

## Supporting Information

# **Ga-Pt Supported Catalytically Active Liquid Metal Solutions (SCALMS) Prepared by Ultrasonication – Influence of Synthesis Conditions on n-Heptane Dehydrogenation Performance**

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## Ultrasonication for Ga and Ga containing metals

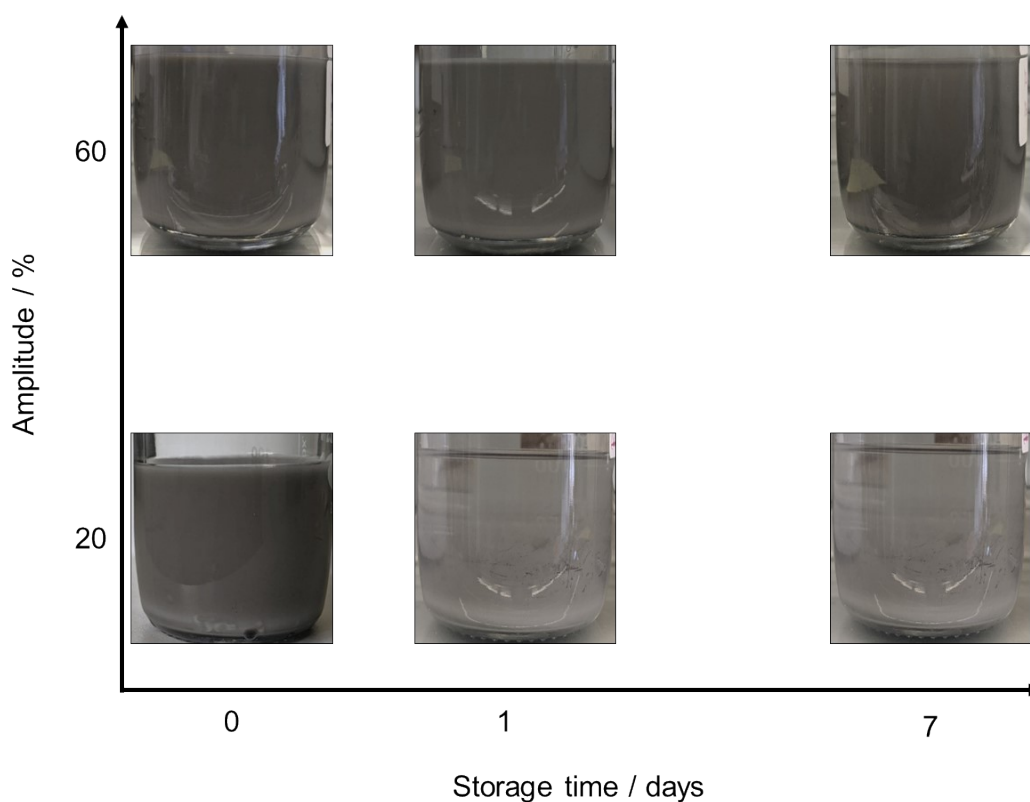
The literature on ultrasonication conditions and the resulting particle sizes reported in the literature for Ga and Ga containing metals are summarized in Table S1.

**Table S1.** Summary table showing ultra-sonication conditions and particle size reported in the literature for Ga and Ga containing metals.

Metal	Solvent	LM conc. (mg mL <sup>-1</sup> )	Stabilizer / conc. (mM)	P (W) / A (%) / T (°C) / t (min.)	Particle size (nm) / technique	Ref.
Ga	Water	~19	none	80 / - / 55 <sup>a</sup> / 6-10	50-10000 / SEM	1
Ga	Isopropanol	~20	C <sub>12</sub> H <sub>25</sub> SH / 300	400 / 40 / 20 / 120	10-400 / SEM	2
Ga	Isopropanol	5	none	450 / 20 / 50 / 120	525 / DLS	§
Ga	Isopropanol	5	none	450 / 40 / 50 / 120	277 / DLS	§
Ga	Isopropanol	5	none	450 / 60 / 50 / 120	206 / DLS	§
Ga	Isopropanol	5	none	450 / 80 / 50 / 120	249 / DLS	§
Ga	Hexane	~12-33	none	80 / - / 55 <sup>a</sup> / 2.5	300-1200 / SEM 400-1000 / DLS	1
Ga	Dodecane	~12-33	none	80 / - / 55 <sup>a</sup> / 2.5	200-1300 / SEM 300-900 / DLS	1
EGaIn	Ethanol (anhydrous)	0.05	none	500 / 25 / - / 10	1890 /	3
EGaIn	Ethanol	0.05	none	500 / 25 / - / 10	148 /	3
EGaIn	Ethanol	~91	C <sub>12</sub> H <sub>25</sub> NOS / 1	700 / 30 / - / 60	180 ± 32	4
EGaIn	Ethanol	~91	none	700 / 30 / - / 60	465 ± 65	4
EGaIn	Ethanol	~91	C <sub>12</sub> H <sub>25</sub> NOS / 1	700 / 30 / - / 30	~ 350	5
EGaIn	Ethanol	~91	C <sub>12</sub> H <sub>25</sub> NOS / 1	700 / 30 / - / 960	50	5
EGaIn	Ethanol	~91	none	700 / 30 / - / 30	~ 650	5
EGaIn	Ethanol	~91	none	700 / 30 / - / 960	50	5
EGaIn	Ethanol	~200	none	55 / 80 / - / 10	~ 105 <sup>b</sup>	6
EGaIn	Ethanol	360	C <sub>12</sub> H <sub>25</sub> SH / 1	Sonication bath - / - / - / 120	100 - 1000 <sup>c</sup>	7
EGaIn	Ethanol	360	C <sub>12</sub> H <sub>25</sub> NOS / 1	Sonication bath - / - / - / 120	< 100 <sup>c</sup>	7
EGaIn	Ethanol	~133	C <sub>12</sub> H <sub>25</sub> SH / 1	Sonication bath - / - / 25 / 60	150 / TEM 176 / DLS 170 / UV-vis	8
EGaIn	Ethanol	~133	C <sub>18</sub> H <sub>37</sub> SH / 1	Sonication bath - / - / 25 / 60	80 / UV-vis	8
EGaIn	Hexanes	250	DPA	500 / 17 / 10 / 120	158.8 / STEM	9
EGaIn	Hexanes	250	none	500 / 17 / 10 / 120	162.8 / STEM	9
GaIn <sup>d</sup>	Water	~60	POMA / 0.033 <sup>e</sup>	700 / 40 / - / 5	~ 170	10
EGaInSn	Ethanol	~10	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> S / 0.05	750 / 40 / 20 / 60	110 / SEM	11

Note: EGaIn = eutectic-GaIn; EGaInSn = eutectic-GaInSn; LM conc. = liquid metal concentration; P = maximum power of horn type ultrasonication device or power input; A = amplitude of sonication; T = temperature of the emulsion, t = duration of ultrasonication. SEM = scanning electron microscopy; STEM = scanning transmission electron microscopy, DLS = dynamic light scattering; UV-vis = Ultraviolet spectroscopy.  $C_{12}H_{25}SH$  = 1-dodecanethiol;  $C_{18}H_{37}SH$  = 1-octadecanethiol;  $C_5H_{10}O_2S$  = ethyl 3-mercaptopropionate;  $C_{12}H_{25}NOS$  = 3-mercapto-N-nonylpropionamide; DPA = Decylphosphonic acid. POMA = poly(1-octadecene-alt-maleic anhydride); a = Ga was melted at 55 °C for 30-40 min prior to sonication. Temperature increased to 64 °C during sonication in water; b = mean diameter of in the supernatant liquid after settling of the larger particles; c = filtered using 0.1  $\mu\text{m}$  Whatmann Luer Lock membrane filter, or separated by mild centrifugation; d = 80 wt.% Ga and 20 wt.% In; e = taking molar mass of POMA as 30000  $\text{g mol}^{-1}$ ; § = this work.

## Stability of the Ga-dispersions

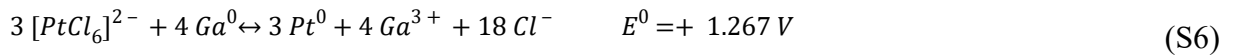
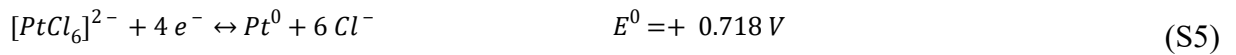
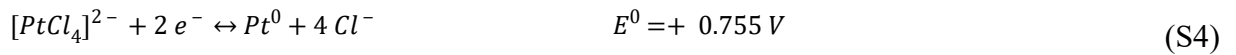
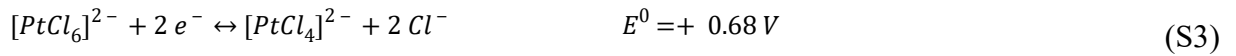
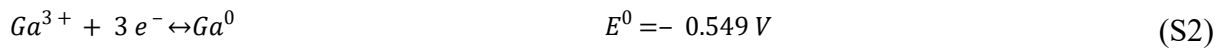


**Figure S1.** Stability of Ga-propan-2-ol dispersions prepared using 80% and 20% sonication amplitude. Dispersions were stored in sample vials.

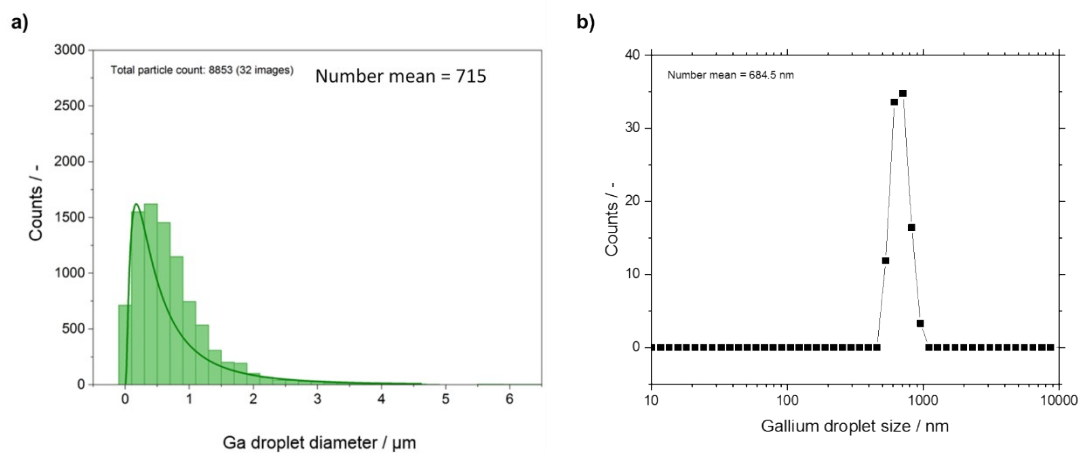
## Nernst equation and galvanic displacement reactions

$$E = \left( E_{Pt^{4+}/Pt^0}^0 - E_{Ga^{3+}/Ga^0}^0 \right) - \frac{RT}{nF} \ln \left( \frac{\theta_0^{Pt}}{\theta^{Pt}} \right) \quad (S1)$$

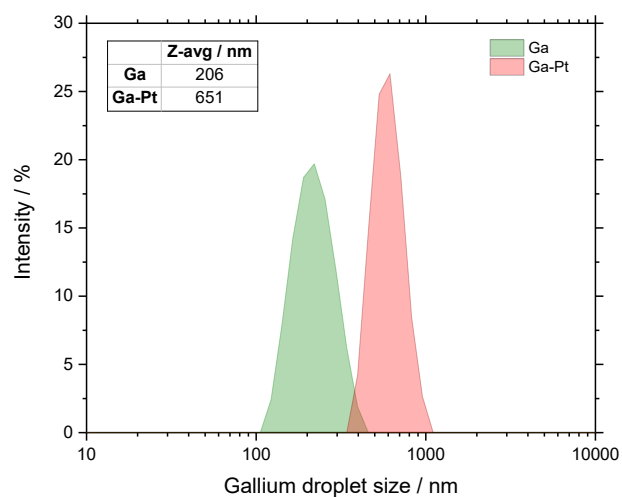
Herein,  $\theta_0^{Pt}$  is the equilibrium coverage of the deposited Pt atoms in the absence of net current,  $\theta^{Pt}$  is the coverage of the Pt atoms while being deposited,  $E_{Pt^{4+}/Pt^0}^0$ ,  $E_{Ga^{3+}/Ga^0}^0$  are the standard reduction potentials of Pt and Ga,  $n$  is the electron transfer number, and  $F$  is the Faraday constant. It is known that  $\theta$  is a function of the activity of the added metal (i.e. here Pt), its concentration at the surface of the sacrificial metal, and the energy transfer coefficient of the GDR. At the beginning of the GDR, the driving force only depends on the difference in  $E^0$  values since the term  $[\frac{RT}{nF} \ln(\frac{\theta^M}{\theta^M})]$  is close to zero.<sup>49</sup> The standard reduction potential of  $Ga^{3+}/Ga^0$  and  $[PtCl_6]^{2-}/Pt^0$  against the standard hydrogen electrode (SHE) are shown in Equations (S3) and (S5), respectively.<sup>50</sup> The redox reaction between  $Ga^0$  and  $Pt^{4+}$  can be represented by Equation (S6).



## Particle size analysis



**Figure S2.** Comparison of particle size analysis of Ga-isopropanol emulsion synthesized using 80% amplitude of ultrasonication via a) SEM and b) DLS imaging.



**Figure S3.** The particle size distribution of Ga droplets after ultrasonication (60% amplitude, 120 min) and after in situ Ga-Pt galvanic displacement in emulsion. Note: Z-avg. = Z-average (intensity-based harmonic mean from DLS measurement).

## Reference catalyst synthesis

The individual building blocks of the SCALMS catalyst system were synthesized individually.

**Ga<sup>0</sup>/Al<sub>2</sub>O<sub>3</sub>:** Ga-emulsion was prepared by ultrasonically dispersing 0.5 g gallium nugget in isopropanol using 60% amplitude and 120 min irradiation time. To this Ga-emulsion, Al<sub>2</sub>O<sub>3</sub> support material was added to achieve approx. 3 wt.-% loading of Ga on alumina. The solvent was then slowly evaporated under vacuum at 313 K using a rotary evaporator. The solid (Ga<sup>0</sup>/Al<sub>2</sub>O<sub>3</sub>) obtained was then calcined for 2 hours at 773 K under ambient conditions.

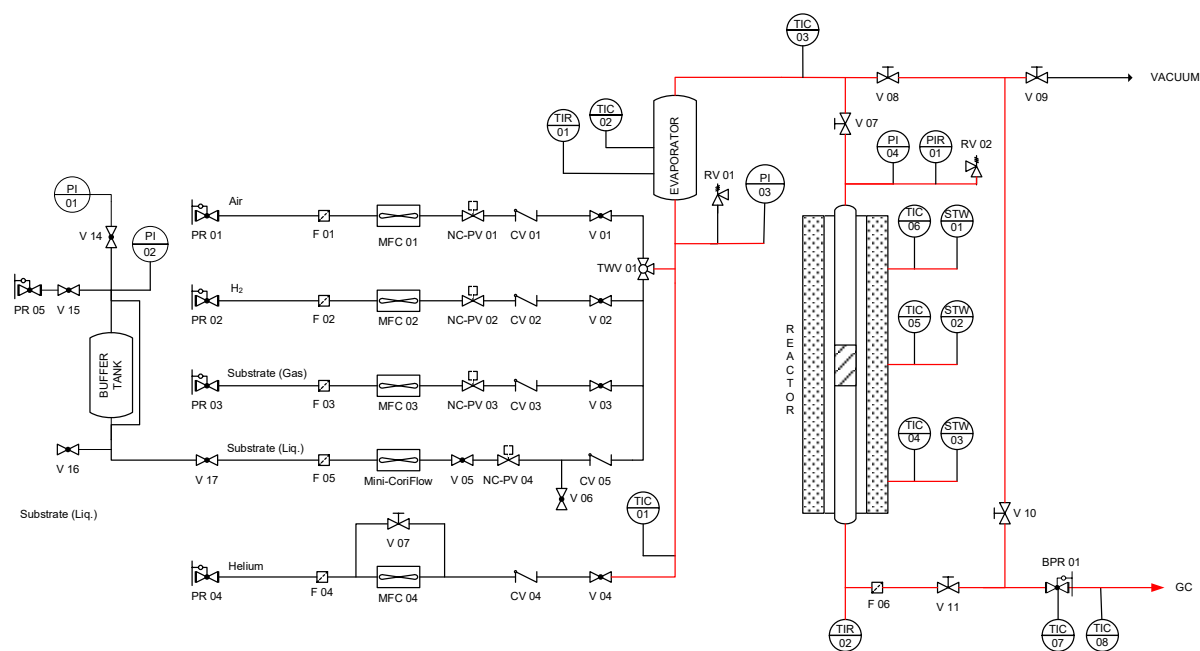
**Ga<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>:** Required amount of Al<sub>2</sub>O<sub>3</sub> support material suspended in isopropanol and to this required amount of Ga precursor (i.e., Ga(NO<sub>3</sub>)<sub>3</sub>) in water was added. The solvent was then slowly evaporated under vacuum at 313 K using a rotary evaporator. The solid (Ga<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>) obtained was then calcined for 2 hours at 773 K under ambient conditions.

**Pt/Al<sub>2</sub>O<sub>3</sub>:** Commercially available Pt/Al<sub>2</sub>O<sub>3</sub> powder (1.0 wt.-% Pt) was purchased from Sigma-Aldrich.

**Pt-Ga<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>:** Ga<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> was prepared as mentioned above and Pt was then added through classical wet-impregnation. Ga<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> was suspended in isopropanol and to this required amount of Pt precursor (i.e. (H<sub>3</sub>O)<sub>2</sub>(PtCl<sub>6</sub>)<sub>x</sub>) in water was added. The solvent was then slowly evaporated under vacuum at 313 K using a rotary evaporator. The solid (Pt-Ga<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>) obtained was then calcined for 2 hours at 773 K under ambient conditions.

The exact loading of Ga was determined by ICP-AES

## Gas-phase dehydrogenation set-up



**Figure S4.** Flow scheme of the continuous gas-phase reactor setup for n-heptane dehydrogenation. Heated lines are shown in red.



**Figure S5.** Image of gas-phase reactor setup used for n-heptane dehydrogenation.

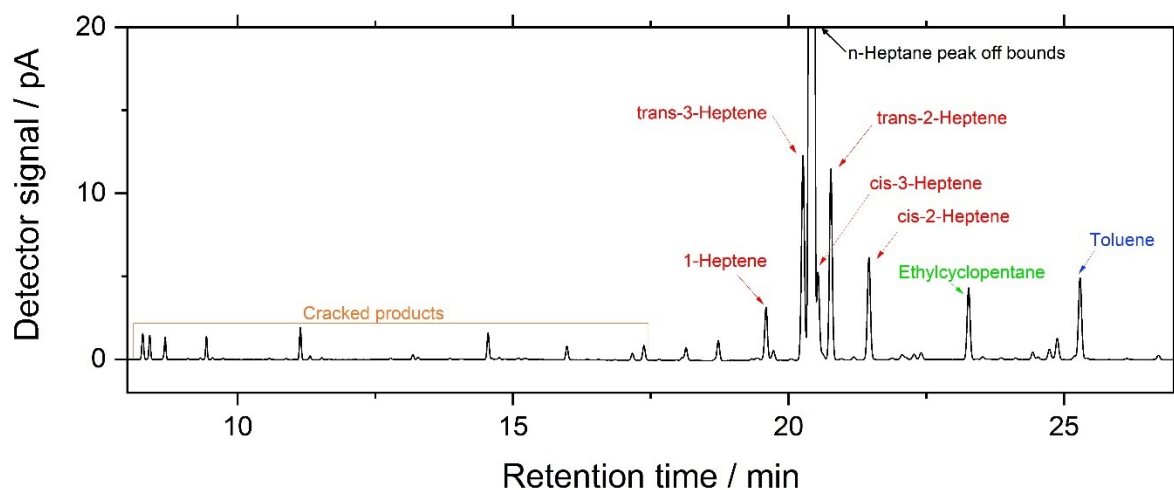
## Catalysts tested in n-heptane dehydrogenation

**Table S2.** Overview of catalysts and their compositions tested in this study.

Catalyst name	Ga	Pt	Ga	Pt	Ga/Pt	Galvanic displacement reaction media
	wt.-%	wt.-%	at.-%	at.-%	-	
Ga <sub>52</sub> Pt SCALMS-A	2.7	0.15	98.1	1.9	52	Isopropanol
Ga <sub>54</sub> Pt SCALMS-B	2.5	0.13	98.2	1.8	54	Water
Ga <sub>53</sub> Pt SCALMS-C	1.7	0.09	98.1	1.9	53	Isopropanol - water
Ga <sub>27</sub> Pt/Al <sub>2</sub> O <sub>3</sub>	2.0	0.21	96.4	3.6	27	Isopropanol - water
Ga <sub>36</sub> Pt/Al <sub>2</sub> O <sub>3</sub>	1.9	0.15	97.3	2.7	36	Isopropanol - water
Ga <sub>53</sub> Pt/Al <sub>2</sub> O <sub>3</sub>	1.7	0.09	98.1	1.9	53	Isopropanol - water
Ga <sub>76</sub> Pt/Al <sub>2</sub> O <sub>3</sub>	2.1	0.08	98.7	1.3	76	Isopropanol - water
Ga <sub>99</sub> Pt/Al <sub>2</sub> O <sub>3</sub>	2.2	0.06	99.0	1.0	99	Isopropanol - water
Ga/Al <sub>2</sub> O <sub>3</sub>	2.3	0	100.0	0.0	0	-
Ga <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	3.0	0	100.0	0.0	0	-
Pt-Ga <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	3.6	0.35	96.6	3.4	29	-
Pt/Al <sub>2</sub> O <sub>3</sub> (commercial)	0	1.0	0	100	0	-

## Reaction product analysis

A sample of gas chromatograph showing the separation and detection of various products formed in n-heptane dehydrogenation is shown in Figure S6.



**Figure S6.** Representative GC chromatogram showing products separation and detection in n-heptane dehydrogenation.



The summary and classification of the different species that were identified by means of GC analysis is shown Table S3.

**Table S3.** Reaction products detected in n-heptane dehydrogenation at 703 K under atmospheric pressure.

Products	Classification	Relevant reactions
Methane, ethane, ethane, propane, propene, cyclopentane, methylcyclopentane, 2-methylpentane, 3-methylpentane, hexane, benzene, n-heptane	Cracked products ( $\leq C6$ )	Hydrocracking Hydrogenolysis
1-heptene, <i>trans</i> -2-heptene, <i>cis</i> -2-heptene, <i>trans</i> -3-heptene, <i>cis</i> -3-heptene	<i>C7 n</i> -alkane	
2,2-dimethylpentane, 3,3-dimethylpentane, 2,3-dimethylpentane, 2-methylhexane, 3-methylhexane	<i>C7 n</i> -alkenes	Dehydrogenation
5-methyl-1-hexene, 3-ethyl-2-pentene, 3-methyl-2-hexene, 2-methyl-2,4-hexadiene, 2,3-dimethyl-1,3-pentadiene	<i>C7 iso</i> -alkanes	Isomerization
<i>Cis</i> -1,3-dimethylcyclopentane, <i>trans</i> -1,3-dimethylcyclopentane, 1,2-dimethylcyclopentane, methylcyclohexane, ethylcyclopentane	<i>C7 iso</i> -alkenes	Dehydrogenation-isomerization
3,5-dimethylcyclopentene, 1-ethylcyclopentene	<i>C7 sub.-cyclo</i> -alkanes	Cyclization
Toluene	<i>C7 sub.-cyclo</i> -alkenes	Dehydrocyclization
	<i>C7 aromatics</i>	Aromatization

Note: *sub.-cyclo* = substituted cyclic

Since the amount of dehydrogenated species within the fractions of isomerized and cyclized compounds was very small (< 1%), they were included in the lumped model. Hence, only six compound classes were discussed:

< C6 cracking, desired n-heptene, isomerized C7, C7 cyclics, C7 aromatics and unspecified

The conversion of *n*-heptane  $X_i$ , the selectivity to *n*-heptenes  $S_k$ , the productivity  $P_k$ , and the cumulative productivity  $P_{k,cum}$  were calculated as follows:

$$X_i = \frac{x_{i,0} - x_i}{x_{i,0}} \quad i = n - \text{heptane} \quad (\text{S7})$$

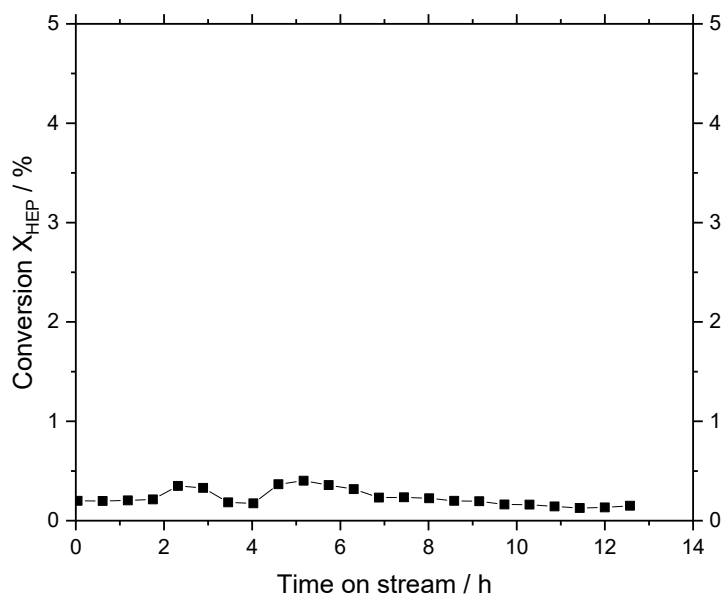
$$S_k = \frac{x_k}{x_{i,0} - x_i} \quad i = n - \text{heptane}, k = n - \text{heptenes} \quad (\text{S8})$$

$$P_k = \frac{F_{m,1} \cdot X_i \cdot S_k}{m_{Pt}} \quad i = n - \text{heptane}, k = n - \text{heptenes} \quad (\text{S9})$$

$$P_{k,cum} = P_k \cdot TOS \quad (\text{S10})$$

Where  $x_{i,k}$  is the mole fraction of component  $i$  and  $k$ ,  $x_{i,0}$  is the mole fraction of component  $i$  in the feed,  $F_{m,i}$  the mass flow rate of *n*-heptane,  $m_{Pt}$  is the mass of platinum in the catalyst bed, and  $TOS$  is the time-on-stream.

## Bare Al<sub>2</sub>O<sub>3</sub> support activity in *n*-heptane dehydrogenation



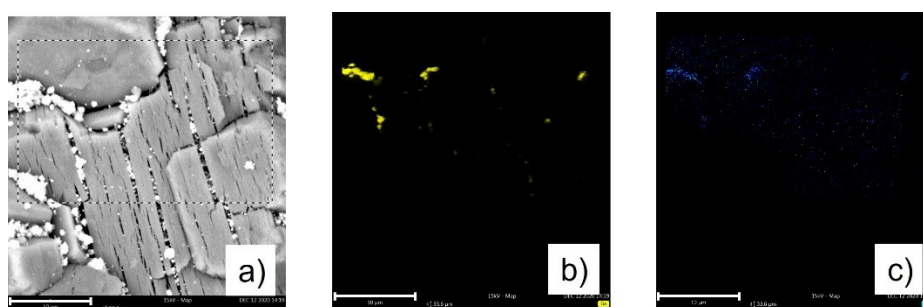
**Figure S7.** Graph showing conversion over time-on-stream in *n*-heptane dehydrogenation using bare Al<sub>2</sub>O<sub>3</sub> (neutral, Sigma Aldrich) support at 430 °C and 1 bar. Reaction conditions: 2.5 mL support material, H<sub>2</sub>/*n*-heptane = 8/1, 0.062 g min<sup>-1</sup> *n*-heptane, 118.87 mL<sub>N</sub> min<sup>-1</sup> H<sub>2</sub>, 14.86 mL<sub>N</sub> min<sup>-1</sup> He, 3320 mL<sub>gas</sub> g<sub>cat-bed</sub><sup>-1</sup> h<sup>-1</sup> GHSV, ~ 1.1 s residence time ( $\tau$ ).

## Comparison between in situ vs. ex situ prepared SCALMS-C in n-heptane dehydrogenation

To study the effect of in situ vs. ex situ Ga-Pt galvanic displacement in n-heptane dehydrogenation we prepared Ga-Pt SCALMS via two routes with identical Ga-to-Pt ratio of 58 and tested in n-heptane dehydrogenation. The catalytic results are shown in Figure S7.

**Table S4.** Composition of Ga-Pt SCALMS prepared via ex situ and in situ galvanic displacement

Ga-Pt galvanic displacement	Ga / wt. %	Pt / wt. %	Ga-to-Pt ratio
<i>ex situ</i> SCALMS-C	1.7	0.09	53
<i>in situ</i> SCALMS-C*	2.79	0.135	58



**Figure S8.** (a) SEM image and EDX mapping of Ga (b) and Pt (c) of Ga-Pt SCALMS-C prepared via ex situ GDR. The scale bar represents 10  $\mu\text{m}$ .

## References

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