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In Situ Raman Spectroscopy of Supported Catalytically Active Liquid Metal Solutions (SCALMS)—Activation and Coking Behavior in Propane Dehydrogenation

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Supported catalytically active liquid metal solutions (SCALMS) represent a new class of catalysts characterized by a highly dynamic catalytic interface due to the liquid state of the active phase. In this study, we have investigated the relevance of H_2 pre-reduction treatment of Ga–Pt SCALMS in propane dehydrogenation reaction (PDH). To elucidate the role of hydrogen during pretreatment and the reason for catalyst deactivation, in situ Raman spectroscopic characterization of silica-supported Ga–Pt SCALMS catalysts was carried out during PDH at 823 K. The results demonstrate that the native passivating ß-Ga_2O_3 skin present in fresh Ga–Pt SCALMS catalyst can be effectively reduced via pretreatment with hydrogen at 823 K. The presence of Pt is crucial for the reduction. With the onset of the PDH reaction, the in situ Raman spectra show the formation of graphitic coke over the applied Ga–Pt-based SCALMS catalysts, which is at least partly due to the reactivity of the applied support material or due to some remaining gallium oxide present in the system. Over long time on stream, the formed graphitic coke accumulates, eventually leading to deactivation of the catalyst.

1. Introduction

Propene is among the most important platform chemicals due to its versatility as a building block for the production of various intermediates and products.[1] Currently, this compound is mostly produced via steam cracking and fluid catalytic cracking of higher hydrocarbons.[2] As the demand for propene is steadily increasing, the search for alternative on-purpose technologies for its production has led to a growing interest in selective propane dehydrogenation (PDH) processes.[3] One major challenge of the current industrial PDH processes is the rapid deactivation of the catalyst by coking. Therefore, all industrial PDH processes currently in use either use sequences of reaction and catalyst regeneration cycles (e.g., Snamprogetti/Yarsintez and Catofin technology), or employ an oxygen/steam-assisted dehydrogenation (e.g., Oleflex and STAR technology) that affects the selectivity of the process.[4]

To overcome some of the limitations associated with high-temperature catalysis, the use of bimetallic catalysts, especially gallium–platinum alloys has been suggested.[5,6] Recently, we have developed the concept of supported catalytically active liquid metal solutions (SCALMS).[7,8] SCALMS materials consist of a small amount of catalytically active metal (e.g., Pd, Rh, Ni, and Pt) dissolved in a low-melting metal matrix (e.g., Ga, Sn, In, or mixtures thereof). These alloys are deposited on a support as small particles and transform into liquid alloy droplets upon heating the SCALMS to operating conditions.[7] In the case of PDH, the catalytically active metal promotes dehydrogenation at the highly dynamic liquid interface of the SCALMS from where the formed propene desorbs.[7–9] The active metal moves then back into the bulk of the matrix metal, while organic compounds do not dissolve in the liquid metal. This protects the active metal from sintering or coking, which are the typical deactivation phenomena in classical heterogeneous catalysis. SCALMS materials with Ga as the liquid metal matrix have been proven effective for a number of dehydrogenation reactions, that is, of propane, butane, heptane, and cyclohexane.[7–11] In all these reactions, SCALMS materials showed high specific activity and excellent selectivity under the harsh operating conditions necessary for thermodynamic reasons. The observed minor deactivation over prolonged time-on-stream was attributed to coking, which, in

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the case of PDH, was stronger when Al_2O_3 was used as support compared to SiO_2-supported systems.[9,12,13] Given the high oxophilicity of Ga, the formation of a thin gallium oxide skin was observed during catalyst preparation and storage under air. This oxide skin was found to be removable by a reductive pretreatment using H_2 at elevated temperatures and it was speculated that the presence of the active noble metal is necessary to achieve this reduction.

In this paper, we report, for the first time, in situ Raman spectroscopy studies to investigate the influence of H_2 pre-treatment on the catalytic performance of GaPt-SCALMS. We determine the role of Pt in reducing the gallium oxide skin and monitor coke formation during PDH reaction.

2. Materials and Methods

All chemicals were purchased from commercial suppliers and used as received. Gallium nuggets (size 3 mm, purity: 99.999%, Alpha Aesar), hexachloroplatinic acid (Pt basis: $\geq$ 37.5%, Sigma–Aldrich), propan-2-ol (purity $\geq$ 99.8%, VWR chemicals), and silica gel spherical (75–200 µm, 287 $m^2\ g^{-1}$, 9 nm pores, Supelco Analytical) were used to prepare the Ga–Pt SCALMS materials.

Two SCALMS materials with Ga to Pt ratios of 46 and 49 (both forming liquid alloys under the typical PDH reaction conditions) were prepared using a top-down approach via ultrasonication.[9] 1 g of gallium was dispersed in 100 mL propan-2-ol using a Branson sonifier equipped with a microtip (450 W, 80% power, 323 K) followed by the addition of the amorphous silica support (final Ga loading was 6.5 wt.%). Pt was introduced via galvanic displacement using hexachloroplatinic acid (see Supporting Information for details).[14]

Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Ciros CCD instrument, Spectro Analytical Instruments GmbH) was carried out to determine the chemical composition of the synthesized SCALMS materials. The instrument was calibrated with standard solutions of Pt and Ga, using their respective emission lines at 214.423 nm and 417.206 nm. The samples were digested in a mixture of $HCl:HNO_3:HF$ in 3:2:1 ratio using microwave heating at 493 K for 20 min.

PDH was investigated under a continuous flow of propane in a lab-scale fixed-bed tubular quartz reactor (length = 65 cm, inner diameter = 1 cm) placed inside an electrically heated tubular split furnace. To evaluate the effect of H_2 pretreatment, one batch of the SCALMS catalyst was first heated under Ar (99.998% purity, Air Liquide) flow to 823 K. Then the sample was treated with 20 vol.% H_2 (99.999% purity, Air Liquide) in Ar for 3 h at 823 K, 0.12 MPa. For comparison, a second batch of catalyst was only heated in Ar flow to 823 K. PDH was subsequently conducted at 823 K, 0.12 MPa for 15 h time on stream using a flow of 8.9 $mL_N \cdot min^{-1}$ of propane (99.95% purity, Air Liquide) and 89.9 $mL_N \cdot min^{-1}$ of argon. A Bruker 456 online GC with a flame ionization detector and a GC-GASPRO column (30 m × 0.32 mm) was used for product analysis.

Raman spectra were acquired in a Renishaw Qontor confocal Raman microscope with a 50x long-distance objective (N. A = 0.35) using 405 nm laser excitation. Measurements under ambient conditions were carried out by placing the powdered sample as a thin layer on a glass slide. For in situ Raman characterization, the sample was loaded into a home-made heated quartz *operando* reactor (5 × 5 mm, length = 17 mm) sandwiched between beds of inert silicon carbide to enhance the heat transfer rate and decrease the void volume.[15] The packed bed was held in place with quartz wool. The sample was submitted to the same operating conditions as for the catalytic tests while Raman spectra were recorded with either 3 or 12 accumulations of 20 s and a laser power of 10% (1.1 mW) and 50% (5.9 mW). Raman shift axis calibration was adjusted with the help of the main silicon band.[16] Spikes were removed with an open-source, in-house algorithm,[17] and baseline subtraction was performed with an asymmetric least square smoothing algorithm.[18]

3. Results and Discussion

As shown in Figure 1, the $Ga_{46}Pt/SiO_2$ catalyst that was prereduced under H_2 showed a significantly higher conversion in PDH compared to the one without such a pretreatment. Moreover, the $Ga_{46}Pt/SiO_2$ SCALMS catalyst reduced under H_2 also showed higher selectivity towards propene. The $Ga_{46}Pt/SiO_2$ SCALMS without H_2 pretreatment also showed a higher cracking activity, which is a typical behavior reported for Ga_2O_3 in PDH.[19]

Next, Raman spectroscopic studies were conducted under different gas atmospheres to elucidate the surface composition of the $Ga_{49}Pt/SiO_2$ SCALMS material. Figure 2 shows the Raman spectra of $Ga_{49}Pt/SiO_2$ under different operating conditions. Under ambient conditions, Raman bands appear at 136, 165, 200, 338, 416, 464, 639, and 751 cm^{-1}; these bands correspond to ß-Ga_2O_3.[20,21] The presence of gallium oxide in $GaPt/SiO_2$ SCALMS synthesized through ultrasonication is attributed to the formation of a thin oxide shell at the surface of the Ga particles, where water, for example, via a galvanic displacement step, acts as an oxidant.[22] Note that this oxidation cannot be prevented. Because of the very high oxophilicity of Ga, even traces of moisture in solvents would lead to this oxide shell formation. The in situ Raman spectra of $GaPt/SiO_2$ SCALMS heated to 823 K under Ar are practically identical to the spectra recorded under ambient conditions, indicating that the heating at 823 K alone does not reduce the ß-Ga_2O_3 under the flow of inert gas. With this oxide skin still intact, the higher cracking activity in PDH can be explained (see selectivity in Figure 1). However, the intensity of the Raman bands recorded in situ at 823 K significantly decreased after introducing H_2 to the system, indicating the reduction of ß-Ga_2O_3 under these conditions. In the case of the reference material Ga/SiO_2, the bands corresponding to ß-Ga_2O_3 observed under ambient conditions are still very intense even after reduction in 20 vol.% H_2/Ar at 823 K (see Supporting Information, Figure S1), indicating that the presence of Pt is essential for the reduction of the gallium oxide in the catalyst. In fact, it has been reported that the presence of Pt facilitate the reduction of GaOx via spill-over mechanism.[6] Note that some coke is already present on both pristine materials, $GaPt/SiO_2$ SCALMS, and Ga/SiO_2, likely formed from the remaining chemicals during the synthesis procedure.

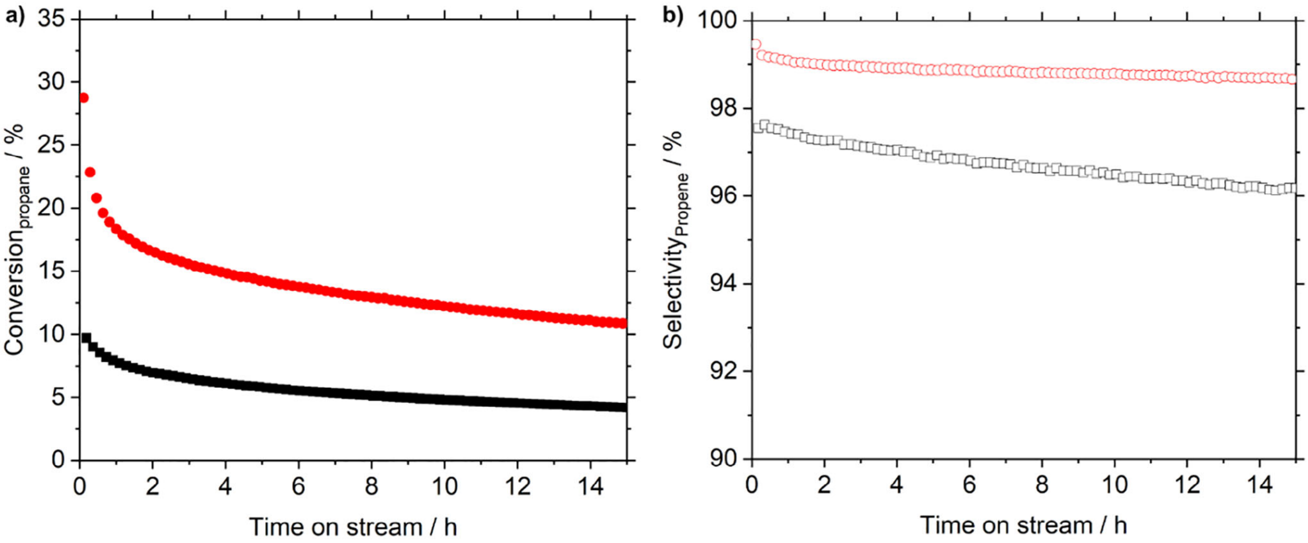

Figure 1. (a) Conversion and (b) selectivity in propane dehydrogenation using $Ga_{46}Pt/SiO_2$ SCALMS materials that were not pretreated (black) or pretreated (red) with a 20 vol.% H_2/Ar flow at 823 K and 0.12 MPa bar for 3 h. PDH conditions: C_3H_8 flow 8.9 $mL_N{\cdot}min^{-1}$, Ar flow 89.9 $mL_N{\cdot}min^{-1}$, 823 K, 0.12 MPa, and GHSV = 3950 $mL_{gas}\,g_{Cat.bed}{}^{-1}h^{-1}$.

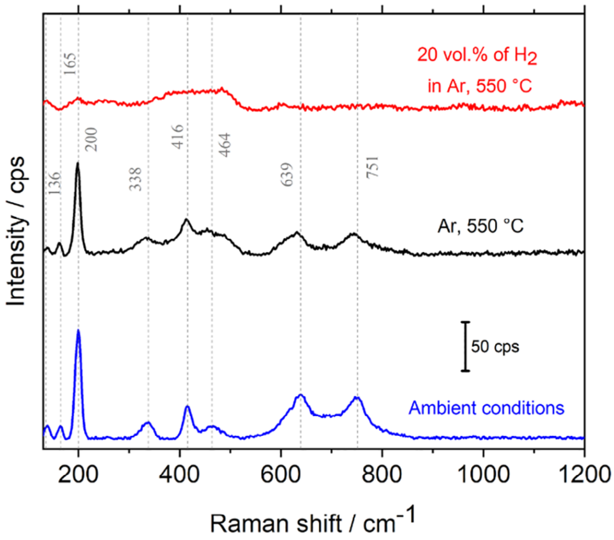

Figure 2. Raman spectra of $GaPt/SiO_2$ SCALMS under different conditions. Blue line: ambient conditions, black line: after Ar flow at 823 K, and red line: after 20 vol.% H_2/Ar flow at 823 K.

After reduction at 823 K in 20 vol.% H_2/Ar, the material was shortly flushed with Ar without changing the temperature and then propane was fed to Raman cell. Figure 3 shows the temporal evolution of the in situ Raman spectra of $Ga_{49}Pt/SiO_2$ SCALMS recorded during this procedure. Note that the broad Raman features apparent in the 300–500 cm^{-1} window and near 600 and 800 cm^{-1} are associated with amorphous silica in the quartz operando reactor window. Interestingly, the initial exposure of the catalyst to pure Ar resulted in the fast reappearance of the bands typical for ß-Ga_2O_3 (see Supporting Information, Figure S2). As Ga is strongly oxophilic, this oxide shell probably forms due to impurities such as trace levels of O_2 or H_2O in the applied flow of Ar.[22,23] The unexpected formation of GaOx in a highly inert atmosphere indicates that even in systems where Ga oxidation would not be expected GaOx may play a role.

Once propane is introduced into the Raman cell and the PDH reaction proceeds, the intensity of the oxide band at 200 cm^{-1} greatly weakens, and reaches a plateau after 40 min of operation (Figure 3a). This reduction is most likely caused by the hydrogen produced in the reaction, which would result in higher selectivity, as the presence of GaOx would lead to a higher proportion of cracking products (see Figure 1b). Concomitantly, the D and G Raman bands of coke grow at 1350 and 1599 cm^{-1}, respectively, after feeding propane to the cell (Figure 3a). The G band corresponds to graphite-type lattice vibrations and the D band to disordered graphite lattice vibrations.[24–27] As shown in Figure 3b, the ratio of integrated areas of peaks at 200 cm^{-1} and the D and G bands indicates that coking occurs immediately and continuously with the onset of PDH. Note that we cannot distinguish between coke forming on Ga or coke forming on the support surface, but given the high dynamic nature of the liquid alloy at 823 K no vicinal sites of Pt are present, hence the formation of coke on the support is more likely.[7–12]

Raman spectra of $GaPt/SiO_2$ SCALMS acquired at different spots within the measurement frame in the *operando* reactor consistently show the formation of D and G bands of graphitic coke (see Supporting Information, Figure S3). As PDH proceeded, the coke overtone band G´ at 2700 cm^{-1} was also observed at certain spots, underlining a large size of coke domains.[28] In previous studies,[9–13] bulk techniques such as high-resolution thermogravimetric analysis coupled with mass spectrometry (HRTGA–MS) reported minimal coke formation on silica-supported GaPt based SCALMS, pointing at the support as the origin of coke. Coherently, we observe the formation and growth of D and G bands corresponding to graphitic coke not only on the $GaPt/SiO_2$ SCALMS, but also on the Pt-free reference material, Ga/SiO_2 (see Supporting Information, Figure S4). Due to the surface sensitivity of Raman spectroscopy to coke, it is

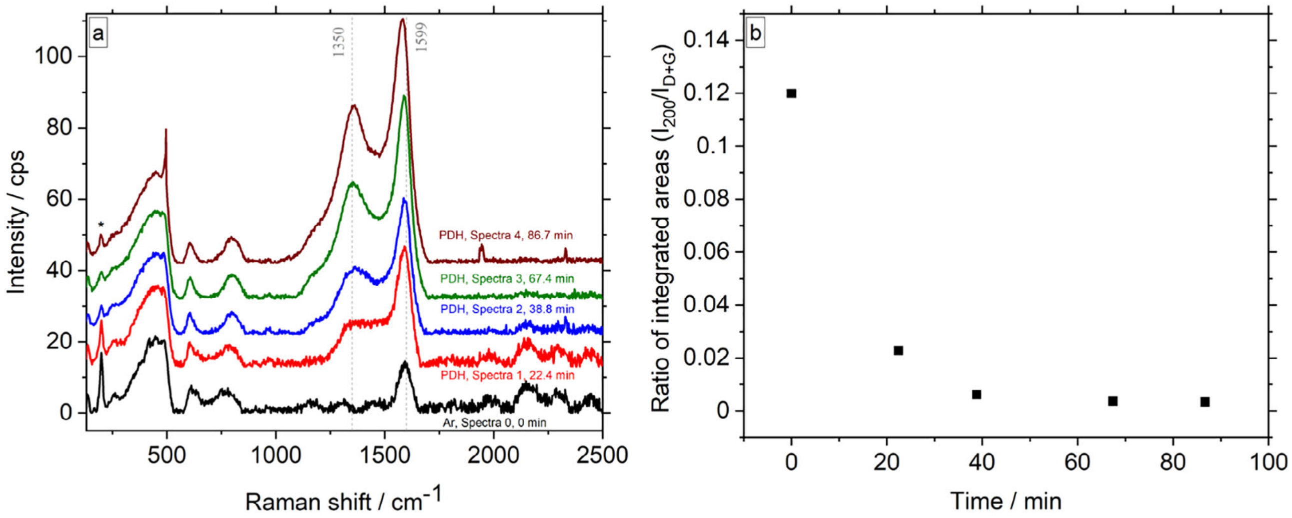

Figure 3. In situ Raman study of GaPt/SiO$_2$ SCALMS under PDH operating conditions (9 vol.% propane/Ar at 823 K and atmospheric pressure). Raman intensity is monitored over time at the same spot within the measurement frame at the *operando* reactor (a). The decline of the Ga oxide band at 200 cm^{-1}, marked with the asterisk in the spectra, and the rise of the G and D bands associated with coke is shown in (b) as the evolution of the ratio between their integrated areas. PDH conditions: C_3H_8 flow 8.9 mL$_N$·min^{-1}, Ar flow 89.9 mL$_N$·min^{-1}, and 823 K, atm.

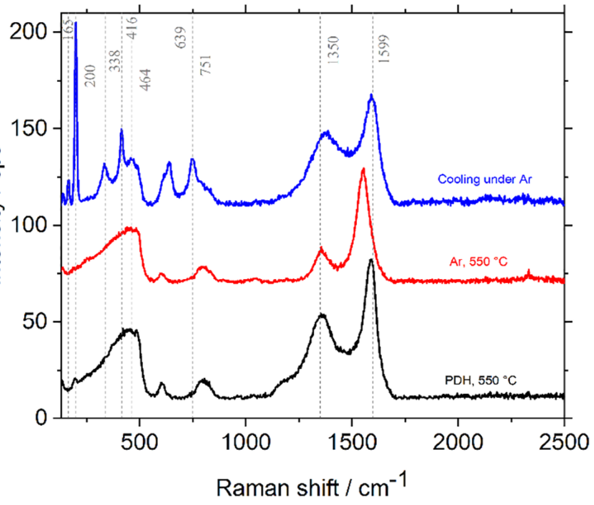

Figure 4. In situ Raman spectra of GaPt/SiO$_2$ SCALMS acquired at different spots within the measurement frame in the *operando* reactor cell during cooling down after replacing the flow of propane by Ar. PDH conditions: C_3H_8 flow 8.9 mL$_N$·min^{-1}, Ar flow 89.9 mL$_N$·min^{-1}, and 823 K, atm.

possible that the observed coke formation is limited to a few atomic layers of carbon.[9] Still, such coke formation can affect the accessibility of the active catalytic sites and thus reduce catalyst activity.

Figure 4 shows Raman spectra of GaPt/SiO$_2$ SCALMS at different spots within the measurement frame in the *operando* reactor cell recorded after PDH while cooling down under Ar gas flow. The ß-Ga_2O_3 bands appear again due to reoxidation. This finding confirms that at 823 K the H_2 generated in the PDH reaction created a reducing environment that suppressed Ga_2O_3. However, Ga_2O_3 forms upon cooling in the absence of this reducing atmosphere. This is attributed to the high affinity of gallium for the ubiquitous oxygen and/or the water present in traces in the argon (99.999% vol.) used for this experiment.

4. Conclusions

In this work, the effect of H_2 pre-treatment on Ga–Pt/SiO$_2$ SCALMS materials was investigated. Ga–Pt/SiO$_2$ SCALMS pretreated under 20 vol.% H_2 flow at 823 K for 3 h exhibited twice as high activity for propane dehydrogenation (PDH) than when the catalyst that was not reduced. In addition, the propene selectivity was slightly higher for the pretreated SCALMS material, while the untreated one resulted in higher cracking activity. Such cracking activity is known for Ga_2O_3 in PDH.

Our in situ Raman spectroscopy studies proved suitable for studying the GaPt/SiO$_2$ SCALMS under different pretreatment and operating conditions. Under ambient conditions, the Raman spectra of the Ga–Pt/SiO$_2$ SCALMS and of the Ga/SiO$_2$ reference material showed the typical bands of ß-Ga_2O_3. The latter forms during the SCALMS synthesis and storage. However, also traces of water or oxygen are sufficient for gallium oxide formation due to the strong oxophilicity of Ga. For Ga–Pt/SiO$_2$ SCALMS, the gallium oxide Raman bands disappear almost completely upon exposure to 20 vol.% hydrogen flow at 823 K, giving us a strong indication that the passivating ß-Ga_2O_3 layer is reduced under these conditions. In contrast, for the Pt-free Ga/SiO$_2$ sample, the gallium oxide bands remain unaffected under the same reducing conditions, indicating that the presence of Pt is required to enable gallium oxide reduction.

The in situ Raman spectra of the SCALMS under PDH conditions revealed a linear growth of the characteristic D and G bands of graphitic coke, indicating its formation and surface accumulation over time. As coking was also observed in the Pt-free Ga/SiO$_2$ reference material in presence of propane, we conclude that at least part of this coke formation is due to the reactivity of the catalyst support or the gallium oxide present. Our surface-sensitive in situ spectroscopic study has therefore provided extremely valuable insights into the activation and deactivation of Ga–Pt/SiO$_2$-SCALMS systems in the

PDH reaction. These insights will help us to select better support materials, develop better synthesis protocols, and define more efficient pretreatment protocols to significantly improve SCALMS-promoted dehydrogenation catalysis in the future.

Author Contributions

Sharanya Nair: Resources, investigation, visualization, formal analysis, and writing—original draft preparation. **Nicolas Coca-Lopez**: Investigation and formal analysis. **Nnamdi Madubuko**: Resources, investigation, formal analysis, and methodology. **Raquel Portela**: Resources, investigation, visualization, and writing—review and editing. **Nicola Taccardi**: Validation, conceptualization, writing—review and editing. **Marco Haumann**: Conceptualization, supervision, writing—review and editing. **Miguel A. Bañares**: Supervision, writing—review and editing. **Peter Wasserscheid**: Writing—review and editing, supervision, and project administration.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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