

Stable and Selective Dehydrogenation of Methylcyclohexane using Supported Catalytically Active Liquid Metal Solutions – Ga₅₂Pt/SiO₂ SCALMS

Oshin Sebastian,^[a] Sharanya Nair,^[a] Nicola Taccardi,^[a] Moritz Wolf,^[a] Alexander Søgaard,^[a] Marco Haumann,^[a] and Peter Wasserscheid*^[a, b]

The use of gallium-rich, Supported Catalytically Active Liquid Metal Solution (SCALMS) is a promising new concept to achieve catalysis with atomically dispersed active metal atoms. Expanding our previous work on short alkane dehydrogenation, we present here the application of SCALMS for the dehydrogenation of methylcyclohexane (MCH) to toluene (TOL) using a Ga₅₂Pt alloy (liquid under reaction conditions) supported on silica. Cycloalkane dehydrogenation catalysis has attracted great attention recently in the context of hydrogen storage concepts using liquid organic hydrogen carrier (LOHC) systems. The system under investigation showed high activity and stable conversion of MCH at 450 °C and atmospheric pressure for more than 75 h time-on-stream ($X_{\text{MCH}} = 15\%$) with stable toluene selectivity (S_{TOL}) of 85%. Compared to commercially available Pt/SiO₂, the SCALMS system resulted in higher yields and robustness. Baseline experiments with Pt-free Ga/SiO₂ under identical conditions revealed the decisive influence of Pt dissolved in the liquid Ga matrix.

Dehydrogenation reactions of cycloalkanes are important transformations in the chemical and refinery industries, e.g. to increase the research octane number of straight-run gasoline in the platforming process.^[1] Furthermore, the reaction has recently gained very high interest in the context of hydrogen storage using reversible catalytic hydrogenation/dehydrogenation cycles in the context of the so-called Liquid Organic Hydrogen Carrier (LOHC) technology.^[2] The endothermic cycloalkane dehydrogenation reaction is thermodynamically favored

at high temperatures and low pressures.^[3] Therefore, the applied catalysts operate under harsh conditions and are prone to deactivation by coke formation.^[4] This makes the design of effective and robust catalysts and processes for cycloalkane dehydrogenation a rewarding research and developmental challenge. Dehydrogenation is typically carried out on noble metal (e.g. Pt) or oxide (e.g. Cr₂O₃) catalysts.^[3,5] Coke formation requires the presence of vicinal sites on the catalyst surface.^[6] Regeneration of the catalyst after coking is possible but causes either reactor downtime or additional investment into stand-by or reserve reactor equipment.

Recently, we reported Supported Catalytically Active Liquid Metal Solutions (SCALMS) as a new class of liquid phase catalysts.^[7] In these materials, a small amount of catalytically active metal is dissolved in a low melting metal matrix, such as liquid gallium. This alloy is supported on a porous support material to maximize the gas-liquid interface. Under reaction conditions, the supported alloy is present in the molten, liquid state. The highly dynamic liquid metal-gas interface of SCALMS enables the catalytically active metal to operate in an atomically dispersed manner at the gas-liquid interface within a matrix of liquid gallium. This particular nature of the active sites has been demonstrated by some of us together with collaboration partners using XPS, DFT, and operando DRIFTS investigations.^[7-8] Concerning catalytic applications, we have applied these SCALMS systems for butane (GaPd on porous glass) and propane (GaRh on Al₂O₃, GaPt on Al₂O₃, GaPt on SiO₂) dehydrogenation reactions already.^[7,9] In the present work, we extend the application of SCALMS systems to the dehydrogenation of cyclic alkanes. In particular, the dehydrogenation reaction of methylcyclohexane (MCH) to toluene (TOL) has been studied due to recent interest in this reaction in the context of reversible hydrogen storage (Liquid Organic Hydrogen Carrier, LOHC concept).^[10]

The results from our dehydrogenation experiments at 450 °C and 1 bar are shown in Figure 1. The absence of blind activity was confirmed for the reactor (empty and filled with SiO₂, see SI for details). The commercial Pt/SiO₂ catalysts showed an initial conversion of 13%, which quickly decreased by half and eventually declined to values below 2% after 12 h time-on-stream (TOS). At the same time, the selectivity of the catalyst toward desired toluene declined from initially 90% to values around 60%. The selectivity of C7 reaction intermediates such as methylcyclohexene and methylcyclohexadiene increased to 23.3% after 12 h TOS. The amount of other by-products from cracking or isomerization was below 5%. In contrast, the

[a] O. Sebastian, S. Nair, Dr. N. Taccardi, Dr. M. Wolf, A. Søgaard, Dr. M. Haumann, Prof. Dr. P. Wasserscheid
Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU)
Lehrstuhl für Chemische Reaktionstechnik (CRT)
Egerlandstr. 3
91058 Erlangen (Germany)
E-mail address:
E-mail: peter.wasserscheid@fau.de

[b] Prof. Dr. P. Wasserscheid
Forschungszentrum Jülich GmbH
Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (IEK 11)
Egerlandstr. 3
91058 Erlangen (Germany)

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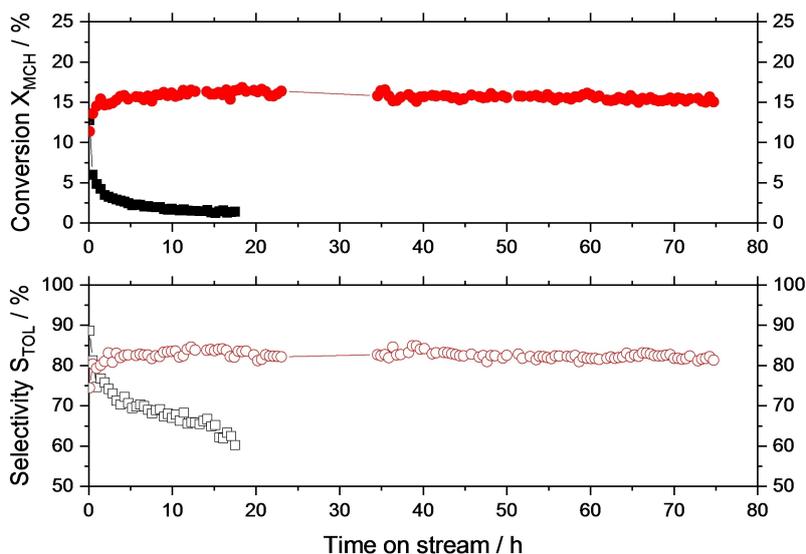


Figure 1. Dehydrogenation of methylcyclohexane (MCH) into toluene (TOL). Comparison between conversion (filled symbols) and selectivity toward toluene (open symbols) for Pt/SiO₂ (black) and Ga₅₂Pt/SiO₂ SCALMS (red) catalysts. Reaction conditions: 4.2 mL catalyst bed volume, T = 450 °C, p_{total} = 1 bar, H₂:MCH:He = 5:1:4 mol mol⁻¹, gas hourly space velocity (GHSV) = 1730 h⁻¹ (under reaction conditions).

Ga₅₂Pt/SiO₂ SCALMS catalyst showed significantly better performance. A Ga/Pt ratio > 50 was chosen as for these Pt concentration Ga–Pt alloys are fully liquid at the reaction temperature, i.e. 450 °C.^[11] After the preparation of catalysts via calcination, it can be assumed that Ga is present as bulk Ga⁰ droplets coated with a thin passivation layer of Ga₂O₃ which is known to be an active alkane dehydrogenation catalyst itself but leads also to the formation of cracking products.^[3,12] For a material such as Ga₅₂Pt/SiO₂ SCALMS, the presence of a hydrogen-activating metal enables the reduction of the oxidic passivation layer under hydrogen atmosphere at 450 °C.^[9b] Hence, we exposed Ga₅₂Pt/SiO₂ SCALMS to a hydrogen pretreatment at 450 °C before MCH dehydrogenation reaction. The initial conversion quickly exceeded 15% and was maintained over 75 h TOS, after which the run was deliberately stopped (average conversion X_{MCH} = 15.6%). Processes, which led to the deactivation of the Pt/SiO₂ catalyst are obviously suppressed in the SCALMS system. Furthermore, the average selectivity toward toluene remained high around 82.4% during the entire time-on-stream. Only a little amount of C7 intermediates (2.4% selectivity) was found. Ring-opening/closing, condensation, or isomerization reaction products were observed in low amounts

(< 5%, see Table 1). Noteworthy, without co-feeding hydrogen, the conversion and toluene selectivity was significantly lowered (see supplementary information, Fig. S7).

In order to elucidate the role of Pt and Ga in the Ga₅₂Pt/SiO₂ SCALMS catalyst, we also prepared a Pt-free Ga/SiO₂ material and exposed the Ga/SiO₂ to the same pretreatment and MCH dehydrogenation reaction conditions. Initially, the conversion was below 0.5% and gradually increased to a low level of around 3% after 18 h TOS, see Table 1. Interestingly, the selectivity towards toluene was comparable with the one of pure Pt/SiO₂, however, it could not compete with the Pt-SCALMS system. Additionally, higher amounts of ≤ C6 compounds were detected (6.2%), which stem from the cracking of the MCH substrate. Formation of C7 paraffins/isoparaffins (e.g. methylhexene or ethylpentene) and C7 isomers (e.g. ethylated cyclopentenes or cyclopentanes) was higher than with the other catalysts. As mentioned above, the ability of oxidic Ga to catalyze alkane dehydrogenation has been already reported,^[3,12] and the presence of Ga^{δ+} species^[9a,13] on the surface of the passivated gallium droplets may be held responsible for the observed catalytic activity. Conversely to the SCALMS system, Ga oxide cannot be fully reduced in the absence of H₂-

Table 1. Dehydrogenation of methylcyclohexane (MCH) into toluene (TOL): Comparison of Pt/SiO₂, Ga/SiO₂, and Ga₅₂Pt/SiO₂ SCALMS catalysts.

Catalyst	Pt [mg]	Ga [mg]	X _{MCH} [%]	S _{TOL} [%]	S _{≤C6} [%]	S _{Bz} [%]	S _{Xy} [%]	S _{C7,ene} [%]	S _{C7,para} [%]	S _{C7,isom} [%]
Pt/SiO ₂	17.0	–	1.6	65.6	3.1	1.1	1.4	23.3	1.5	4.0
Ga/SiO ₂	–	59.4	3.0	69.3	6.2	0.5	0.7	9.0	5.6	8.7
Ga ₅₂ Pt/SiO ₂	7.6	140.0	16.5	84.6	4.2	1.3	2.1	2.4	1.9	3.6

Pt = amount of Pt in reactor, Ga = amount of Ga in reactor, X = conversion at 12 h, S = selectivity at 12 h, MCH = methylcyclohexane, TOL = toluene, ≤ C6 = cracking products C1–C6 (excluding benzene), Bz = benzene, Xy = xylenes, C7,ene = methylcyclohexenes, C7,para = C7 paraffins, C7,isom = C7 isomerization compounds from ring opening or closing reaction. Reaction conditions: 4.2 mL catalyst bed volume, T = 450 °C, p_{total} = 1 bar, H₂:MCH:He = 5:1:4 mol mol⁻¹, gas hourly space velocity (GHSV) = 1730 h⁻¹ (under reaction conditions).

activating metal atoms (such as Pt in the case of Ga₅₂Pt/SiO₂).^[9b,13,14] The dehydrogenation activity of gallium oxide is accompanied by a significant tendency to promote by-product formation, via cracking and/or isomerization reactions. Similar results have been previously observed for the dehydrogenation of propane.^[9a]

Clearly, the use of Pt together with Ga in the form of SCALMS catalyst brings significant advantages for the dehydrogenation of methylcyclohexane under the here-applied conditions. From the conversion and selectivity data, the productivity (in kg_{TOL} kg_{Pt}⁻¹ h⁻¹) of the different catalysts with respect to the desired toluene product can be calculated (see SI for details). Summing up of these values over time-on-stream results in a cumulative productivity value (in kg_{TOL} kg_{Pt}⁻¹) that enables a proper comparison of the different catalytic systems under investigation as shown in Figure 2. The deactivation and loss of selectivity of the commercial Pt/SiO₂ catalyst result in a leveling off of the cumulative productivity to a value of 20 kg_{TOL} kg_{Pt}⁻¹ after 18 h TOS. The stable conversion and selectivity of Ga₅₂Pt/SiO₂ SCALMS catalyst, in contrast, leads to a linear increase in cumulative productivity reaching 140 kg_{TOL} kg_{Pt}⁻¹ after 18 h TOS and close to 700 kg_{TOL} kg_{Pt}⁻¹ after 75 h TOS. To the best of our knowledge, these results represent the most productive SCALMS system in the dehydrogenation of alkanes.^[15]

We have postulated in previous papers describing SCALMS systems for the catalytic dehydrogenation of short alkanes that the liquid nature of the gallium matrix under reaction conditions prevents to a large extent deactivation via coke formation.^[9,16] First, Pt is present in an atomically dispersed form under the SCALMS conditions. Since vicinal sites are required for coking, coke formation cannot be triggered easily in SCALMS systems. Second, Pt comes into contact with the substrate MCH only when it appears dynamically at the alloy/gas interface.^[7-9] After product desorption, Pt dives back into

statistically preferred Ga matrix,^[7] while hydrocarbon compounds do not dissolve in liquid gallium. Lastly, the dynamics of the liquid gallium surface prevents the blocking of the active Pt atoms via agglomeration of coke precursors.

We were therefore interested to analyze the spent SCALMS after MCH dehydrogenation for carbon deposition by means of temperature-programmed oxidation (TPO). As shown in Figure 3, only minor amounts of coke were indeed found on the Ga₅₂Pt/SiO₂ SCALMS system after MCH dehydrogenation experiments over 75 h time-on-stream as evidenced by a net weight loss of only 0.06 wt% in our TPO experiment. Taking into account the initial increase of the sample weight upon first exposure of the catalyst to 21% O₂/He the observed weight variation of the spent SCALMS in the TPO experiment increases to 0.18 wt%. The initial weight gain could be due to the oxidation of the SCALMS surface. However, the formation of metastable oxygen functionalities of the carbon deposits will also increase the weight during the heating ramp.^[9b,16-17] Simultaneous gasification of said intermediates resulting in CO₂ was observed at temperatures exceeding 200 °C even though the weight was increasing until reaching 350 °C due to the continuous formation of intermediates. Complete combustion of carbon deposits dominates the weight change at temperatures >400 °C as confirmed by means of mass spectrometry. The profile of CO₂ formation (m/z=44) suggests two major species of coke. Both species are highly reactive excluding polyaromatic condensation as formation mechanism of coke, which would result in less reactive, graphitic carbon.

Interestingly, no detectable carbon deposits were identified on the commercial Pt/SiO₂ catalyst after catalytic application even though strong deactivation was observed. This is not unexpected as MCH conversion declines very rapidly and therefore little amount of intermediates that may lead to the formation of coke is present. We assume that the rapid

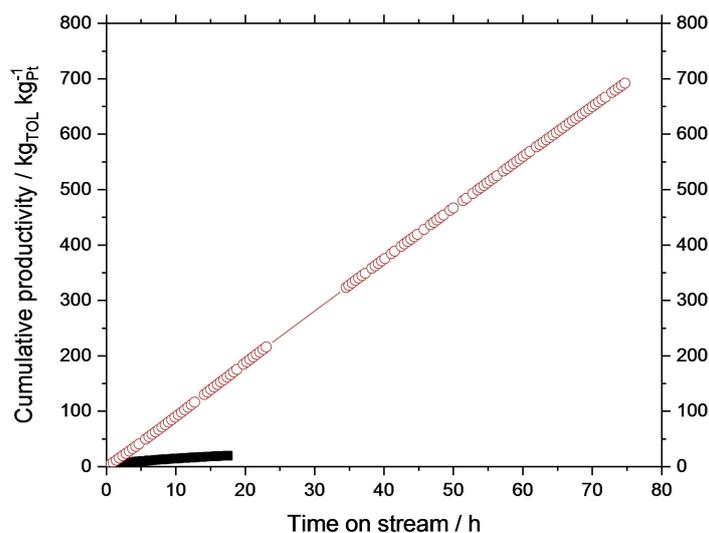


Figure 2. Dehydrogenation of methylcyclohexane (MCH) to toluene (TOL). Comparison between the cumulative productivity for toluene formation with Pt/SiO₂ (black) and Ga₅₂Pt/SiO₂ SCALMS (red) as catalysts. Reaction conditions: 4.2 mL catalyst bed volume, T = 450 °C, p_{total} = 1 bar, H₂:MCH:He = 5:1:4 mol mol⁻¹, gas hourly space velocity (GHSV) = 1730 h⁻¹ (under reaction conditions).

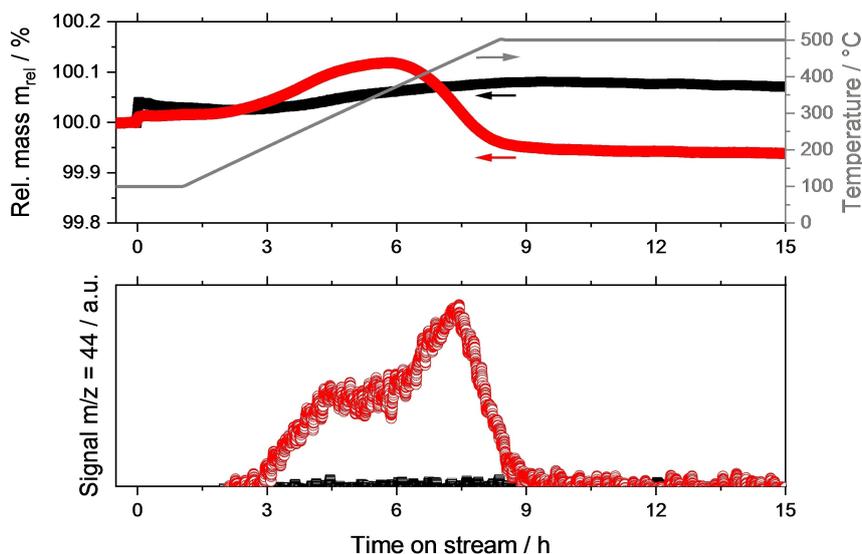


Figure 3. Sample weight relative to the weight prior to exposure to 21% O₂/He at 100 °C (filled symbols) and formation of CO₂ (open symbols) during temperature-programmed oxidation of spent Pt/SiO₂ (black) and Ga₅₂Pt/SiO₂ SCALMS (red) catalysts after dehydrogenation of methylcyclohexane as monitored via high-resolution thermogravimetry coupled with mass spectrometry. Reaction conditions: 0.2 g spent catalyst, 1 °C min⁻¹, $p_{\text{total}} = 1$ bar, O₂:He = 0 (TOS < 0) and 0.26 (TOS > 0) mol mol⁻¹, 100 mL_N min⁻¹.

deactivation of the classical heterogeneous Pt/SiO₂ could essentially be caused by 2 phenomena:

1. Small amount of carbon species may form in the early stage of the catalytic reaction and strongly adsorb on Pt surface and cause poisoning of the active sites.^[6]
2. The Pt particles undergo sintering. Both phenomena seem to apply for the pure Pt catalyst as the EDX mapping showed less dispersed Pt on the surface of the spent catalyst, while CO-TPD experiment hint for a significant poisoning of the Pt-sites. (For details see supplementary information Figures S8, S9, and S10).

In contrast, although significant CO₂ formation is observed in TPO of SCALMS, the catalytic activity in MCH dehydrogenation remained almost constant for 75 h time-on-stream. Thus, the SCALMS concept seems to effectively prevent deactivation. In fact, despite the formation of some reactive carbon deposits, they cannot strongly adsorb and poison the surface of the liquid alloy. Moreover, being in a liquidus regime, the active metal is always present atomically dispersed at the surface,^[7-8,9a] *de facto* avoiding sintering phenomena.

In conclusion, we have demonstrated the first application of SCALMS in the dehydrogenation of cyclic alkanes. This was demonstrated for Ga₅₂Pt/SiO₂, which showed stable conversion and selectivity in the dehydrogenation of methylcyclohexane to toluene at 450 °C and atmospheric pressure over 75 h time-on-stream with a cumulative productivity of 700 kg_{TOL} kg_{Pt}⁻¹. Under the applied conditions, this SCALMS system significantly outperformed the corresponding Pt/SiO₂ and Ga/SiO₂ systems with comparable amounts of Pt and Ga, respectively. Thus our results demonstrate the high potential of the SCALMS concept for aromatization reactions of cycloalkanes that are technically relevant for the refinery industry and also for future hydrogen storage applications. Further studies exploring other supports,

liquid metals, variation of Ga/Pt ratio, and reaction conditions (temperature, partial pressure of MCH and H₂, residence time, etc.) are currently ongoing.

Experimental Section

The SCALMS materials under investigation were prepared by the deposition of (Et₃N)GaH₃ onto mesoporous silica followed by thermal decomposition to yield Ga decorated silica (Ga/SiO₂).^[7] Pt deposition was achieved via partial galvanic displacement followed by calcination at 500 °C overnight. The desired Ga to Pt atomic ratio of 52 was obtained by adjusting the amount of stock solution added (here: H₂PtCl₆), see SI for details. The chemical composition of the SCALMS material was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Cirox CCD instrument, Spectro Analytical Instruments GmbH). Additionally, commercially available Pt/SiO₂ was purchased from Sigma-Aldrich for benchmark experiments. The dehydrogenation of MCH was carried out in a fixed-bed tubular reactor at 450 °C and atmospheric pressure (see SI for details). Prior to the dehydrogenation experiment, the catalyst was reduced *in situ* in an equimolar H₂-He gas mixture (24.50 mL_N min⁻¹ He and 24.50 mL_N min⁻¹ H₂) at 450 °C and atmospheric pressure for 2 hours. The reaction gas had a molar ratio of H₂:MCH:He = 5:1:4 (19.60 mL_N min⁻¹ He, 24.50 mL_N min⁻¹ H₂, 0.02 g min⁻¹ MCH). The product gas stream was analyzed by an online GC equipped with FID. Additionally, the condensed product stream was analyzed using offline GC-MS. The spent catalysts were subjected to temperature-programmed oxidation (TPO) using high-resolution thermogravimetric analysis coupled with mass spectrometry (HRTGA-MS) in a XEMIS sorption analyzer (Hiden Isochema) to investigate the amount of coke formed.^[16]

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Conflict of Interest

The authors declare no conflict of interest.

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