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Heterogeneously catalyzed decarbonylation of thioesters by supported Ni, Pd, or Rh nanoparticle catalysts

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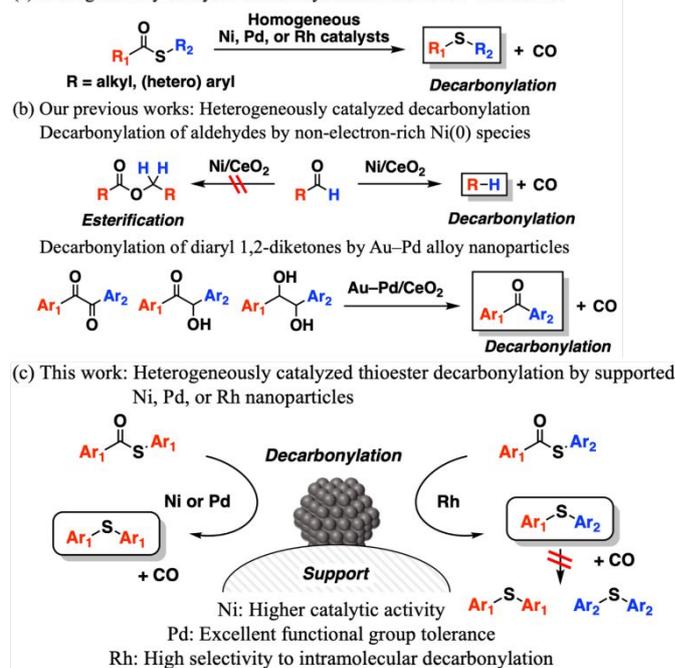
Decarbonylation of thioesters has been actively studied using homogeneous metal catalysts as an attractive approach to synthesize thioethers, which are widely utilized in various fields, because the decarbonylation ideally requires no additives and produces CO as the sole theoretical byproduct. However, heterogeneously catalyzed decarbonylation of thioesters has not been reported to date, despite its importance for construction of environmentally-friendly and practical catalytic systems. This study demonstrated a heterogeneously catalyzed system for decarbonylation of various aryl thioesters to produce thioethers and CO by utilizing CeO_2- or hydroxyapatite-supported Ni, Pd, or Rh nanoparticle catalysts. The Ni catalysts showed high catalytic activity, while the Pd catalysts possessed excellent functional group tolerance. The Rh catalysts were suitable for the selective decarbonylation of unsymmetrically substituted thioesters.

Introduction

Thioethers are widely utilized in various fields of chemistry, pharmaceuticals, agrochemicals, and materials science.[1] Although transition-metal-catalyzed cross-coupling reactions between (pseudo)halides and thiols represent the efficient and well-developed thioether synthetic methods,[1a,b,2] there are some disadvantages in the conventional reactions; (i) prefunctionalization of substrates to (pseudo)halides is required, and (ii) a stoichiometric amount of base is indispensable.[2b,3] Instead, decarbonylation of thioesters has attracted much attention as an alternative approach to synthesize thioethers because thioesters can be obtained from carboxylic acids, which are easily obtained, derivatized, and inexpensive.[4] Additionally, the decarbonylation ideally requires no additives and produces carbon monoxide (CO) as the sole theoretical byproduct.[5] Since Yamamoto and co-workers reported the first example of decarbonylation of thioesters in the presence of stoichiometric amounts of Rh complexes or catalytic amounts of Pd complexes in 1987,[6a] significant progress has been made in developing thioester decarbonylation as tractable and efficient thioether synthetic methods using different Rh,[6b] Pd,[6a,c–g] and Ni[6d,h–n] homogeneous catalysts (Scheme 1a) (Table S1). However, to our knowledge,

Scheme 1 Previous works on decarbonylation reactions and

overview of this study.

heterogeneously catalyzed decarbonylation of thioesters has not been reported so far. Regardless of the kind of carbonyl compounds, most of transition-metal catalyzed liquid-phase decarbonylation reactions have been developed by homogeneous catalysts,[5] and there are few examples of heterogeneously catalyzed decarbonylation, which are limited to some substrates such as aldehydes[7a–c] and acyl chlorides.[7d,e] On the other hand, we have recently developed selective decarbonylation of aldehydes by a heterogeneous Ni catalyst, in which non-electron-rich Ni(0) species inhibited a problematic

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† Footnotes relating to the title and/or authors should appear here.
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esterification (Scheme 1b),[8a] and diaryl 1,2-diketone decarbonylation via oxidative addition by a multifunctional heterogeneous Au–Pd alloy nanoparticle catalyst (Scheme 1b).[8b] On the basis of these findings, we speculated that supported Ni and Pd nanoparticles were effective for decarbonylation of thioesters as the heterogeneous catalysts.

Herein, we report the first example of heterogeneously catalyzed decarbonylation of various aryl thioesters by CeO_2- or hydroxyapatite (HAP)-supported Ni or Pd nanoparticle catalysts (Scheme 1c). The Ni nanoparticle catalysts exhibited higher catalytic activity for the thioester decarbonylation than the corresponding Pd nanoparticle catalysts, while the Pd nanoparticle catalysts demonstrated wider substrate scopes and excellent functional group tolerance. In addition, we also report selective intramolecular decarbonylation of unsymmetrically substituted aryl thioesters to afford unsymmetrically substituted aryl thioethers by an HAP-supported Rh nanoparticle catalyst, whereas symmetrically substituted aryl thioethers were also obtained as the byproducts via C–S bond metathesis in the case of supported Ni or Pd nanoparticle catalysts (Scheme 1c). In general, the catalytic performances of heterogeneous catalysts tend to be worse than those of the corresponding homogeneous ones; however, as summarized in Table S1, the thioether yields and substrate scopes demonstrated in the present heterogeneous catalytic systems are comparable to those demonstrated by previous homogeneously catalyzed systems.

Results and Discussion

A CeO_2-supported Ni nanoparticle catalyst (Ni/CeO_2) and an HAP-supported Pd nanoparticle catalyst (Pd/HAP) were prepared based on our previous reports with some modifications.[8a,9] Briefly, Ni/CeO_2 was prepared via reduction of a supported Ni hydroxide precursor (Ni(OH)$_x$/CeO_2) by sodium naphthalenide (NaNaph),[8a] and Pd(OH)$_x$/HAP was reduced by $NaBH_4$ to afford Pd/HAP (For the details, see ESI).[9] We confirmed the existence and high dispersion of zero-valent Ni species on the surface of Ni/CeO_2 from the DRIFT spectrum measured after CO adsorption (~16 Torr) which showed only linearly adsorbed CO on Ni(0) species without bridged adsorption modes of CO (Fig. S1).[10] Although both linearly and bridged CO adsorption modes on Pd(0) species were observed in the DRIFT spectrum of Pd/HAP,[11] based on our previous reports, the mean diameter of Pd nanoparticles on Pd/HAP was revealed to be ~4 nm, and no peaks derived from Pd species were observed in the X-ray diffraction (XRD) pattern.[9] Therefore, on the basis of the observations mentioned above and our previous reports, it was suggested that the highly dispersed zero-valent Ni and Pd species were successfully prepared.

The effect of catalysts on the decarbonylation of thioesters was investigated using *S*-(4-methylphenyl) 4-methylbenzenecarbothioate (**1a**) as the substrate under the reaction conditions indicated in Table 1.[§] The catalysts shown in Table 1 were prepared by the same method as that of Ni/CeO_2

or Pd/HAP. The decarbonylated product *p*-tolyl sulfide (**2a**) was obtained in 90% yield in the presence of Ni/HAP with no byproducts such as *p*-toluenethiol (**3a**), which could be produced via hydrolysis of **1a** (Table 1, entry 1).[§§] When using Pd/HAP, **2a** was produced in a moderate yield (Table 1, entry 2), while supported Rh or Ru nanoparticle catalysts exhibited almost no catalytic performance (Table 1, entries 3 and 4). Then, the effect of supports on Ni-catalyzed decarbonylation of **1a** was examined under milder reaction conditions (Table 1, entries 5–8). When using Ni/HAP or Ni/CeO_2, decarbonylation of **1a** efficiently proceeded to afford **2a** in excellent yields with high selectivity even at 140 °C (Table 1, entries 5 and 6). The catalytic performance of Ni nanoparticle catalysts prepared using other supports such as TiO_2 and Al_2O_3 was much lower than that of Ni/HAP and Ni/CeO_2 (Table 1, entries 7 and 8). In addition, the hydrolysis product **3a** was observed in the presence of Ni/TiO_2 and Ni/Al_2O_3. Thus, Ni/HAP and Ni/CeO_2 were the optimized catalysts for thioester decarbonylation in terms of catalytic activity and selectivity to the desired decarbonylation. The solvent affected this Ni nanoparticles-catalyzed thioester decarbonylation, and low-polar solvents tended to be effective (Table S2). After optimizing the reaction conditions for decarbonylation of **1a** in the presence of supported Pd nanoparticle catalysts, Pd/HAP also exhibited the high catalytic performance to produce **2a** in 93% yield (Table 1, entry 9). This decarbonylation did not proceed in the presence of only HAP, CeO_2, or supported Ni hydroxide catalysts (Table 1, entries 10–13), although Pd(OH)$_x$/HAP produced decarbonylated product **2a** in almost the same yield as that in the presence of Pd/HAP (Table 1, entries 2 and 14), which was probably due to *in situ* reduction of Pd species in Pd(OH)$_x$/HAP (Fig. S2).[12] Therefore, the active species for this reaction were

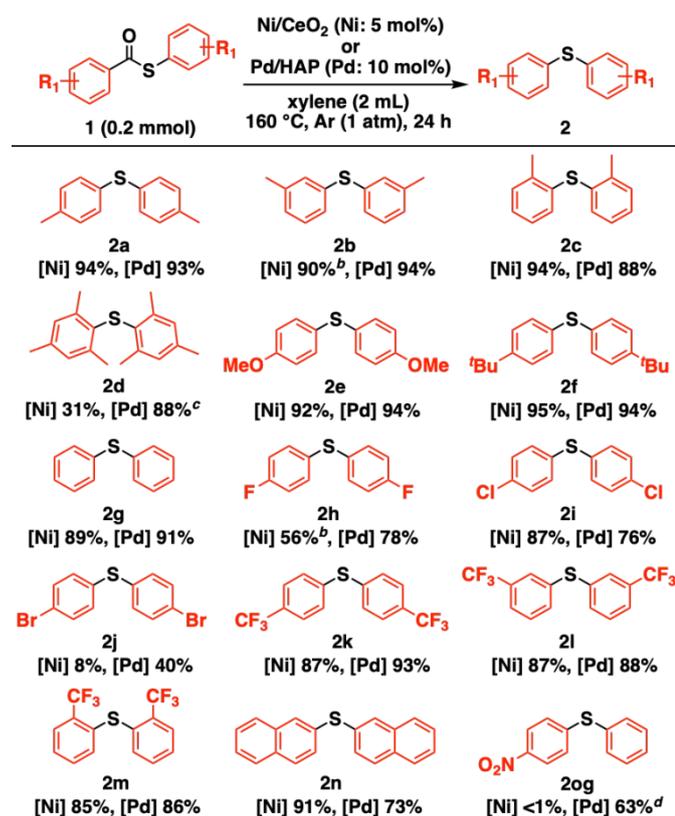**Table 1** Effect of catalysts on the decarbonylation of **1a**.[a]
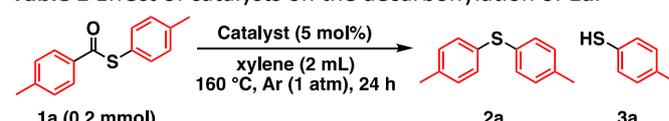
entry	catalyst	yield (%)	
		2a	**3a**
1	Ni/HAP	90	<1
2	Pd/HAP	25	<1
3	Rh/HAP	2	<1
4	Ru/HAP	<1	<1
5[b]	Ni/HAP	86	<1
6[b]	Ni/CeO_2	79	<1
7[b]	Ni/TiO_2	6	21
8[b]	Ni/Al_2O_3	6	8
9[c]	Pd/HAP	93	<1
10[d]	HAP	<1	<1
11[d]	CeO_2	<1	<1
12	Ni(OH)$_x$/HAP	<1	<1
13	Ni(OH)$_x$/CeO_2	1	<1
14	Pd(OH)$_x$/HAP	27	<1

[a]Conditions: **1a** (0.2 mmol), catalyst (5 mol%), xylene (2 mL), Ar (1 atm), 160 °C, 24 h. [b]140 °C. [c]Pd/HAP (Pd: 10 mol%). [d]HAP or CeO_2 (80 mg). Yields were determined by GC using 1,3,5-trimethoxybenzene as an internal standard.

suggested to be reduced Ni species and Pd species.

The substrate scope for decarbonylation of thioesters to afford symmetrically substituted aryl thioethers using Ni/CeO$_2$ and Pd/HAP as the catalysts was shown in Scheme 2. This system was applicable to symmetrically methyl-substituted aryl thioesters at *para-*, *meta-*, or *ortho-* positions, and the decarbonylated products were obtained in excellent yields (**2a–2c**). Pd/HAP could be applied to decarbonylation of a bulky thioester with mesityl group to afford the corresponding thioether, while Ni/HAP exhibited lower catalytic performance (**2d**). Both Pd/HAP and Ni/CeO$_2$ worked well to afford 4,4'-dimethoxy-substituted, 4,4'-*tert*-butyl-substituted, or non-substituted aryl thioethers in good yields (**2e–2g**). Halogenated aryl thioesters were also applied to this decarbonylation, and 4,4'-difluoro- or 4,4'-dichloro-substituted aryl thioesters were tolerated to give the corresponding decarbonylated products (**2h**, **2i**). This system was successfully applied to trifluoromethyl-substituted aryl thioesters at any positions (**2k–2m**). In addition, a thioether with 2-naphthyl group was also produced in a good yield (**2n**). Further studies revealed that both Pd/HAP and Ni/CeO$_2$ catalyzed decarbonylation to produce **2k** efficiently even at 120 °C (Scheme S1). We also succeeded in the gram-scale synthesis; **2k** was produced in 91% isolated yield (1.17 g, Scheme S2).

Ni/HAP and Ni/CeO$_2$ were superior to Pd/HAP in terms of catalytic activity for the decarbonylation of thioesters (Table 1, entries 1 and 2, Fig. S3), while Pd/HAP exhibited better functional group tolerance. In fact, 4,4'-dibromo-substituted aryl thioesters (**1j**) were moderately decarbonylated by Pd/HAP (**2j**), while its functional group could not be retained in the presence of Ni/CeO$_2$ (Scheme 2). In addition, an unsymmetrically substituted aryl thioester with a nitro group (**1og**), which is strongly electron-withdrawing and easy to be reduced, was successfully decarbonylated by Pd/HAP (**2og**), while **1og** was hardly converted into **2og** by Ni/HAP or Ni/CeO$_2$ (Scheme 2 and Table 2, entries 1–3). The choice of not only active metal species but also supports was important for the functional group tolerance, and HAP was the best for the selective conversion into **2og** among the examined supports (Table 2, entries 3–5). In addition to **2og**, symmetrical thioethers (**2g**, **2o**) were also observed as the byproducts by Pd/HAP (Table 2, entry 3), which decreased the selectivity to intramolecular decarbonylation toward **2og** (the details will be discussed below).

Then, the decarbonylation of unsymmetrically substituted aryl thioesters was examined using *S*-(4-methylphenyl)benzenecarbothioate (**1ga**) as the substrate in the presence of HAP-supported Ni, Pd, or Rh nanoparticle

Scheme 2 Substrate scope of Ni or Pd-catalyzed decarbonylation of thioesters.[a] [a]Conditions: **1** (0.2 mmol), Ni/CeO$_2$ (Ni: 5 mol%) or Pd/HAP (Pd: 10 mol%), xylene (3 mL), 160 °C, Ar (1 atm), 24 h. [b]Ni/CeO$_2$ (Ni: 10 mol%). [c]Pd/HAP (Pd: 20 mol%). [d]Pd/HAP (Pd: 10 mol%), 140 °C. GC yields are shown using 1,3,5-trimethoxybenzene as an internal standard.

Table 2 Effect of catalysts on the decarbonylation of **1og**.[a]

entry	catalyst	yield (%)		
		2og	**2o**	**2g**
1	Ni/HAP	<1	<1	<1
2	Ni/CeO$_2$	<1	<1	<1
3	Pd/HAP	63	19	28
4	Pd/CeO$_2$	13	<1	9
5	Pd/TiO$_2$	<1	<1	9

[a]Reaction conditions: **1og** (0.2 mmol), catalyst (5 mol%), xylene (2 mL), Ar (1 atm), 140 °C, 24 h. Yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.

Table 3 Effect of catalysts on the decarbonylation of **1ga**.[a]

entry	catalyst	yield (%)		
		2ga	**2g**	**2a**
1	Ni/HAP	61	14	19
2	Pd/HAP	52	23	19
3	Rh/HAP	20	<1	2
4[b]	Rh/HAP	79	4	3

[a]Conditions: **1ga** (0.2 mmol), catalyst (Ni: 5 mol%, Pd: 10 mol%, or Rh: 3 mol%), xylene (2 mL), Ar (1 atm), 160 °C, 24 h. Yields were determined by GC using 1,3,5-trimethoxybenzene as an internal standard. [b]Rh/HAP (Rh: 11 mol%), 180 °C.
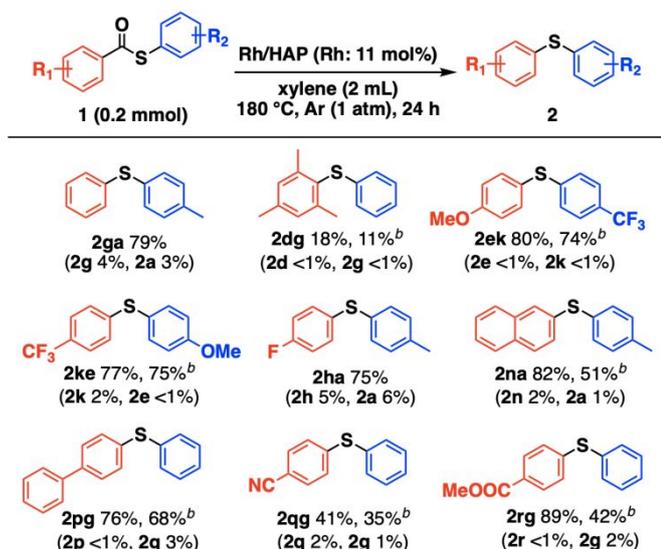
Scheme 3 Substrate scope of Rh-catalyzed intramolecular decarbonylation of unsymmetrically substituted thioesters.[a] [a]Conditions: **1** (0.2 mmol), Rh/HAP (Rh: 11 mol%), xylene (2 mL), 180 °C, Ar (1 atm), 24 h. GC yields are shown using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield.

catalysts (Table 3).[§§§] Intramolecular decarbonylated product **2ga** was produced in moderate yields as well as symmetrical thioethers (**2g**, **2a**) when utilizing Ni/HAP or Pd/HAP (Table 3, entries 1 and 2), while Rh/HAP exhibited much higher selectivity to intramolecular decarbonylation toward **2ga** (Table 3, entry 3). In fact, Rh/HAP hardly catalyzed C–S bond metathesis of aryl thioethers between **2a** and **2g**, while the metathesis reaction moderately proceeded when using Ni/HAP or Pd/HAP (Table S3), possibly because C–S bond oxidative addition to Rh/HAP was more difficult than that to Ni/HAP and Pd/HAP. Under the optimized conditions using Rh/HAP, intramolecular decarbonylated product **2ga** was obtained in 79% yield with high selectivity (Table 3, entry 4).

Then, the substrate scope for decarbonylation of thioesters to afford unsymmetrically substituted aryl thioethers using Rh/HAP as the catalyst was investigated (Scheme 3). This system was applicable to decarbonylation of various unsymmetrically substituted aryl thioesters with methyl, methoxy, trifluoromethyl, fluoro, phenyl, cyano, and ester groups (**2ga**, **2ek**, **2ke, 2ha, 2pg, 2qg, 2rg**) with excellent intramolecular selectivity. An unsymmetrically substituted thioether with 2-naphthyl group was also produced in a high yield (**2na**) although the yield of aryl thioether with mesityl group was low probably due to its steric hindrance (**2dg**).

In order to confirm whether the observed catalysis of Pd/HAP for thioester decarbonylation was heterogeneous or not, hot filtration of the catalysts during the reactions and ICP-AES analysis of the reaction solutions were conducted. Pd/HAP-catalyzed decarbonylation of *S*-phenyl benzenecarbothioate (**1g**) was immediately stopped after hot filtration of the catalyst (Fig. 1). In addition, ICP-AES analysis revealed that Pd species were hardly leached into the reaction solution after decarbonylation of **1g** (Pd: below the detection limit). These

results indicated that Pd/HAP functioned as a heterogeneous catalyst. As with the case of Pd/HAP, Ni/CeO$_2$ and Rh/HAP were confirmed to function as the heterogeneous catalysts for the present decarbonylation by hot filtration during the reaction (Figs. S4 and S5) and ICP-AES analysis of the filtrate after the reaction (Ni: 0.08% of the Ni species used for the decarbonylation, Rh: 0.04% of the Rh species used for the decarbonylation). Additionally, Pd/HAP could be easily retrieved by simple filtration and reused at least 5 times without loss of the final yield of **2k** after regeneration of the catalyst via calcination followed by reduction (Fig. 2).
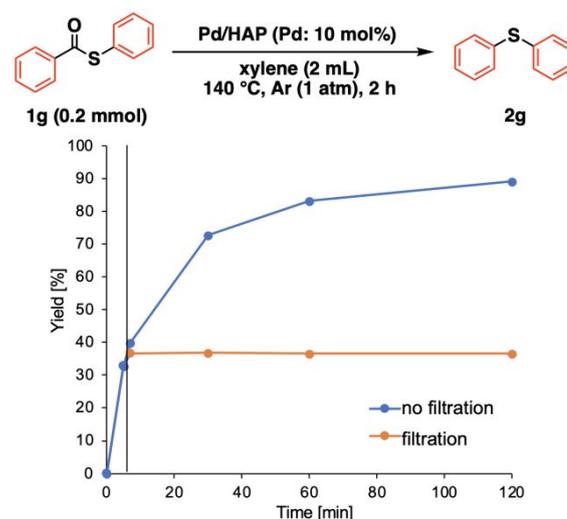

Fig. 1 Effect of removal of Pd/HAP on the decarbonylation of **1g**. Reaction conditions: **1g** (0.2 mmol), Pd/HAP (Pd: 10 mol%), xylene (2 mL), Ar (1 atm), 140 °C. Yields of **2g** were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.
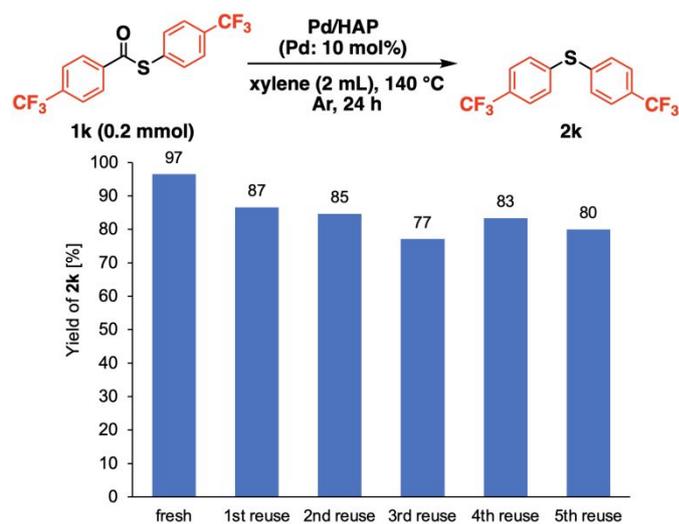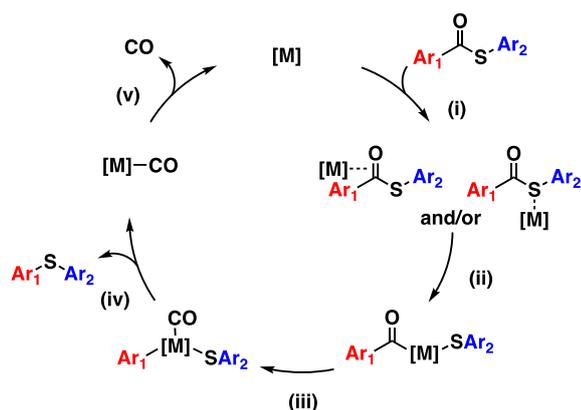

Fig. 2 Reuse experiments on the decarbonylation of **1k** in the presence of Pd/HAP. Reaction conditions: **1k** (0.2 mmol), Pd/HAP (Pd: 10 mol%), xylene (2 mL), Ar (1 atm), 140 °C for 24 h. Yields of **2k** were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.

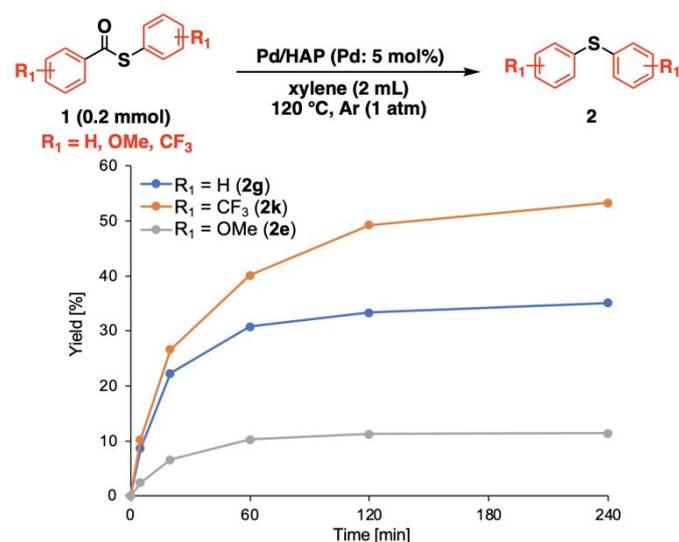**Scheme 4** Proposed mechanism for decarbonylation of thioesters to thioethers.

Fig. 3 Reaction profiles of Pd/HAP-catalyzed decarbonylation of non-substituted (**1g**) or 4,4'-substituted thioesters (**1e**, **1k**) independently. Reaction conditions are shown in the figure. Yields of were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.

CO was determined by GC-BID analysis of the gas phase after the decarbonylation of **1g** using Pd/HAP or Ni/CeO$_2$, and the amount of CO was almost the same as that of produced **2g**, which suggested that this reaction proceeded through decarbonylation via oxidative addition (Fig. S6). Based on the previous reports on thioester decarbonylation[6] and the results mentioned above, the proposed mechanism of Ni-, Pd-, or Rh-catalyzed decarbonylation of thioesters was depicted in Scheme 4. The proposed mechanism is as follows: (i) coordination of the carbonyl group and/or S-atom of thioesters to low-valent metal species, (ii) C(carbonyl)–S bond oxidative addition of thioesters to the active species, (iii) CO extrusion from the oxidative adducts, (iv) reductive elimination to afford decarbonylated products, and then (v) catalyst regeneration through CO desorption from the active species. The initial rate of **1g** decarbonylation hardly depended on the initial

concentration of **1g**, indicating (i) coordination step efficiently proceeded in the reaction conditions (Fig. S7). We measured the reaction profiles for Ni/CeO$_2$- or Pd/HAP-catalyzed thioester decarbonylation using non-substituted (**1g**) or 4,4'-substituted aryl thioesters (**1e**, **1k**) as the substrates independently to gain the insights into the electronic effect of the substrates (Figs. 3 and S8). As a result, more electron-withdrawing group accelerated the reaction in both cases, suggesting that (ii) oxidative addition or (iii) CO extrusion is the turnover-limiting step.

Conclusions

In conclusion, we have successfully developed intramolecular decarbonylation of symmetrically substituted aryl thioesters using CeO$_2$- or HAP-supported Ni or Pd nanoparticle catalysts, which is the first example of heterogeneously catalyzed thioester decarbonylation. These systems exhibited wide substrate scope with excellent functional group tolerance. In addition, selective intramolecular decarbonylation of various unsymmetrically substituted aryl thioesters in the presence of an HAP-supported Rh nanoparticle catalyst was also highlighted. This report demonstrated the applicability of heterogeneous catalysts to decarbonylation of carbonyl compounds other than well-studied aldehydes, which will offer a methodology for developing more challenging molecular transformations using heterogeneous catalysts.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

§ 1,3,5-trimethoxybenzene was used as the internal standard for the GC analysis, and it was confirmed that the addition of 1,3,5-trimethoxybenzene did not affect the present decarbonylation reactions (Table S4).
§§ In the absence of supported metal species, **3a** was formed from **1a** in the presence of Al$_2$O$_3$ while CeO$_2$ did not afford **3a** at

all (Table S5), indicating that **3a** was produced via hydrolysis catalyzed by acid-base sites of supports using water contained in the solid catalysts.

§§§ The average diameter of Rh nanoparticles in Rh/HAP was determined to be 2.4 nm (σ = 0.7 nm) by TEM observation (Fig. S9).

1 (a) C.-F. Lee, Y.-C. Liu and S. S. Badsara, *Chem. Asian J.*, 2014, **9**, 706–722; b) I. P. Beletskaya and V. P. Ananikov, *Chem. Rev.*, 2011, **111**, 1596–1636; (c) K. L. Dunbar, D. H. Scharf, A. Litomska and C. Hertweck, *Chem. Rev.*, 2017, **117**, 5521–5577; (d) E. A. Ilardi, E. Vitaku and J. T. Njardarson, *J. Med. Chem.*, 2014, **57**, 2832–2842.

2 (a) S. V. Ley and A. W. Thomas, *Angew. Chem. Int. Ed.*, 2003, **42**, 5400–5449; (b) T. Kondo and T. Mitsudo, *Chem. Rev.*, 2000, **100**, 3205–3220; (c) C. C. Eichman and J. P. Stambuli, *Molecules*, 2011, **16**, 590–608.

3 P. Chauhan, S. Mahajan and D. Enders, *Chem. Rev.*, 2014, **114**, 8807–8864.

4 (a) M. Kazemi and L. Shiri, *J. Sulphur Chem.*, 2015, **36**, 613–623; (b) Q. Wu, Y.-H. Zhao, C. Lu-Lu, H.-Y. Li and H.-X. Li, *Org. Chem. Front.*, 2022, **9**, 2977–2985; (d) C. Liu and M. Szostak, *ChemCatChem* 2021, **13**, 4878–4881.

5 H. Lu, T.-Y. Yu, P.-F. Xu and H. Wei, *Chem. Rev.*, 2021, **121**, 365–411.

6 (a) K. Osakada, T. Yamamoto and A. Yamamoto, *Tetrahedron Lett.*, 1987, **28**, 6321–6324; (b) H. Cao, X. Liu, F. Bie, Y. Shi, Y. Han, P. Yan, M. Szostak and C. Liu, *J. Org. Chem.*, 2021, **86**, 10829–10837; (c) T. Kato, H. Kuniyasu, T. Kajiura, Y. Minami, A. Ohtaka, M. Kinomoto, J. Terao, H. Kurosawa and N. Kambe, *Chem. Commun.*, 2006, 868–870; (d) N. Ichiishi, C. A. Malapit, Ł. Woźniak and M. S. Sanford, *Org. Lett.*, 2018, **20**, 44–47; (e) S.-F. Wang, C.-E. Li, Y.-C. Liu, D. M. Reddy, R. S. Basha, J. K. Park, S. Lee and C.-F. Lee, *Asian J. Org. Chem.*, 2020, **9**, 1826–1833; (f) H. Cao, X. Liu, F. Bie, Y. Shi, Y. Han, P. Yan, M. Szostak and C. Liu, *Org. Chem. Front.*, 2021, **8**, 1587–1592; (g) S. Yang, X. Yu and M. Szostak, *ACS Catal.*, 2023, **13**, 1848–1855; (h) E. Wenkert and D. Chianelli, *J. Chem. Soc. Chem. Commun.*, 1991, 627–628; (i) C. Liu and M. Szostak, *Chem. Commun.*, 2018, **54**, 2130–2133; (j) K. Ishitobi, R. Isshiki, K. K. Asahara, C. Lim, K. Muto and J. Yamaguchi, *Chem. Lett.*, 2018, **47**, 756–759; (k) Z.-J. Zheng, C. Jiang, P.-C. Shao, W.-F. Liu, T.-T. Zhao, P.-F. Xu and H. Wei, *Chem. Commun.*, 2019, **55**, 1907–1910; (l) C. E. Brigham, C. A. Malapit, N. Lalloo and M. S. Sanford, *ACS Catal.*, 2020, **10**, 8315–8320; (m) J.-Y. Zhou, R. Tian and Y.-M. Zhu, *J. Org. Chem.*, 2021, **86**, 12148–12157; (n) T. Xu, X. Zhou, X. Xiao, Y. Yuan, L. Liu, T. Huang, C. Li, Z. Tang and T. Chen, *J. Org. Chem.*, 2022, **87**, 8672–8684.

7 (a) S. Chen, R. Wojcieszak, F. Dumeignil, E. Marceau and S. Royer, *Chem. Rev.*, 2018, **118**, 11023–11117; (b) M. Besson, P. Gallezot and C. Pinel, *Chem. Rev.*, 2014, **114**, 1827–1870; (c) N. An, D. Ainembabazi, C. Reid, K. Samudrala, K. Wilson, A. F. Lee and A. Voutchkova-Kostal, *ChemSusChem*, 2020, **13**, 312–320; (d) J. Tsuji, K. Ohno and T. Kajimoto, *Tetrahedron Lett.*, 1965, **6**, 4565–4568; (e) J. D. Rich, *Organometallics*, 1989, **8**, 2609–2615.

8 (a) T. Matsuyama, T. Yatabe, T. Yabe and K. Yamaguchi, *ACS Catal.*, 2021, **11**, 13745–13751; (b) T. Matsuyama, T. Yatabe, T. Yabe and K. Yamaguchi, *ACS Catal.*, 2022, **12**, 13600–13608.

9 (a) W.-C. Lin, T. Yatabe and K. Yamaguchi, *Chem. Commun.*, 2021, **57**, 6530–6533; (b) Y. Koizumi, X. Jin, T. Yatabe, R. Miyazaki, J. Hasegawa, K. Nozaki, N. Mizuno and K. Yamaguchi, *Angew. Chem. Int. Ed.*, 2019, **58**, 10893–10897.

10 (a) Y. Bai, J. Zhang, G. Yang, Q. Zhang, J. Pan, H. Xie, X. Liu, Y. Han and Y. Tan, *ACS Catal.*, 2018, **8**, 6367–6374; (b) Y. Chen, B. Qiu, Y. Liu and Y. Zhang, *Appl. Catal. B*, 2020, **269**, 118801.

11 (a) A. Mansouri and N. Semagina, *Appl. Catal. A*, 2017, **543**, 43–50; (b) Z. Di, H. Chen, R. Zhang, H. Wang, J. Jia and Y. Wei, *Appl. Catal. B*, 2022, **304**, 120843.

12 (a) X. Jin, K. Taniguchi, K. Yamaguchi, K. Nozaki and N. Mizuno, *Chem. Commun.*, 2017, **53**, 5267–5270; (b) X. Jin, Y. Koizumi, K. Yamaguchi, K. Nozaki and N. Mizuno, *J. Am. Chem. Soc.*, 2017, **139**, 13821–13829; (c) M. Takabatake, A. Hashimoto, W.-J. Chun, M. Nambo, Y. Manaka and K. Motokura, *JACS Au*, 2021, **1**, 124–129.