FULL PAPER



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Supported rhodium liquid metal catalysts for the hydroformylation of olefins

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National Natural Science Foundation of China, Grant/Award Number: 21676140; State Key Laboratory of Materials-Oriented Chemical Engineering, Grant/ Award Number: ZK201711 The hydroformylation of olefins in supported room temperature liquid metals was developed, and the supported Rh liquid metal catalysts (Rh SLMCs) showed unprecedented activity and high selectivity for the hydroformylation of olefins to aldehydes. The turnover frequency is up to 7000 h⁻¹, much higher than that of homogeneous RhCl₃ + 3PPh₃ catalyst. Moreover, the Rh SLMCs can be recovered conveniently without obvious deactivation, and the total turnover number is up to 250 000. The active Rh(I) catalyst formed *in situ* can be reduced back to Rh(0) by the free electrons in liquid metal when H₂/CO gas is emitted, and thus Rh is not leaked into the organic solvent. Long-chain olefins, cycloolefins and styrenes were applied, and the corresponding aldehydes were obtained in good to excellent yields.

KEYWORDS

aldehydes, hydroformylation, liquid metal, olefins, rhodium

1 | INTRODUCTION

Room temperature liquid metals $(RTLMs)^{[1-3]}$ are different from molecular liquids and ionic liquids,^[4–6] and RTLMs behave as flowing metal cations in free electrons and reactions in RTLMs are probably also different from reactions in traditional solvents. It is interesting to study organic reactions in RTLMs, but only few reports of dehydrogenation in liquid metal at high temperature (>400°C) have been published to date.^[7,8] Generally, RTLMs can dissolve catalytic active metals, and RTLMs are insoluble in organic solvents. On the other hand, active metals in liquid metal (metal solutions) should be atomically dispersed, and supported metal solutions can be contacted well with reactants. Gallium and gallium-based eutectic alloys such as GaIn (containing gallium and indium) and galinstan (containing gallium, indium and tin) are liquid at room temperature (or close to room temperature). The liquid metal galinstan (GaInSn eutectic alloy made of 68.5% Ga, 21.5% In and 10% Sn by weight) has a broad temperature range of liquid phase with a melting point at about 10°C. In addition, it is generally chemically stable and a series of previous studies have proven that such an alloy is safe for humans under normal circumstances.^[9]

Single-atom catalysts (SACs), with isolated atoms dispersed on supports, are emerging as a new frontier in the catalysis field.^[10-14] SACs are usually more active than the corresponding nanocatalysts^[15-18] (nanoparticles and nanoclusters on supports) owing to the atomic dispersion. In addition, SACs often offer high selectivity towards a specific product due to the atomic dispersion on supports. Thus, we can consider that SACs are similar to the homogeneous analogues but with separable properties like heterogeneous catalysts. Recently, we reported some nanocatalysts based on Pd, Rh and Ir for cross-coupling reactions and reductive amination reactions, and we are attempting to improve the catalyst performance further.^[19–21] If catalyst metals (such as Rh, Ru or Pd) are dissolved in RTLMs, the catalyst metals are homogeneous in liquid metals, and reactions can be conducted in RTLMs or at the surface of the RTLMs. Therefore the catalyst metals are atomically dispersed in the RTLMs (metal solution), and also the catalysts can be separated easily as the metal solution are insoluble in organic solvents. The liquid metal catalysts are SACs also for the corresponding reactions, and the atomic dispersion of the catalyst metal can be maintained, which can avoid the aggregation of the SACs. To increase the contact surface of the catalyst metals with organic reactants, catalyst metals in RTLMs can be dispersed on supports.

Rhodium-catalyzed hydroformylation of olefins is one of the most important industrial processes, with more than 10 million tons of aldehydes produced globally annually. The aldehydes produced from the hydroformylation of olefins^[22-25] are value-added fine chemicals that are employed in the synthesis of pharmaceuticals, agrochemicals, flavorings and food additives.^[26,27] But most industrial processes use homogeneous Rh catalysts, and the catalyst separation issue remains a problem.^[28] Some efforts have been devoted to develop heterogeneous catalysts for the hydroformylation of olefins. Supported Rh nanocatalysts were developed but with limited activity and selectivity for the hydroformylation of olefins.^[29-33] Besides, Rh SACs were reported also for the hydroformylation of olefins with good activity.^[34,35] and the Rh SACs can be recycled easily without evident deactivation.

In the work reported herein, the hydroformylation of olefins in supported RTLM (galinstan) was developed, and the supported Rh liquid metal catalysts (Rh SLMCs) showed unprecedented activity and high selectivity for the hydroformylation of olefins to aldehydes (Scheme 1). Moreover, the Rh SLMCs can be recovered conveniently without obvious deactivation. The active species, Rh(I), formed *in situ* can be reduced back to metal Rh(0) by the free electrons and dissolved into liquid metal after emitting CO/H_2 gas, and thus no Rh leaked into the solution and the Rh SLMCs can be recovered without deactivation.

2 | EXPERIMENTAL

2.1 | Catalyst Synthesis

2.1.1 | Synthesis of liquid metal galinstan

GaInSn alloy was synthesized based on a previously reported method with a slight change.^[9] Typically, 6.7 g of gallium, 2.05 g of indium and 1.25 g of tin metals were added to a 100 ml Schlenk tube under argon. After the Schlenk tube was heated at 100°C with stirring for 12 h, the mixture was cooled to room temperature and 10.0 g of liquid metal galinstan was obtained.



SCHEME 1 SLMCs for the hydroformylation of olefins.

2.1.2 | Procedure for preparation of Rh SLMCs

A typical procedure for the preparation of the catalysts was as follows. An amount of 12 ml of a toluene solution of rhodium acetate (Rh(Ac)₂; 5.0 mg of Rh) was added into galinstan liquid metal (1.0 g) in a stainless steel autoclave with a polytetrafluoroethylene (PTFE) liner and with a magnetic stirring bar. After stirring for 12 h at 100°C, the reaction mixture was cooled to room temperature. Subsequently, silica (4.0 g) was added and the whole reaction mixture was stirred at room temperature for 3 h. The obtained precipitate was filtered and washed with toluene, then dried under vacuum at 60°C for 6 h. This afforded Rh-SLMC-0.1% (Rh-SLMC-0.1% catalyst contains 0.1 wt% Rh and 20 wt% galinstan). Samples with various Rh weight loading (0.5 and 0.03%) were prepared similarly (Rh-SLMC-0.5% catalyst contains 0.5 wt% Rh and 20 wt% galinstan; Rh-SLMC-0.03% catalyst contains 0.03 wt% Rh and 20 wt% galinstan).

2.1.3 | Preparation of Rh-SLMC/C-0.1%

An amount of 12.0 ml of $Rh(Ac)_2$ solution (5.0 mg of Rh) in toluene was added into galinstan liquid metal (1.0 g) in a stainless steel autoclave with a PTFE liner and with a magnetic stirring bar. After stirring for 12 h at 100°C, the reaction mixture was cooled to room temperature. Subsequently, activated carbon (4.0 g) was added and the reaction mixture was stirred at room temperature for 3 h. The obtained precipitate was filtered and washed with toluene, then dried under vacuum at 60°C for 6 h. The resulting catalyst is designated as Rh-SLMC/C-0.1% (containing 0.1 wt% Rh).

2.1.4 | Preparation of 0.1% Rh in galinstan

An amount of 12.0 ml of $Rh(Ac)_2$ solution (1.0 mg of Rh) in toluene was added into galinstan liquid metal (1.0 g) in a stainless steel autoclave with a PTFE liner and with a magnetic stirring bar. After stirring for 12 h at 100°C, the reaction mixture was cooled to room temperature. The resulting catalyst is denoted as 0.1% Rh in galinstan (containing 0.1 wt% Rh).

2.1.5 | Preparation of galinstan/SiO₂

An amount of 12.0 ml of toluene was added into galinstan liquid metal (1.0 g) in a stainless steel autoclave with a PTFE liner and with a magnetic stirring bar. After stirring for 12 h at 100°C, the reaction mixture was cooled to room temperature. Subsequently, silica (4.0 g) was added and the whole reaction mixture was stirred at room temperature

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for 3 h. The obtained precipitate was filtered and washed with toluene, then dried under vacuum at 60° C for 6 h. The resulting catalyst is denoted as galinstan/SiO₂.

2.1.6 | Preparation of the 0.1%Rh/SiO₂

Silica (1.0 g) was dispersed into 15.0 ml of ethanol and the suspension was stirred at room temperature for 15 min. Then, 5 ml of $RhCl_3 \cdot 3H_2O$ solution (1.0 mg of Rh) in ethanol was added dropwise (1.0 ml min⁻¹) to the suspension. The resulting slurry was stirred for 3 h and ethanol was removed slowly under vacuum. The remaining solid sample obtained was dried at 60°C for 12 h. The dried sample was reduced using H_2 at 200°C for 3 h, affording 0.1%Rh/SiO₂ (containing 0.1 wt% Rh).

2.2 | Catalytic Hydroformylation of Olefins

The hydroformylation of olefins was conducted in a 30.0 ml stainless steel autoclave equipped with a stirring bar. In a typical procedure, 5.0 mmol of styrene, 10.0 mg of Rh-SLMCs-0.1% (about 10^{-5} mmol Rh metal) and 4.0 ml of toluene were added into the autoclave. Then, the autoclave was flushed five times with 1.0 MPa H₂, and charged successively with 2.0 MPa H₂ and 2.0 MPa CO gas. After the autoclave was sealed, it was heated to 100°C in an oil bath for 8 h. After reaction, 0.3 ml of *n*-hexadecane was added as the standard. The products were qualitatively analyzed using GC-MS. Products were quantitatively analyzed using an Agilent 7890A gas chromatograph equipped with an HP-5 capillary column and flame ionization detector.



FIGURE 1 Preparation of Rh SLMCs: (a) galinstan liquid metal with toluene; (b) galinstan liquid metal with toluene solution of rhodium acetate; (c) Rh metal in galinstan solution dispersed in toluene; (d) Rh metal solution under toluene after centrifugation at 6000 rpm.



FIGURE 2 SEM images of Rh-SLMC-0.1: (a) Rh-SLMC-0.1%, scale bar = 100 μ m; (b) Rh-SLMC-0.1%, scale bar = 1 μ m; (c) recycled Rh-SLMC-0.1%, scale bar = 100 μ m; (d) recycled Rh-SLMC-0.1%, scale bar = 1 μ m.

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The catalyst Rh-SLMCs-0.1% was separated by filtration and washed with *n*-hexane. The recovered Rh-SLMCs-0.1% was used again for a subsequent reaction under the same conditions.

2.3 | Catalyst Characterization

X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Ka radiation. X-ray diffraction (XRD) patterns were collected with a Bruker D8 Advance powder diffractometer using Ni-filtered Cu Ka radiation source at 40 kV and 20 mA, from 5° to 95° with a scan rate of 0.5° min⁻¹. The base pressure was about 3×10^{-9} mbar. Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4800 field-emission scanning electron microscope. Brunauer-Emmett-Teller (BET) surface areas were measured at the temperature of liquid nitrogen using a Micromeritics ASAP2010 analyzer. The samples were degassed at 150°C to a vacuum of 10^{-3} Torr before analysis. The amount of Rh was measured using a Jarrell-Ash 1100 inductively coupled plasma atomic emission spectrometry (ICP-AES) instrument.

3 | **RESULTS AND DISCUSSION**

3.1 | Analysis of Preparation Process of Rh SLMCs

The Rh SLMCs were prepared by supporting the Rh galinstan liquid metal solution on supports. Rh(Ac)₂ solution in toluene was added into the galinstan liquid metal in a stainless steel autoclave with a PTFE liner and magnetic stirring bar. When the reaction mixture was heated, $Rh(Ac)_2$ was reduced to Rh metal by Ga metal (excess Ga added), and then Rh metal was dissolved into galinstan liquid metal. So Rh in galinstan liquid metal solution was obtained. Silica was added into the mixture of the liquid metal solution and toluene with stirring, and then the Rh SLMCs were obtained after removal of the toluene by filtration. The process of the preparation of the Rh SLMCs is shown in Figure 1. The galinstan liquid metal with toluene is shown in Figure 1(a), with the galinstan liquid metal layer being under the toluene layer. When rhodium acetate was dissolved in the upper toluene layer, we can see the green rhodium acetate toluene solution on the galinstan liquid metal layer (Figure 1b). When the galinstan liquid metal with rhodium acetate toluene solution was heated, the rhodium acetate was reduced to Rh metal and dissolved in galinstan liquid metal. The Rh metal solution in galinstan liquid metal can be dispersed in toluene (Figure 1c). And then the Rh metal solution in galinstan liquid metal can be obtained after separation of the toluene by centrifugation (Figure 1d). The Rh SLMCs can be obtained by dispersion of the Rh liquid metal solution on silica.

3.2 | Characterization of Catalysts

The Rh SLMCs were characterized using SEM. Figure 2 shows SEM images of Rh-SLMC-0.1%. The Rh solution in galinstan liquid metal was dispersed well on the silica (Figure 2a,b), and small spheres of about 100 nm of the liquid metal phase were found on the surface of silica. Moreover, the appearance of the recycled Rh-SLMC-0.1% catalyst was similar to that of the fresh catalyst, and the liquid metal phase was also dispersed as small spheres of about 100–200 nm on the silica (Figure 2c,d). A small liquid sphere was analyzed using SEM/energy-dispersive X-ray spectroscopy, and the amount of Rh was about 0.05 at% and 0.26 wt%, which is in agreement with the Rh liquid metal solution. In addition, Ga, In and Sn were found in the liquid metal sphere. And no



FIGURE 3 (a) N_2 adsorption/desorption isotherm and pore size distribution of silica; (b) N_2 adsorption/desorption isotherm and pore size distribution of Rh-SLMC-0.1%.

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Rh was found in the silica surface without liquid metal sphere (supporting information, Figure S1).

Nitrogen adsorption/desorption analysis showed typical type IV isotherms for Rh-SLMC-0.1% and silica gel (Figure 3). The BET specific surface of Rh-SLMC-0.1% is about 235 m² g⁻¹ with an average pore diameter of 9.4 nm, which is slightly decreased from the parent silica gel (307 m² g⁻¹ with pore diameter of 9.6 nm). Rh is present in the Rh-SLMC-0.1% catalyst as both Rh(0) and Rh³⁺ states as determined from XPS spectra, although the signals are not strong. But the recycled Rh-SLMC-0.1% catalyst contained mainly Rh(0) (Figure 4). From the XRD patterns of silica and Rh-SLMC-0.1%, we can see a new weak peak of Ga₂O₃ formed possibly by the partial oxidation of Ga with air (Figure 5).

3.3 | Catalytic Performance of Rh SLMCs for Hydroformylation of Olefins

The hydroformylation of styrene was studied as a model reaction for the optimization of reaction conditions. Firstly, the amount of Rh in the Rh-SLMC catalysts was studied, and Rh-SLMC-0.1% was found to be good for

the hydroformylation of styrene (Table 1, entries 1–3). Similar catalyst Rh-SLMC/C-0.1% with activated carbon as support was not as good due to the poor wettability of the galinstan with activated carbon, as some liquid metal was left out beside the supported Rh-SLMC/C-



FIGURE 5 XRD patterns of Rh-SLMC-0.1% and silica.



FIGURE 4 XPS spectra of Rh: (a) fresh Rh-SLMC-0.1% catalyst; Rh 3d: 307 eV and 313.4 eV are Rh⁰; 309.1 eV and 314.8 eV are Rh³⁺;^[34,35] (b) recycled Rh-SLMC-0.1% catalyst; Rh 3d: 306.7 eV and 311.5 eV are Rh⁰; 308.8 eV is Rh³⁺;^[34,35] (c) fresh Rh-SLMC-0.1% catalyst; Ga 3d: 18.3 eV is Ga⁰; 20.3 eV is Ga³⁺; 25.0 eV is O 2s signal;^[36] (d) recycled Rh-SLMC-0.1% catalyst; Ga 3d: 18.6 eV is Ga⁰; 20.6 eV is Ga³⁺; 25.0 eV is O 2s signal;^[36]

TABLE 1 Hydroformylation of styrene with various catalysts^a

Entry	Catalyst	l:b ^b	S (%) ^c	Y (%) ^d	TOF (h ⁻¹) ^e
1	Rh-SLMC-0.5%	1.1	99	56	3601
2	Rh-SLMC-0.1%	1.1	99	99	6367
3	Rh-SLMC-0.03%	1.1	99	90	5788
4	Rh-SLMC/C-0.1%	1.1	99	19	1222
5	RhCl ₃	1.0	83	9	579
6	$RhCl_3 + 3PPh_3$	1.0	94	37	2380
7	0.1%Rh/SiO ₂	1.0	99	31	1994
8	0.1% Rh in galinstan	1.1	99	29	1865
9	Galinstan/SiO ₂	_	0	0	0

^aReaction conditions: 5.0 mmol of styrene; styrene/Rh = 51450 (mol/mol); 4.0 ml of toluene; 2.0 MPa H_2 , 2.0 MPa CO; at 100°C; for 8 h.

^bl:b = linear:branch.

^cSelectivity.

^dYields determined by GC.

 $^{\rm e}\!{\rm TOF}$ (turnover frequency) denotes moles of aldehyde (l + b) produced per mole of Rh catalyst per hour.

0.1% catalyst after dispersion of Rh liquid metal solution on activated carbon (Table 1, entry 4). Additionally, RhCl₃ only and homogeneous RhCl₃ with PPh₃ catalysts were found to be of low selectivity and low activity for the hydroformylation (Table 1, entries 5 and 6). The 0.1% Rh/SiO₂ without galinstan and the Rh solution (0.1% Rh in galinstan) without support are not as active as the Rh-SLMC-0.1% catalyst (Table 1, entries 7 and 8). Also, galinstan/SiO₂ without Rh was completely inactive (Table 1, entry 9). Although recently Rh SACs have been found to be highly active for hydroformylation, the turnover frequency (TOF) of Rh-SLMC-0.1% catalyst is up to 6367 h⁻¹, which is much higher than that of SACs and homogeneous Rh catalysts (Table 2, summary of recently reported results).

Next, the process of the hydroformylation of styrene catalyzed by Rh-SLMC-0.1% based on reaction time was studied (Figure 6). Styrene was converted to the

TABLE 2 Representative Rh nanoparticle-catalyzedhydroformylation of styrene

Entry	Catalyst	l:b	Selectivity (%)	TOF (h ⁻¹)	Ref.
1	Rh-SLMC-0.1%	1.1	99	6367	This work
2 ^a	0.006%Rh/ ZnO-nw	1.0	99	3333	[35]
3 ^a	Rh/ZIF-8	0.4	99	42	[31]
5 ^a	Rh-PPh ₃ /SiO ₂	0.2	99	239	[32]
6 ^a	Rh/Al ₂ O ₃	0.5	99	3200	[33]

^aReported TOF value.





FIGURE 6 Hydroformylation of styrene as a function of reaction time. Reaction conditions: 5.0 mmol of styrene; styrene/Rh = 51450 (mol/mol); 4.0 ml of toluene; 2.0 MPa H_2 , 2.0 MPa CO; at 100°C.

corresponding aldehydes (l + b) smoothly with good selectivity. The selectivity to aldehydes (l + b) was kept high from the start to the end (complete conversion). And the reaction rate was stable in the first 6 h (at about 90% conversion), and then went slightly down in the last 2 h (from 90to 100% conversion).

With the optimized reaction conditions in hand, the application scope of the Rh-SLMC-0.1% catalyst was investigated for the hydroformylation and the results are listed in Table 3. The hydroformylation of 4-chlorostyrene gave the corresponding aldehydes in 99% yield, and the TOF was up to 7004 h^{-1} (Table 3, entry 2), which is much higher than that with homogeneous $RhCl_3 + 3PPh_3$ catalyst (2500 h^{-1}). Moreover, the selectivity of homogeneous $RhCl_3 + 3PPh_3$ catalyst for the hydroformylation of styrene (94% to aldehydes, 6% to ethyl benzene) and 4chlorostyrene (92% to aldehydes, 8% to ethyl benzene) was lower than that of the Rh-SLMC-0.1% catalyst (Table 3, entries 1 and 2). Additionally, the hydroformylation of cyclopentene and cyclohexene gave the corresponding aldehydes in good yields in 18 h (Table 3, entries 3 and 4). But the hydroformylation of cyclooctene gave cyclooctanecarbaldehyde in 82% yield even at lower substrate-to-catalyst ratio (Table 3, entry 5). Aliphatic olefins, such as *n*-hexene, *n*-octylene and *n*dodecene, were converted to the corresponding aldehydes in good yields at high TOFs (Table 3, entries 5-8). Moreover, the hydroformylation of 3-hydroxy-2studied, methylpropene was with 4-hydroxy-3methylbutanal being obtained in good yield (Table 3, entry 9). Also, the hydroformylation of 2-phenyl-1-propene gave 3-phenylbutanal in 80% yield (Table 3, entry 10). From these results, most of the olefins can be converted to the corresponding aldehydes with excellent selectivity.

TABLE 3 Rh-SLMC-0.1%-catalyzed hydroformylation of various olefins^a

$R \longrightarrow + CO/H_2 \xrightarrow{\text{Rh-SLMC-0.1}} R \xrightarrow{\text{CHO}}$									
Entry	Product	S:C ^b	Time (h)	l:b ^c	C (%) ^d	S (%, l + b) ^e	TOF $(h^{-1})^{f}$		
1	CHO	51450	8	1.1	100	99 (94) ^h	6367 (2380) ^h		
2	CHO	56595	8	1.0	100	99 (92) ^h	7004 (2500) ^h		
3	СНО	51450	18	/	99	99	2801		
4	СНО	51450	18	/	98	99	2773		
5	СНО	5145	18	/	83	98	232		
6	n-C ₄ H ₉	51450	8	1.0	100	98	6303		
7 ^g	n-C ₆ H ₁₃ CHO	51450	10	1.0	98	98	4941		
8	n-C ₁₀ H ₂₁ CHO	12862	12	1.2	98	98	1029		
9	—————————————————————————————————————	5145	18	>99	83	98	232		
10	СНО	12862	12	>99	81	99	859		

 aReaction conditions: 4.0 ml of toluene; 2.0 MPa H_2; 2.0 MPa CO; at 100°C.

^bS:C = substrate (mol):catalyst (Rh mol).

^cl:b = linear:branch.

^dConversions determined by GC.

^eSelectivity.

^fTOF (turnover frequency) denotes moles of aldehyde produced per mole of Rh catalyst per hour.

^g4.0 ml of *n*-hexane as solvent.

^hHomogeneous catalyst (RhCl₃+ 3PPh₃) was used.

3.4 | Reusability of Catalyst Rh-SLMC-0.1%

The reusability of Rh-SLMC-0.1% was tested for the hydroformylation of styrene and the results are shown in Figure 7. Rh-SLMC-0.1% can be reused at least five times without obvious loss of reactivity. The slight deactivation of the Rh-SLMC-0.1% catalyst may be due to the loss of the catalyst in the recycling processes. The total turnover number (TON) is up to 250 000, which is unprecedentedly high compared to similar catalysts. Moreover, no Rh was detected (ICP-AES) in the solution after removal of the catalyst by filtration.

3.5 | Proposed Mechanism of Hydroformylation of Olefins over Rh SLMCs

The mechanism of the Rh-SLMC-0.1%-catalyzed hydrformylation of styrene was studied, and some control



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FIGURE 7 Recycling experiment for Rh-SLMC-0.1%. Reaction conditions: 5.0 mmol of styrene; styrene/Rh = $51450 \pmod{mol/mol}$; 4.0 ml of toluene; 2.0 MPa H₂, 2.0 MPa CO; at 100° C; for 8 h.





FIGURE 8 Proposed mechanism of hydroformylation of olefins over Rh SLMCs.

experiments were conducted. When hydrogenation of styrene (the reaction without CO gas, under 2.0 MPa H_2) was conducted (same reaction conditions as Table 1, entry 2, but without CO), the conversion of styrene to ethylbenzene was only about 2% (supporting information, Table S1, entry 1). The result implied that the Rh-SLMC-0.1% catalyst was firstly activated by CO gas, and the hydrogenation byproduct, ethylbenzene, was low. Moreover, the recycled Rh-SLMC-0.1% catalyst was found mainly to be Rh(0) metal state from XPS spectra (Figure 4). The active Rh(I) was reduced back to Rh(0) metal by free electrons and dissolved in liquid metal when the CO/H₂ gas was given out, since the active Rh center should be Rh(I) and liquid metal has free electrons. As the liquid metal phase is not soluble in toluene, the Rh-SLMC-0.1% catalyst can be recovered without Rh loss. A possible mechanism is presented (Figure 8).

4 | CONCLUSIONS

In summary, we developed the hydroformylation of olefins in supported RTLM (galinstan) firstly, and the Rh SLMCs showed high activity and high selectivity for the hydroformylation of olefins to aldehydes. The TOF is up to 7000 h⁻¹, much higher than that of homogeneous RhCl₃ + 3PPh₃ catalyst and SACs. Long-chain olefins, cyclo-olefins and styrenes were applied, and the corresponding aldehydes were obtained in good to excellent yields. Moreover, the Rh SLMCs can be recovered conveniently without obvious deactivation, and the total TON is up to 250 000. The active species, Rh(I), formed *in situ* can be reduced back to metal Rh(0) by free electrons and dissolved into liquid metal after emitting CO/H₂ gas, and thus no Rh leaked into the solution and the Rh SLMCs can be recovered without deactivation. We believe more organic reactions in liquid metals will be developed, and more insights can be obtained in the near future.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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