding NEB. ** The furnace used in the thermal method are pre-heated from room temperature (25 °C) to 550 °C by the heating rate of 10 °C /min. *** The energy out is calculated as the enthalpy of combustion of the produced hydrogen.

Supplementary Table 4. The composition of petrol determined by GCMS. (The percentage is the area% obtained from GCMS)

Compounds	Percentage (%)
Isobutane	2.14
Butane, 2-methyl-	13.22
Pentane, 3-methyl-	4.55
Hexane	4.11
(2,2-Dimethylcyclopropyl)-methanol	1.15
Cyclopentane, methyl-	2.16
Hexane, 2-methyl-	2.1
Hexane, 3-methyl-	3.7
Benzene	0.87
Pentane, 2,2,3,4-tetramethyl-	1.15
Heptane	2
Cyclohexane, methyl-	1.69
Cyclopentane, propyl-	0.39
1-Heptene, 4-methyl-	0.47
Heptane, 3-ethyl-5-methylene-	0.56
Heptane, 2-methyl-	1.31
Heptane, 3-methyl-	1.1
Toluene	19.86
Octane	0.93
Ethylbenzene	3.35
o-Xylene	13.12
o-Xylene	4.83

Benzene, propyl-	0.88
Benzene, 1-ethyl-3-methyl-	2.99
Benzene, 1-ethyl-2-methyl-	1.18
Benzene, 1,2,4-trimethyl-	1.21
Benzene, 1-ethyl-2-methyl-	0.86
Benzene, 1,2,3-trimethyl-	4.92
Benzene, 1,2,4-trimethyl-	0.69
2,4-Dimethylstyrene	0.18
Azulene	0.13
n-Hexadecanoic acid	0.43
Octadecanoic acid	0.12
Sum	**98.35**

Supplementary Table 5. The chemical compounds analysis on extra-heavy crude oil.

Analysis of light fractions wt.%	
C	84.020
H	11.220
S	4.750
S/C	0.04
H/C	1.60
Density	0.913

Supplementary Table 6. The chemical compounds analysis on crude oil.

Analysis of light fractions wt.%	
C	84.160
H	12.700
S	3.140
S/C	0.03
H/C	1.81
Density	0.86

Supplementary Table 7. The energy requirement and energy output for the combustion of H_2 produced via the diesel cracking

Compounds	Formula	Percentage (%)	Energy requirement MJ/kg	H_2 product* Nm^3/kg	Energy output MJ/kg
Nonane	C_9H_{20}	0.97	2.15	1.75	22.24
1-Octanol, 2-butyl-**	$C_{12}H_{26}O$	1.43	2.86	1.56	19.90
Decane	$C_{10}H_{22}$	2.39	2.12	1.73	22.06
Benzene, 1,2,3-trimethyl-	C_9H_{12}	1	0.46	1.14	14.48
Decane, 4-methyl-	$C_{11}H_{24}$	0.82	2.11	1.72	21.90
1-Iodo-2-methylnonane***	$C_{10}H_{21}$	1.15	2.12	1.73	22.06
Undecane	$C_{11}H_{24}$	3.48	2.09	1.72	21.90
Octane, 2,3,6,7-tetramethyl-	$C_{12}H_{26}$	1.81	2.12	1.71	21.77
Undecane, 2-methyl-	$C_{12}H_{26}$	0.95	2.10	1.71	21.77
Dodecane	$C_{12}H_{26}$	4.49	2.07	1.71	21.77
Tridecane	$C_{13}H_{28}$	5.92	2.05	1.70	21.67
Tetradecane	$C_{14}H_{30}$	7.22	2.04	1.69	21.57
Hexadecane	$C_{16}H_{34}$	17.56	2.01	1.68	21.42
Octadecane	$C_{18}H_{38}$	13.06	1.99	1.67	21.30
Heptadecane	$C_{17}H_{36}$	6.75	2.00	1.68	21.36
Nonadecane	$C_{19}H_{40}$	5.26	1.98	1.67	21.25
9-Octadecenoic acid, methyl ester, (E)- ****	$C_{19}H_{36}O_2$	8.01	2.11	1.36	17.32
Octadecanoic acid, methyl ester	$C_{19}H_{38}O_2$	1.84	2.83	1.43	18.16
Heneicosane*****	$C_{21}H_{44}$	12.3	2.02	1.66	21.16

Eicosane	$C_{20}H_{42}$	2.26	1.98	1.66	21.20
Tetracosane	$C_{24}H_{50}$	1.32	1.95	1.65	21.06
Sum	**(-)**	**99.99**	**2.04**	**1.65**	**20.97**

Notes: * Assumption that there is no water formation during the diesel cracking; ** data of 1-dodecanol; *** data of n-decane; **** data of gas state; ***** data of 2,6,10,14-Tetramethylheptadecane

Supplementary Table 8. Theoretical hydrogen densities of various hydrogen storage materials.

Materials	Gravimetric Density (kg-H_2/kg)	Volumetric Density (kg-H_2/m^3)
DoE target	7.5	70
Petrol	14.84	109.29
diesel	16.35	124.69
CH_4 (liq.)	25	107.30
C_4H_{10} (liq.)	17.3	98.40
CH_4	25	0.179
C_2H_6	20	0.268
C_3H_8	18.18	0.357
C_4H_{10}	17.24	0.446
C_5H_{12}	16.67	104.33
C_6H_{14}	16.28	107.28
C_7H_{16}	16	109.44
C_8H_{18}	15.79	111.00
C_9H_{20}	15.63	112.19
$C_{10}H_{22}$	15.49	113.10
$C_{11}H_{24}$	15.38	113.85
$C_{12}H_{26}$	15.29	114.55
$C_{13}H_{28}$	15.22	115.04
$C_{14}H_{30}$	15.15	115.76
$C_{15}H_{32}$	15.09	116.08
$C_{16}H_{34}$	15.04	116.29
$C_{17}H_{36}$	15	116.55
CH_3OH	12.9	93.80

$NaBH_4$	10.7	114

Supplementary Table 9. Experimental hydrogen densities of diesel, petrol and hexadecane obtained over 5 wt.% Fe/SiC catalysts.

Materials	**Gravimetric Density (kg-H_2/kg)**	**Volumetric Density (kg-H_2/m^3)**
DoE target	7.5	70
Diesel	8.57	71.28
Petrol	9.27	71.39
Hexadecane	9.75	75.36

Supplementary Table 10. BET surface area of Fe/SiC and Fe/AC catalysts.

Samples	**BET Surface Area [m^2/g]**
SiC	0.3
Fe/SiC (Fresh)	0.9
Fe/SiC (Spent)	1.3
AC	875
Fe/AC (Fresh)	517
Fe/AC (Spent)	452

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