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Forum Article

Direct Heterogenization of the Ru-Macho Catalyst for the Chemoselective Hydrogenation of *α,β*-Unsaturated Carbonyl Compounds

Sudakar Padmanaban,[†] Gunniya Hariyanandam Gunasekar,[†] and Sungho Yoon*

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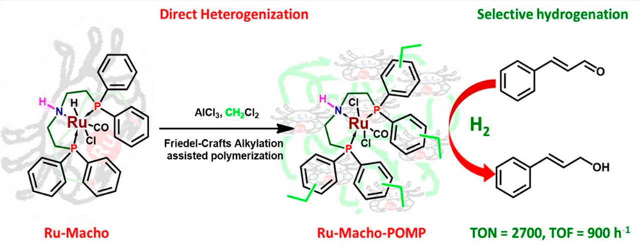
ABSTRACT: In this study, a commercially available homogeneous pincer-type complex, Ru-Macho, was directly heterogenized via the Lewis acid-catalyzed Friedel−Crafts reaction using dichloromethane as the cross-linker to obtain a heterogeneous, pincer-type Ru porous organometallic polymer (Ru-Macho-POMP) with a high surface area. Notably, Ru-Macho-POMP was demonstrated to be an efficient heterogeneous catalyst for the chemoselective hydrogenation of *α,β*-unsaturated carbonyl compounds to their corresponding allylic alcohols using cinnamaldehyde as a model compound. The Ru-Macho-POMP catalyst showed a high turnover frequency (TOF = 920 h^{-1}) and a high turnover number (TON = 2750), with high chemoselectivity (99%) and recyclability during the selective hydrogenation of *α,β*-unsaturated carbonyl compounds.



■ INTRODUCTION

The chemoselective hydrogenation of *α,β*-unsaturated carbonyl compounds to their corresponding unsaturated alcohols is an important class of organic reactions because the resulting allylic alcohols are important intermediates in the synthesis of numerous fine chemicals and pharmaceutical agents, agrochemicals, and perfumes.[1−10] The chemoselective hydrogenation of a carbonyl group of the *α,β*-unsaturated carbonyl compounds is challenging because reduction of the olefin group is kinetically faster than that of the carbonyl group. Additionally, hydrogenation of the C═C group relative the C═O group is thermodynamically preferred by a factor of 35 kJ mol^{-1}.[11] Therefore, developing highly efficient catalysts for the chemoselective reduction of *α,β*-unsaturated carbonyl compounds to allylic alcohols is highly desirable.[12−16]

In this context, numerous heterogeneous and homogeneous catalysts have been studied for chemoselective reduction of the carbonyl group of the *α,β*-unsaturated carbonyl compounds.[1−3,10−12,17−52] Here, the homogeneous catalysts show admirable reactivity for the chemoselective hydrogenation of carbonyl compounds. Alternatively, the heterogeneous catalysts exhibit noticeable benefits, including multiple-recycling ability, facile separation of products and catalysts, and easy handling, that underline the demand for developing highly efficient heterogeneous catalysts for the chemoselective reduction of *α,β*-unsaturated carbonyl compounds.

Pincer-type metal complexes are an indispensable class of catalytic materials for a variety of chemical transformations. A plethora of pincer-type ligand-based transition-metal complexes have been used as catalysts for the hydrogenation of various functional groups.[53−57] One of the notable pincer-type complexes is the commercially available Ru-Macho complex, which is a highly robust catalyst for several transformations, including the reduction of carbon dioxide, ester, and carbonyl compounds, as well as the dehydrogenation of amines, alcohols, and formic acid.[34,58−80]

Considering the efficiency and high catalytic activity of the Ru-Macho complex in a variety of chemical transformations and its commercial availability, it is suitable for use in industrial-level hydrogenation processes.[81] Furthermore, a Ru-Macho-based complex has been reported as an active catalyst for the base-free transfer hydrogenation of *α,β*-unsaturated carbonyl compounds to their corresponding alcohols, which suggests the possibility of using Ru-Macho complexes in large-scale hydrogenation processes.[25]

However, the homogeneous nature of the complex complicates the catalyst isolation and recycling in an industrial process and increases the operational cost. Notwithstanding its variety of catalytic applications, the homogeneous Ru-Macho complex has been reported to be unstable under basic conditions and forms various impurities, including dimeric Ru complexes.[82,83] Therefore, to conveniently achieve the benefits of both homogeneous and heterogeneous catalytic

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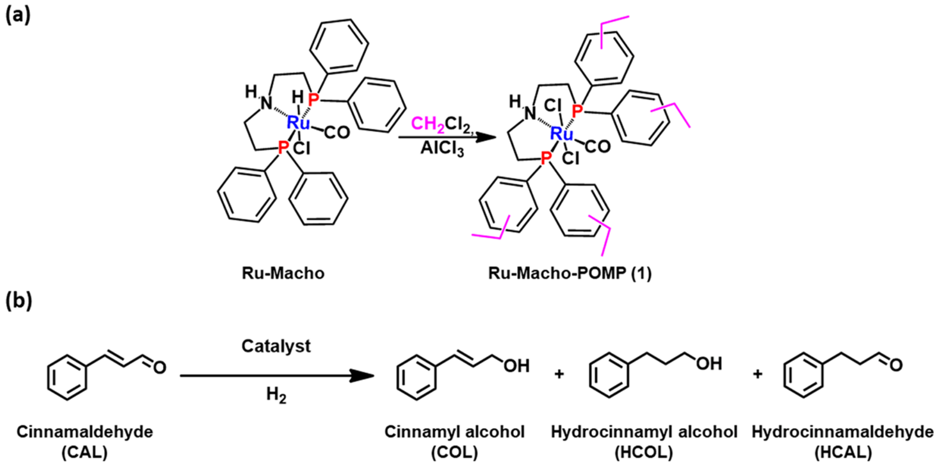
Scheme 1. Schematic Representations for (a) the Heterogenization of Ru-Macho to Ru-Macho-POMP (Catalyst 1) and (b) the Catalytic Hydrogenation of CAL



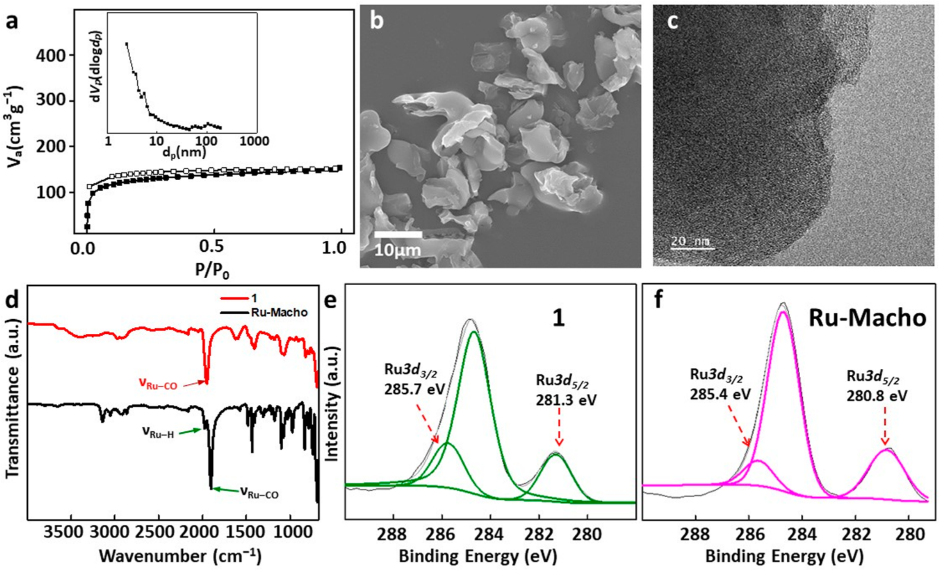


Figure 1. (a) N_2 sorption curve of catalyst **1**. The inset shows the pore-size distributions obtained via the BJH analysis method. (b) SEM image of catalyst **1**. (c) TEM image of catalyst **1**. (d) FTIR spectra of the homogeneous Ru-Macho complex (black line) and catalyst **1** (red line). Ru 3d core region from the XPS spectra of (e) catalyst **1** and (f) the Ru-Macho complex.

processes in further exploration studies, heterogenization of the Ru-Macho complex is highly desirable.

Recently, the Lewis acid-catalyzed Friedel−Crafts reaction (FCR) has been considered to be a potential approach to directly heterogenizing active homogeneous catalysts because it is a simple and economically viable method.[84−88] Additionally, the FCR-assisted aryl knitting strategy promotes the development of heterogenized catalysts with very high surface area, porosity, and robustness, which are beneficial for enhanced catalytic performance.[56,57,84,85,89−93] In this context, the commercially available homogeneous pincer-type complex Ru-Macho is heterogenized via the FCR to prepare a heterogeneous pincer-type porous organometallic polymer, Ru-Macho-POMP (catalyst **1**; Scheme 1a). The catalytic ability of the as-prepared catalyst **1** for the chemoselective hydrogenation of *α*,*β*-unsaturated carbonyl compounds was investigated using cinnamaldehyde (CAL) as a model compound (Scheme 1b). Additionally, the scope and limitations of catalyst **1** for the selective hydrogenation of carbonyl groups in the presence of other reducible groups were explored for carbonyl compounds containing cyano, nitro, ester, carboxylic acid, and aryl bromide groups.

■ RESULTS AND DISCUSSION

Initially, catalyst **1** was prepared via the Friedel−Crafts-assisted aryl knitting method using $AlCl_3$ as a Lewis acid catalyst and dichloromethane as a linker (Scheme 1a). The as-formed catalyst **1** is insoluble in most organic solvents and water. The porous properties of catalyst **1** were analyzed through N_2 sorption isotherms. The N_2 sorption isotherm for catalyst **1** shows the features of a type I isotherm (Figure 1a).[94] The steep adsorption at $P/P_0 \approx 0.1$, as well as the pore size determined via the Barrett−Joyner−Halenda (BJH) analysis method (Figure 1a, inset), indicates that the material is microporous, with appreciable amounts of mesoporous voids in it.[94] The surface area and total pore volume of catalyst **1**, as determined by the Brunauer−Emmett−Teller analysis, are 465 $m^2\ g^{-1}$ and 0.23 $cm^3\ g^{-1}$, respectively. The high surface area of

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Table 1. Chemoselective Hydrogenation of CAL by Catalyst **1**[a]

							selectivity (%)[b]		
entry	solvent	base	time (h)	pH_2 (MPa)	T (°C)	conversion (%)[b]	COL	HCOL	TON[c]
1	H_2O	KOH	1	1.0	40	2	99	1	4
2	MeOH	KOH	1	1.0	40	98	99	1	190
3	ethanol	KOH	1	1.0	40	85	93	7	160
4	isopropyl alcohol	KOH	1	1.0	40	68	99	1	130
5	THF	KOH	1	1.0	40	98	99	1	190
6	toluene	KOH	1	1.0	40	3	99	1	5
7	MeOH	Et_3N	1	1.0	40	3	100	0	5
8	MeOH	$KHCO_3$	1	1.0	40	2	99	1	4
9	MeOH	K_2CO_3	1	1.0	40	91	95	5	170
10	MeOH	K_3PO_4	1	1.0	40	95	95	5	180
11[d]	MeOH		1	1.0	40	70	0	0	0
12	MeOH	KOH	1	1.0	80	>99	83	17	160
13	MeOH	KOH	1	1.0	20	52	>99	trace	100
14	MeOH	KOH	1	2.0	40	99	99	1	195
15	MeOH	KOH	1	0.5	40	97	99	1	190
16[e]	MeOH	KOH	3	1.0	40	56	98	2.0	2750 (TOF = 920 h^{-1})
17[f]	MeOH	KOH	1	1.0	40	>99	83	17	160

[a]Reaction conditions: catalyst:substrate:base = 1:200:200; 4.0 mL of solvent. [b]Measured via ^1H NMR spectroscopy. [c]TON = [COL]/[Ru]. [d]Only acetal formation was observed. [e]Catalyst:substrate:base = 1:5000:5000; [f]Homogeneous Ru-Macho was used as a catalyst in place of catalyst **1**. TOF = TON/h.

catalyst **1** and well-maintained porosity are highly beneficial in catalysis to facilitate the mass transfer while maintaining the heterogeneity of the catalyst.

The morphology and crystallinity of catalyst **1** were probed via scanning electron microscopy (SEM), transmission electron microscopy (TEM), and powder X-ray diffraction (PXRD) analyses. The PXRD analysis of catalyst **1** reveals a broad reflex at $2\theta = 22°$, demonstrating that Ru-Macho-POMP is an amorphous carbonaceous solid (Figure S1). Additionally, the reflexes corresponding to Ru metal were not observed in the PXRD pattern of catalyst **1**, thereby indicating a homogeneous distribution of the Ru moiety in the POMP.[95]

The SEM image of catalyst **1** shows that the particles are formed as polydispersed blocks with irregular shapes (Figure 1b), while the TEM images further reveal the porosity of catalyst **1** (Figure 1c). Moreover, in line with the PXRD pattern, the energy-dispersive X-ray spectroscopy (EDX) analysis further supported the homogeneous distribution and coherence existence of the P, N, Cl, and Ru atoms in catalyst **1** (Figure S2).

The Fourier transform infrared (FTIR) spectra of catalyst **1** and that of the homogeneous Ru-Macho catalyst are compared in Figure 1d, which shows that the structural integrity of the Ru-Macho complex was maintained during polymerization. The FTIR spectrum of catalyst **1** shows the alkyl and aryl C−H bands between 2880 and 3080 cm^{-1} and the P−Ph band at 1100 cm^{-1}. However, the Ru−CO band at 1902 cm^{-1} in the Ru-Macho complex shifts to 1952 cm^{-1} after polymerization. This increased stretching frequency of the CO ligand in catalyst **1** indicates that the electron density on the Ru atom decreases after polymerization. Furthermore, the Ru−H band at 1974 cm^{-1} in the homogeneous Ru-Macho complex disappeared during polymerization, and the corresponding Ru−H band was not observed in catalyst **1**. This may be due to exchange of the hydride ligand with chloride ions during the $AlCl_3$-assisted polymerization. To verify this, a controlled experiment was performed using MeI as the alkylating agent in the Friedel−Crafts alkylation process in the presence of $AlCl_3$, and the reaction progress was monitored via ^1H NMR spectroscopy (Figure S3). Notably, the intensity of the original hydride peaks of the Ru-Macho complex that resonated at −12.2 and −15.1 ppm gradually decreased, and after 12 h, the hydride peaks completely disappeared. This experiment also supports the replacement of hydride ligands with other halide ions to form a ruthenium halogen complex during the FCR-assisted aryl knitting heterogenization of Ru-Macho complexes.

The solid-state ^{13}C cross-polarization magic-angle-spinning (CP/MAS) NMR spectral analysis of catalyst **1** showed the presence of aromatic phenyl rings at $\delta = 150-120$ ppm (Figure S4). The C sp^3 atoms of the ethyl units and the C atoms of the methylene linker units from CH_2Cl_2 were observed at $\delta = 52$, 42, and 35 ppm. In addition, the solid-state $^{31}P\{^1H\}$ CP/MAS NMR spectrum of catalyst **1** showed the resonance of the Ru-PPh_2 unit as a broad peak at $\delta = 65$ ppm (Figure S5).

The inductively coupled plasma optical emission spectrometry analysis of catalyst **1** revealed that the Ru content in the POMP after heterogenization was 9.0 wt %. The coordination environment of the Ru atom of catalyst **1** was probed via X-ray photoelectron spectroscopy (XPS) analysis. The deconvoluted Ru 3d core region shows the Ru $3d_{5/2}$ component at a binding energy (BE) of 281.3 eV, indicating that the Ru atom in catalyst **1** is in the 2+ oxidation state (Figure 1e).[96] However, for the homogeneous Ru-Macho complex, the $3d_{5/2}$ component is observed at a slightly lower BE of 280.8 eV, suggesting that the electron density on the metal center decreases after FCR-assisted polymerization (Figure 1f).

The aforementioned is attributed to the fact that the hydride ligand in the Ru-Macho complex is converted to Ru−Cl during polymerization. This result is consistent with the FTIR spectral results of catalyst **1**. These results again support that catalyst **1** is formed as shown in Scheme 1a.

After preparation of the heterogenized Ru-Macho-POMP catalyst **1**, its catalytic activity in the selective hydrogenation of carbonyl compounds was investigated using CAL as a model compound because the C=C group in CAL is highly activated toward hydrogenation by a catalyst.[27,30] In the case of the

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hydrogenation of CAL, along with the expected product cinnamyl alcohol (COL), the byproducts hydrocinnamaldehyde (HCAL) and hydrocinnamic alcohol (HCOL) are often observed (Scheme 1b).

Initially, the catalytic ability of catalyst **1** for the chemoselective hydrogenation of CAL to COL was tested in water (H_2O) with a substrate-to-catalyst ratio (S/C) of 200 in the presence of 100 mol % potassium hydroxide (KOH) at 40 °C under 1.0 MPa of H_2 pressure for 1 h. However, the use of H_2O as a solvent results in negligible formation of COL, although with high selectivity (99%; Table 1, entry 1), which is possibly due to the low dispersibility of catalyst **1** in H_2O arising from its low density. Therefore, other organic solvents were tested for their suitability in the chemoselective hydrogenation of CAL to COL using catalyst **1** (Table 1, entries 2−6). As seen in Table 1, catalyst **1** was inactive in the nonpolar solvent toluene. Notably, the catalytic conversion considerably increases in polar solvents, such as alcohols and tetrahydrofuran (THF). Among the tested alcoholic solvents, methanol (MeOH) showed the highest conversion (98%) and selectivity (99%) toward COL with a high turnover number (TON) of 190. The higher solubility of the base and H_2 gas in MeOH might be responsible for this high reactivity. Additionally, the aprotic polar solvent THF showed a reactivity similar to that of MeOH; however, the latter was preferred as a solvent in this study because the simple alcohol is an environmentally benign and greener solvent compared to THF.

The influence of a base on the selective hydrogenation of CAL to COL by catalyst **1** was then studied using a series of inorganic and organic bases, such as Et_3N, $KHCO_3$, K_2CO_3, K_3PO_4, and KOH (Table 1, entries 2 and 7−10). It is observed that the addition of a strong base is favorable for the conversion of CAL to COL because in the presence of the organic base Et_3N or the mild inorganic base $KHCO_3$ catalyst **1** shows negligible reactivity in the hydrogenation of CAL (<5% conversion; Table 1, entries 7 and 8).

The role of a base in the activation of Ru-Macho and related PN^HP-Ru complexes has been reported in the literature.[25,34,58−80] The base assists in the initial formation of the "activated Ru-Macho" via dehydrochlorination, as shown in Scheme S1. In the case of **1**, a series of dehydrochlorination and hydrogenation steps may be required to form the catalytically active Ru−H intermediate (Scheme S2), which necessitates the presence of a base in the current study. In line with this, in the absence of a base additive, only the acetal product formed from the reaction of CAL and MeOH was detected, and no COL formation was observed (Table 1, entry 11).

The reaction temperature significantly affects the outcome of the CAL reduction by catalyst **1**. At a higher temperature of 80 °C, 17% HCOL was formed as a result of additional reduction of the resulting COL (Table 1, entry 12). The selectivity for COL was only 83% in this case. However, decreasing the reaction temperature to 20 °C showed a reduction in the reaction rate, although the selectivity for COL was maintained over 99% (Table 1, entry 13). Therefore, the optimum temperature was maintained at 40 °C in this study.

Interestingly, catalyst **1** shows similar reactivity under different H_2 pressures ranging from 0.5 to 2.0 MPa (Table 1, entries 2, 14, and 15). Under a higher pressure of 2.0 MPa, only a negligible amount of HCOL was observed, whereas employing lower H_2 pressures of 1.0 and 0.5 MPa has shown similar TON and selectivity for COL formation. This indicates that a fast hydride-transfer reaction may occur from the Ru-metal center to the carbonyl group of CAL, even under low H_2 pressure. The reactivity of catalyst **1** was further investigated with an increased S/C of 5000 under optimal reaction conditions (Table 1, entry 16). A high TON of 2750 was obtained after 3.0 h with a very high TOF of 920 h^{-1}, and the selectivity of the allylic alcohol product was maintained at 98%, demonstrating that catalyst **1** was durable and active. However, the initial TOF after 9% conversion under the similar conditions of Table 1, entry 16, was determined to be 380 h^{-1}.

Additionally, the homogeneous catalyst Ru-Macho had shown hydrogenation activity superior to that of catalyst **1**; however, because of the high reactivity in the homogeneous conditions, the selectivity for COL was only 83% and a 17% HCOL formation was observed (Table 1, entry 17).

After exploration of the catalytic activity of catalyst **1** for the selective hydrogenation of CAL, the scope and limitations of catalyst **1** for the selective hydrogenation of carbonyl groups in the presence of various other reducible functional groups, such as nitrile, nitro, halogen, ester, carboxylic acid, and olefin, were also evaluated under the optimized conditions. The results are summarized in Table S1.

As seen in Table S1, the heterogenized catalyst **1** exhibited high chemoselectivity for hydrogenation of the carbonyl group over nitrile, carboxylic ester, and carboxylic acid functional groups (Table S1, entries 1−3). Both the nitrile and ester groups were tolerated during hydrogenation of the carbonyl group with excellent conversion rates (Table S1, entries 1 and 2). Although the homogeneous Ru-Macho complex was reported to be an active catalyst for the hydrogenation of nitrile and ester functional groups, the soothingly mild reaction conditions required for the reduction of aldehyde and keto groups inherited high chemoselectivity in the case of catalyst **1**.

The carboxylic group was not affected under the hydrogenation conditions; however, it was shown to affect the reaction rate (64%) for hydrogenation of the carbonyl group of 4-carboxybenzaldehyde (Table S1, entry 3).

However, when 4-bromobenzaldehyde was employed as a substrate, hydrodebromination also occurred along with the reduction of a carbonyl group (Table S1, entry 4). Similarly, in the case of 4-nitrobenzaldehyde as the substrate, hydrogenation of both the nitro and carbonyl functional groups occurred (Table S1, entry 5). Thus, carbonyl compounds containing the highly labile arylhalogen and nitro groups are unsuitable substrates for the selective hydrogenation by catalyst **1**. Furthermore, *p*-anisaldehyde and *o*-tolualdehyde are amenable substrates and are completely converted to the corresponding alcohols (Table S1, entries 6 and 7). Acetophenone, a ketone, was also smoothly hydrogenated to 1-phenylethanol by catalyst **1** (Table S1, entry 8). The heterocyclic carbonyl compound furfural was hydrogenated to furfuryl alcohol by catalyst **1** with a 100% conversion rate (Table S1, entry 9).

The chief benefit of a heterogeneous catalyst entails its usage in multiple-recycling runs with appreciable reactivity. Therefore, the recyclability of catalyst **1** in the chemoselective reduction of CAL was evaluated. As shown in Figure 2, catalyst **1** had shown recyclable catalytic activity at a reduced S/C of 100 for at least four cycles with high chemoselectivity. Markedly, after the fourth cycle, the conversion of CAL remained at 94% with a 97% chemoselectivity. Notably, the TEM−EDX analysis of the spent catalyst **1** suggested that Ru was maintained in the POMP support (Figure S6), which

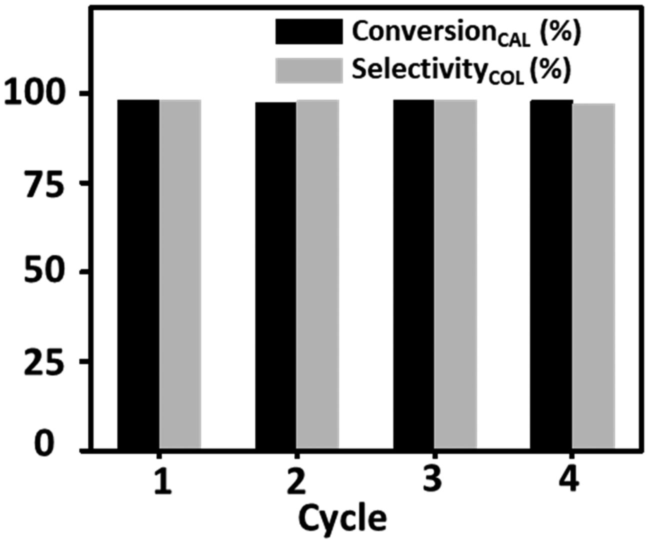

Figure 2. Recyclability of catalyst **1** for the chemoselective hydrogenation of CAL.

agreed with the observed recyclability. The FTIR spectrum of the spent catalyst suggested that the Ru−CO bond was retained without any changes (Figure S7). Additionally, no band corresponding to Ru−H species was observed for the spent catalyst.

■ CONCLUSIONS

The highly active homogeneous Ru-Macho catalyst was directly heterogenized by the Friedel−Crafts method to prepare a heterogeneous hydrogenation catalyst **1**, Ru-Macho-POMP. The scope and limitations of catalyst **1** in the selective hydrogenation of a carbonyl group in the presence of other reducible functional groups were evaluated. Catalyst **1** showed excellent selectivity and high turnovers in hydrogenation of the carbonyl group of *α*,*β*-unsaturated carbonyl compounds. The milder reaction conditions along with the high reactivity in multiple cycles suggest the possibility of heterogenization of the active homogeneous catalysts for the chemoselective hydrogenation of carbonyl compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03681.

> General considerations, experimental procedures, PXRD pattern, SEM and TEM images, NMR and FTIR data of catalyst **1**, activation of Ru-Macho precatalyst, presumed activation of **1**, chemoselective hydrogenation, and ^{1}H NMR data of the products (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Sungho Yoon − *Department of Chemistry, Chung-Ang University, Seoul 06974, Republic of Korea*; orcid.org/0000-0003-4521-2958; Email: sunghoyoon@cau.ac.kr

Authors

Sudakar Padmanaban − *Department of Chemistry, Chung-Ang University, Seoul 06974, Republic of Korea; Department of Chemistry, Seoul National University, Seoul 08826, Republic of Korea*; orcid.org/0000-0001-8625-8480

Gunniya Hariyanandam Gunasekar − *Clean Energy Research Centre, Korea Institute of Science and Technology, Cheongryang, Seoul 136-791, Republic of Korea*; orcid.org/0000-0002-2519-3238

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c03681

Author Contributions

†These authors contributed equally.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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