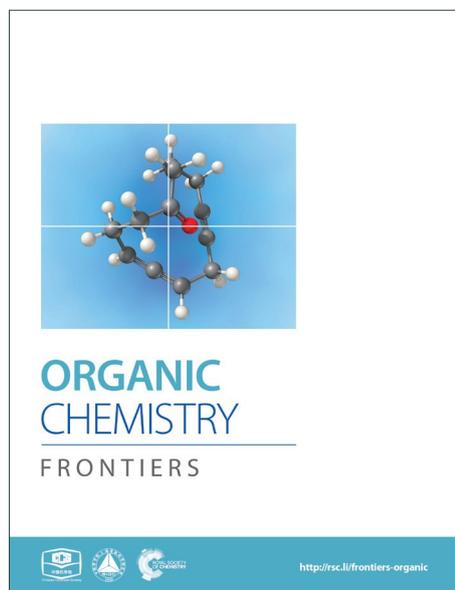
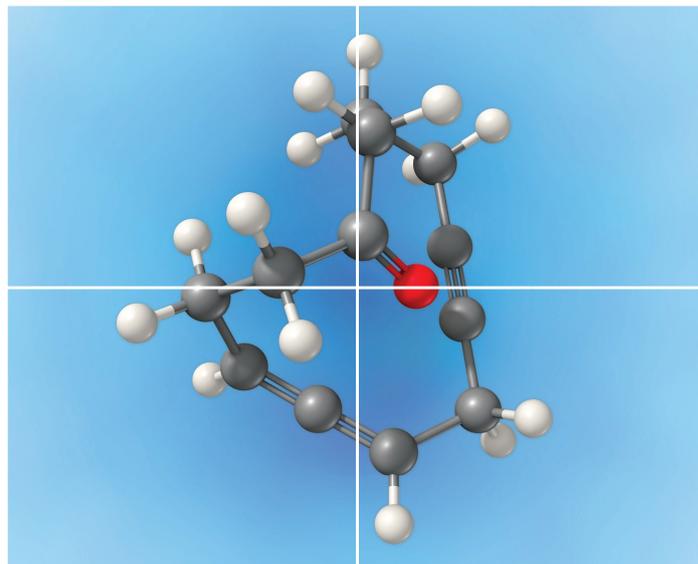


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Aerobic oxidation of cyclohexanones to phenols and aryl ethers over supported Pd catalysts

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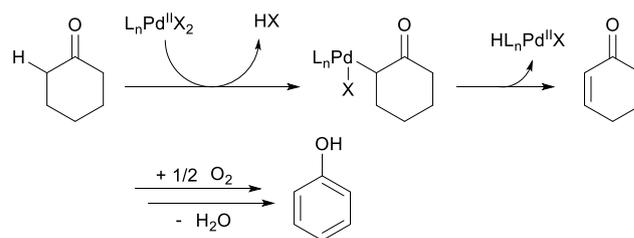
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Transformation of cyclohexanone to phenols and aryl ethers over supported Pd catalysts using molecular oxygen as the sole oxidant was developed. Several metal oxide supported Pd catalysts were used to activate the C–H bond in cyclohexanone to produce cyclohexenone and phenol through oxidation. Although the selectivity of cyclohexenone was difficult to control, phenol was obtained in excellent yield with a broad substrate scope. A novel catalytic system, using ZrO₂ supported Pd(OH)₂, was proposed for the synthesis of aryl ethers, and the products were obtained in moderate to excellent yields. Orthoesters, such as trimethyl orthoformate (TMOF), triethyl orthoformate (TEOF), and triisopropyl orthoformate (TIPOF), enabled nucleophilic addition and elimination after activation of cyclohexanone over Pd catalyst to produce the corresponding aryl ethers. TIPOF was also used as dehydrating reagent to promote the reaction of cyclohexanone with alcohols for the preparation of versatile aryl ethers.

Introduction

Over the past decades, Pd-catalyzed aerobic oxidation reactions have been widely developed.¹ Dehydrogenation of ketones to synthesize enones is one of the important reactions, since enones are regarded as useful building blocks in organic synthesis.² Li and Wang reported a direct aerobic dehydrogenation of aldehyde to the corresponding enones catalyzed by Pd(OAc)₂/amine, but only moderate product yields were obtained.³ On the other hand, synthesis of phenols from cyclohexanones have also appeared via enone formation by Pd-catalyzed aerobic oxidation of cyclohexanones.^{4,5} One of our authors developed a Pd(TFA)₂/bipy catalytic system for synthesizing cyclohexenones from cyclohexanones with a yield of up to 84%.^{4a} In that report, phenol was partly formed as a by-product. Stahl and co-workers reported the oxidative dehydrogenation of cyclohexanones over Pd(DMSO)₂(TFA)₂ and Pd(TFA)₂/2-dimethylaminopyridine (2-Me₂Npy) catalytic systems to produce cyclohexenones^{4c} and phenols^{5b}, respectively. In general, the cyclic enones and phenols were formed by a Pd^{II}-catalyzed α-hydrogen activation of cyclohexanones followed by β-hydride elimination or further dehydrogenation, and oxygen was used to re-oxidize the Pd⁰ species (Scheme 1). Stahl concluded that DMSO inhibited to form Pd black, and soluble Pd^{II} species was highly active for the oxidation of cyclohexanone to cyclohexenone.^{4d,6} In contrast, soluble Pd nanoparticles (NPs) were formed in Pd(TFA)₂/2-Me₂Npy system, and they were more active for the oxidation of cyclohexenone to phenol than Pd^{II} species.^{5c} Although Pd NP-mediated oxidation of cyclohexanones to phenols has been proposed, active catalysts are limited to

pseudo-homogeneous Pd NPs. Heterogeneous catalysts, such as Pd/C, has not yet been scarcely reported for this reaction in spite of their advantages, such as easy catalyst separation.

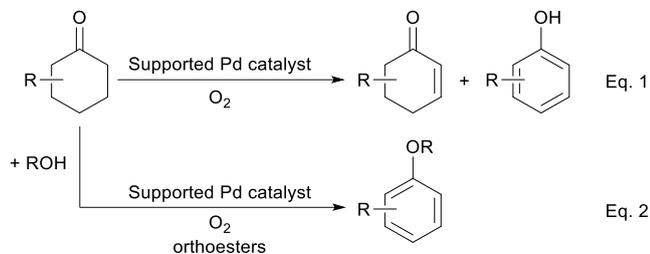


Scheme 1 Proposed mechanism for the Pd-catalyzed dehydrogenation of cyclohexanone by Stahl and co-workers.

Aryl ethers are also important compounds for organic synthesis⁷ and are usually obtained via Williamson ether synthesis⁸ or Ullmann coupling reactions⁹. However, both of these methods generally use halogen-containing substrates and need a stoichiometric amount of base to promote the reaction. Li and co-workers reported a method to prepare aryl ethers from cyclohexanones catalyzed by homogeneous Cu catalysts in the presence of N-hydroxyphthalimide (NHPI) as a co-catalyst.¹⁰ Since cyclohexenones can be obtained by Pd-catalyzed aerobic oxidation of cyclohexanones, direct transformation of aryl ethers from cyclohexanones is more simple and straightforward. Recently, Lemaire and co-workers reported the synthesis of aryl ethers from cyclohexanones over Pd/C.¹¹ The proposed mechanism involved activation of the carbonyl group in cyclohexanone by Pd, followed by reaction

with alcohols to form the hemiacetal intermediate. Elimination of hemiacetal to enol ethers and subsequent dehydrogenation yielded aryl ethers. In the previous reports,^{10,11} alcohols were limited to those having high boiling points (>100 °C), and simple alcohols, such as methanol and ethanol, were not described.

In this work, using metal oxide supported Pd catalysts, we studied the aerobic oxidation of cyclohexanones to synthesize cyclic enones and phenols (Scheme 2, Eq. 1). Moreover, preparation of aryl ethers from cyclohexanones in simple alcohols is developed over supported Pd catalysts under oxygen atmosphere in the presence of orthoesters, such as trimethyl orthoformate (TMOF) and triisopropyl orthoformate (TIPOF) (Eq. 2).



Scheme 2 Aerobic oxidation of cyclohexanones over supported Pd catalysts.

Results and Discussion

Preparation and characterization of catalysts

Metal oxides, such as TiO₂, Al₂O₃, CeO₂, and ZrO₂, supported Pd(OH)₂ catalysts were prepared by the deposition-precipitation (DP) method using PdCl₂ as the precursor according to the literature with modifications.¹² Metal oxide supported PdO and Pd catalysts were prepared from supported Pd(OH)₂ catalysts by calcination in air and reduction with pure H₂, respectively (also see supplementary information). High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image of 10 wt% Pd(OH)₂/ZrO₂ revealed that Pd NPs were well dispersed on the surface of ZrO₂, and the mean diameter was calculated to be 1.8 ± 0.9 nm (Figure S1). On the other hand, HAADF-STEM image of 10 wt% Pd/ZrO₂ showed that Pd NPs were aggregated to large particles during the H₂ reduction at 200 °C (Figure S2).

Characterization of supported Pd catalysts was performed by X-ray absorption fine structure (XAFS) at BL14B2 of SPring-8 (Hyogo, Japan).¹³ To identify the chemical state of Pd in supported Pd(OH)₂ and Pd catalysts, Pd *K*-edge X-ray absorption near edge structure (XANES) spectra was measured (Figure S3). As we have previously reported, the chemical state of Pd in Pd(OH)₂/ZrO₂ and Pd/ZrO₂ were confirmed to be Pd^{II} and Pd⁰, respectively. In the radial structure functions (RSF) (Figure S4), two peaks were observed at 1.5 and 2.9 Å (phase-uncorrected) in PdO, and these peaks corresponded to Pd–O bond of the first coordination shell and both of Pd–Pd and Pd–O bond of the second one, respectively. Due to the fact that both of Pd–Pd and Pd–O bond at 2.9 Å was small as well as reference of Pd(OH)₂, Pd(OH)₂ might be present in Pd(OH)₂/ZrO₂ as major species, although the formation of PdO could not be fully excluded by XAFS.¹⁴

Synthesis of cyclohexenones and phenols

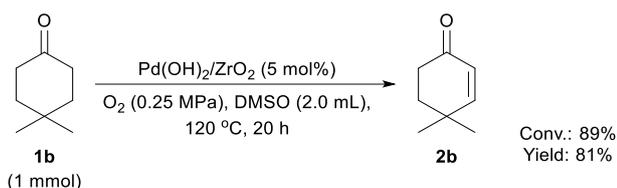
Catalytic performance of supported Pd(OH)₂ catalysts was evaluated by the transformation of cyclohexanone into cyclohexenone and phenol (Table 1). Initially, several metal oxide supported Pd(OH)₂ catalysts were screened in DMSO (Table 1, entries 1–4). Among these catalysts, the basic metal oxide (CeO₂) and the relatively acidic metal oxide (TiO₂) supported Pd(OH)₂ showed lower catalytic activity than amphoteric metal oxides (Al₂O₃ and ZrO₂) as the support. However, the selectivity to enone and phenol over Pd(OH)₂/Al₂O₃ was lower than Pd(OH)₂/ZrO₂. Thus, ZrO₂ was selected as a suitable support. Other solvents such as 1,4-dioxane, EtOAc, toluene, and PhCl were also investigated for the reaction with supported Pd(OH)₂ catalysts, whereas the selectivity to cyclohexenone or phenol were found to be unsatisfactory (Table S1, entries 1–6). When the catalytic amount of Pd decreased from 5 mol% to 2 mol%, the selectivity to cyclohexenone was increased to 26% yield (Table 1, entry 5). When Pd(OH)₂/ZrO₂ was reduced to Pd/ZrO₂ using H₂, the selectivity for phenol was improved (Table 1, entry 6). Decreasing the reaction temperature improved the cyclohexenone yield to 34% (Table, entry 7). Although we tried to further improve the selectivity of cyclohexenone, subsequent oxidation of cyclohexanone to phenol could not be avoided. Only exception is 4,4-dimethylcyclohexenone (**2b**) which was obtained in 81% yield, due to the absence of hydrogen atom at the 4-position (Scheme 3). In this case, 4,4-dimethylcyclohexa-2,5-dien-1-one was not formed, suggesting that the second oxidation to dienone did not proceed when the substrate cannot be aromatized.

Then we focused on the synthesis of phenol. Selectivity of phenol was significantly affected by the pressure of O₂. Neither cyclohexenone nor phenol was obtained under atmospheric pressure of O₂ (Table S1, entries 7), an increase in O₂ pressure to 0.5 MPa gave phenol in excellent yield to 99% (Table, entry 8).

Table 1 Aerobic oxidation of cyclohexanone.^a

Entry	Catalyst	Temp. (°C)	Time (h)	Conv. (%) ^b	Yield of 2a (%) ^b	Yield of 3a (%) ^b
1	Pd(OH) ₂ /Al ₂ O ₃	120	8	99	8	18
2	Pd(OH) ₂ /CeO ₂	120	15	44	7	22
3 ^c	Pd(OH) ₂ /TiO ₂	120	20	70	7	25
4	Pd(OH) ₂ /ZrO ₂	120	15	90	15	38
5 ^d	Pd(OH) ₂ /ZrO ₂	120	15	73	26	40
6	Pd/ZrO ₂	120	15	86	12	54
7	Pd/ZrO ₂	100	24	81	34	36
8 ^e	Pd/ZrO ₂	100	24	100	<1	99

^a Reaction conditions: cyclohexanone (1 mmol), catalyst (Pd 5 mol%), DMSO (2.0 mL), O₂ (0.25 MPa). ^b Calculated on the basis of GC analysis using tridecane as an internal standard. ^c Catalyst (Pd 8 mol%). ^d Catalyst (Pd 2 mol%). ^e O₂ (0.5 MPa).



Scheme 3 Synthesis of 4,4-dimethylcyclohexenone.

Next, we examined the scope of substrates for phenol synthesis (Table 2). For methyl substituted cyclohexanones, the corresponding phenols were obtained in good to excellent yield (Table 2, entries 1–3); the reactivity order was 4- > 3- > 2-substituted cyclohexanones, and this might be ascribed to the steric effect on 3- and 2-substituted cyclohexanones for further oxidation to cyclohexa-2,5-dien-1-ones, which was considered to be formed faster than cyclohexa-2,4-dien-1-one as an intermediate before phenol formation. Other 4-substituted cyclohexanones were also tested (Table 2, entries 4–6). 4-Ethylcyclohexanone (**1f**) and 4-*t*-butylcyclohexanone (**1g**) exhibited excellent reactivity to form the corresponding phenols. 4-Phenylcyclohexanone (**1h**) was transformed to 4-phenylphenol (**3h**) in 82% yield by using high loading Pd catalyst. Low reactivity was observed in 3,5-dimethylcyclohexanone (**1i**) (Table 2, entry 7). 2-Phenyl substituted cyclohexanone (**1j**) were examined (Table 2, entry 8), but this compound showed poor reactivity.

In order to elucidate the chemical state of Pd for the synthesis of phenol, the Pd/ZrO₂ catalyst was tested by Pd *K*-edge XANES before and after the reaction, and the chemical states of Pd both on the fresh and the recycled catalysts were confirmed to be Pd⁰ (Figure S5a). In RSF of Pd/ZrO₂ after use, magnitude of the peak at 2.5 Å, which corresponds to the Pd–Pd bond as seen in Pd foil, decreased as compared to fresh catalyst (Figure S5b). In the *k*³-weighted EXAFS oscillations, the amplitude of the catalyst after reaction was also lower than the fresh catalyst (Figure S5c). This result indicated that possibility of the Pd NPs size was decreased during the reaction. Additionally, in the X-ray diffraction (XRD) patterns of fresh Pd/ZrO₂, the diffraction peaks at 40, 46 and 68° were assigned to (111), (200), and (220) crystalline planes of the face-centered cubic (*fcc*) lattice of Pd (PDF-2 Database, No. 01-087-0645) (Figure S6a). In contrast, these diffraction peaks were not present in the XRD patterns of the used Pd/ZrO₂ (Figure S6b). From these results, we suggest that Pd was dissolved into the solution during the reaction and was re-deposited on ZrO₂ as small Pd NPs. The microwave plasma-atomic emission spectrometry (MP-AES) analysis result demonstrated that only 0.6 wt% Pd was lost from the fresh catalyst (Table S2). Although the reaction would proceed via quasi-homogeneous catalysis, most of Pd could be recovered after the reaction as supported catalysts. In addition, the recyclability of Pd/ZrO₂ for synthesis of phenol was studied. Although the yield of phenol was slightly decreased at the fourth run, the catalyst showed good recyclability (Figure 1).

Table 2 Substrate scope for synthesis of substituted phenols from cyclohexanones.^a

Entry	Substrate	Product	Conv. (%) ^b	Yield (%) ^b
1	1c	3c	87	63
2	1d	3d	89	78
3	1e	3e	100	99
4	1f	3f	100	99
5	1g	3g	100	99
6 ^c	1h	3h	98	82
7	1i	3i	19	13
8	1j	3j	66	46

^a Reaction conditions: substrate (1 mmol), 10 wt% Pd/ZrO₂ (Pd 5 mol%), DMSO (2.0 mL), O₂ (0.5 MPa), 100 °C, 24 h. ^b Calculated on the basis of GC analysis using tridecane as an internal standard. ^c Catalyst (Pd 8 mol%).

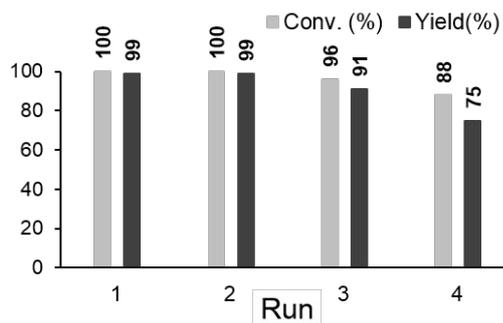


Figure 1 Recyclability of Pd/ZrO₂ in phenol synthesis. Reaction conditions: cyclohexanone (1 mmol), 10 wt% Pd/ZrO₂ (Pd 5 mol%), DMSO (2.0 mL), O₂ (0.5 MPa), 100 °C, 24 h.

Synthesis of aryl ethers

The reaction of cyclohexanone and methanol into anisole was explored under oxidative conditions. In the absence of additives, the reaction proceeded over 2 mol% Pd(OH)₂/ZrO₂ at 140 °C to afford anisole in 37% yield (Table 3, entry 1). Several additives such as Na₂SO₄ and molecular sieve 4Å were added as dehydrating reagent, but the conversion decreased markedly (Table 3, entries 2 and 3). However, the reaction proceeded very well, yielding anisole in 60% yield, when using trimethyl orthoformate (TMOF) as the additive (Table 3, entry 4). The reaction also proceeded in the absence of methanol to form anisole (Table 3, entry 5). We suggest that TMOF, which is commonly used for introduction of a protecting group in aldehydes, worked as both dehydrating and nucleophilic reagents during the reaction. After the optimization of reaction conditions, 96% yield of anisole was achieved under the following reaction conditions: 0.5 MPa of O₂, at 140 °C for 6 h (Table 3, entry 6). ZrO₂ supported PdO and Pd catalysts also promoted this reaction to give anisole in good yields (Table 3, entries 7 and 8).

Table 3 Synthesis of anisole from cyclohexanone.^a

Entry	Catalyst	MeOH (eq)	Additive (eq)	Conv. (%) ^b	Yield (%) ^b
1	Pd(OH) ₂ /ZrO ₂	40	--	100	37
2	Pd(OH) ₂ /ZrO ₂	40	Na ₂ SO ₄	19	0
3	Pd(OH) ₂ /ZrO ₂	40	MS 4Å ^c	23	2
4	Pd(OH) ₂ /ZrO ₂	40	TMOF	100	66
5	Pd(OH) ₂ /ZrO ₂	--	TMOF	91	70
6	Pd(OH) ₂ /ZrO ₂	--	TMOF	100	96
7	PdO/ZrO ₂ ^d	--	TMOF	100	92
8	Pd/ZrO ₂ ^e	--	TMOF	100	77

^a Reaction conditions: cyclohexanone (1 mmol), 10 wt% Pd(OH)₂/ZrO₂ (Pd 2 mol%), MeOH, additives, O₂ (0.5 MPa). ^b Calculated on the basis of GC analysis using tridecane as an internal standard. ^c Molecule sieve 4Å (100 mg) was added. ^d The catalyst was calcined at 300 °C for 4 h from Pd(OH)₂/ZrO₂. ^e The catalyst was reduced using H₂ (20 mL/min) at 200 °C for 2 h from Pd(OH)₂/ZrO₂.

With the optimized reaction conditions in hand, several substituted cyclohexanones were investigated. Methyl (**1d** and **1e**) and phenyl (**1j**) substituted cyclohexanones were transformed into their corresponding aryl ethers in moderate yields (Table 4, entries 1–3). 1-Tetralone (**1k**), which contains a benzocyclohexanone structure, exhibited better reactivity than other substrates and gave 1-methoxynaphthalene (**4k**) in 78% yield (Table 4, entry 4). Moreover, other orthoester reagents, including triethyl orthoformate (TEOF) and triisopropyl orthoformate (TIPOF), could be used instead of TMOF. Ethoxybenzene and isopropoxybenzene were obtained as the products in 49 and 11% yield, respectively (Table 4, entries 5 and 6). Relatively low product yields compared to high conversions were due to the formation of phenols as by-products.

Table 4 Scope of substrates for synthesis of aryl ethers.^a

Entry	Substrate	R'	Product	Conv. (%) ^b	Yield (%) ^b
1		Me		91	66
2		Me		85	45
3		Me		100	22
4		Me		95	78
5		Et		92	49
6		ⁱ Pr		79	11

^a Reaction conditions: substrate (1 mmol), 10 wt% Pd(OH)₂/ZrO₂ (Pd 2 mol%), orthoester reagent (1.5 mL), O₂ (0.5 MPa), 140 °C, 6 h. ^b Calculated on the basis of GC analysis using tridecane as an internal standard.

Next, we tested the recyclability of the catalyst in anisole synthesis (Figure 2). Although the catalytic activity was gradually decreased with consecutive runs, 80% yield was maintained for the fourth run. The reasons for the decrease in the catalytic activity were probably due to the leaching of Pd and/or aggregation of Pd species. Consequently, the reaction solution was measured by MP-AES, and the concentration of residual Pd in the solution after filtration was determined to be 1.33 ppm (in 1.5 mL TMOF). Moreover, after the removal of the catalyst by filtration at 42% conversion, the reaction of the filtrate stopped (Figure 3). These results proved that the loss of Pd could not be the cause of the decrease in catalytic activity.

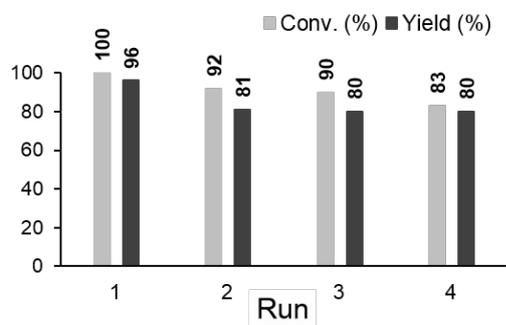


Figure 2 Recyclability of Pd(OH)₂/ZrO₂ in anisole synthesis. Reaction conditions: cyclohexanone (1 mmol), 10 wt% Pd(OH)₂/ZrO₂ (Pd 2 mol%), TMOF(1.5 mL), O₂ (0.5 MPa), 140 °C, 6 h.

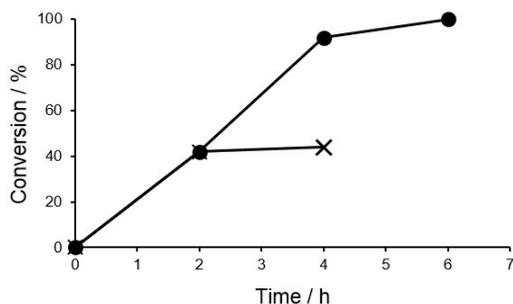


Figure 3 Synthesis of anisole from cyclohexanone in the presence of Pd(OH)₂/ZrO₂ (●) and after the removal of Pd(OH)₂/ZrO₂ at 2 h by filtration (×). Reaction conditions: cyclohexanone (1 mmol), 10 wt% Pd(OH)₂/ZrO₂ (Pd 2 mol%), TMOF (1.5 mL), O₂ (0.5 MPa), 140 °C

Since TIPOF possesses lower reactivity to produce the isopropoxybenzene than TMOF and TEOF, we considered that TIPOF could be used as a dehydrating reagent in the presence of the alcohols to synthesize aryl ethers without the formation of isopropoxybenzene (Table 5). The ratio of alcohols and TIPOF was optimized to 6:1. In entry 1, anisole was obtained in 74% yield, which was lower than the yield obtained using only TMOF. For other primary alcohols, we evaluated ethanol, propanol, and butanol (Table 5, entries 2–4). The corresponding products, ethoxybenzene, propoxybenzene, and butoxybenzene, were obtained in good yields, and only small amounts of isopropoxybenzene and phenol (4–11% yield) were detected as by-products. This reaction also proceeded with 2-propanol to produce isopropoxybenzene (Table 5, entry 5), although the reaction only gave **4o** in 23% yield due to the steric hindrance in the formation of the acetal intermediate. Furthermore, higher alcohols, such as *n*-heptanol and *n*-octanol, were also employed, and the corresponding aryl ethers were afforded in good yields (Table 5, entries 6 and 7).

Table 5 Synthesis of aryl ethers from cyclohexanone with alcohols.^a

Entry	ROH	Product	Conv. (%) ^b	Yield (%) ^b
1	MeOH		100	74
2 ^c	EtOH		100	83
3	ⁿ PrOH		100	76
4	ⁿ BuOH		91	73
5	ⁱ PrOH		51	23
6 ^d	ⁿ Heptanol		95	78
7 ^d	ⁿ Octanol		98	79

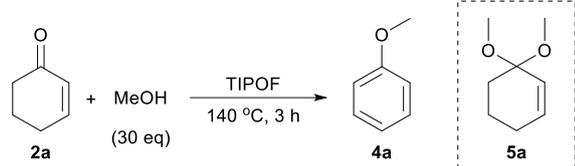
^a Reaction conditions: cyclohexanone (1 mmol), 10 wt% Pd(OH)₂/ZrO₂ (Pd 2 mol%), ROH (30 eq), TIPOF (5 eq), O₂ (0.5 MPa), 140 °C, 6 h. ^b Calculated on the basis of GC analysis using tridecane as an internal standard. ^c 8 h. ^d Alcohol (15 eq).

Possible reaction pathway

In order to investigate the reaction pathway for the synthesis of aryl ethers, several experiments were performed by using cyclohexanone (**2a**) as the starting material in the absence of Pd (Table 6). When both TIPOF and ZrO₂ were used in this process, the reaction proceeded efficiently, affording the anisole (**4a**) with a good yield in 2 h (Table 6, entry 1). Due to orthoesters can facilitate the formation of acetals from

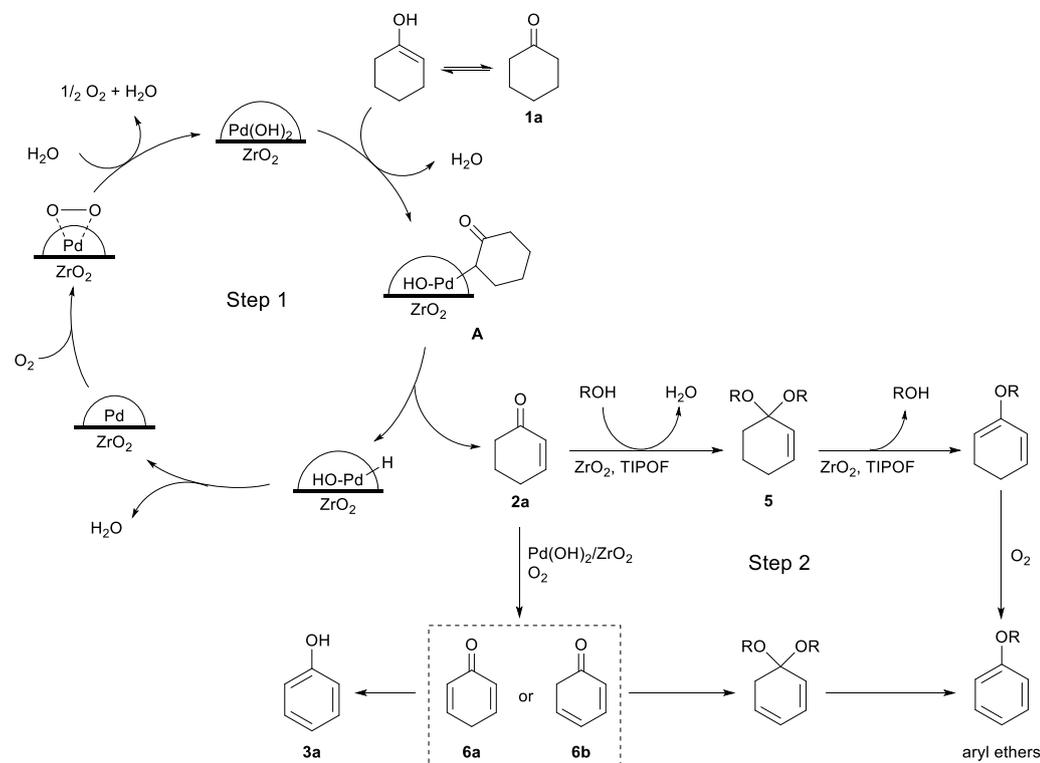
aldehydes and ketones, a comparative test was carried out (Table 6, entry 2) using the reaction conditions as entry 1 in absence of ZrO_2 . The anisole yield was slightly decreased, indicating that ZrO_2 is required for this reaction. Since ZrO_2 has both Lewis acid and base sites, we assumed that ZrO_2 acted as a Lewis acid to promote the formation of the acetal intermediate and/or as a Lewis base for the production of anisole by eliminations. Additionally, cyclohexenone did not react with methanol in the absence of ZrO_2 and TIPOF (Table 6, entry 3). Also, molecular oxygen was appeared to be essential to produce aryl ethers, because only dimethylacetal (**5a**) was detected under N_2 atmosphere (Table 6, entry 4).

Table 6 Synthesis of anisole started from cyclohexenone.



Entry	ZrO_2	TIOPF (eq)	Gas (MPa)	Yield (%) ^a
1	20 mg	5	O_2 (0.5)	77
2	--	5	O_2 (0.5)	35
3	--	--	O_2 (0.5)	0
4	--	5	N_2 (0.1)	0

^a Calculated on the basis of GC analysis using tridecane as an internal standard.



Scheme 4 Suggested reaction pathway for synthesis of cyclohexenone, phenols, and aryl ethers from cyclohexanone.

The proposed reaction pathway for the synthesis of cyclohexenone, phenol, and aryl ethers is presented in Scheme 4. The mechanism for the synthesis of cyclohexenone (**2a**) from cyclohexanone (**1a**) has been studied in previous reports.^{4c,5b} Similarly, cyclohexanone is activated by $Pd(OH)_2$ on metal oxide surface to produce Pd-enolate intermediate (**A**), and cyclic enone is formed, followed by β -hydride elimination. Pd^0 is regenerated to Pd^{II} by oxidation with molecular oxygen. In the second step, the cyclic enone reacts with alcohol to form acetal (**5**), and aryl ether is obtained by further elimination and oxidation. These steps are promoted by ZrO_2 as Lewis acid-base catalyst and by orthoesters as efficient dehydrating reagent. Alternatively, cyclic enone could be oxidized to dienones when the six-membered ring could be aromatized, and dienones were tautomered to phenol.

Conclusions

In conclusion, we have developed a method for the direct aerobic oxidation of cyclohexanones to cyclic enones, phenols, and aryl ethers over supported Pd^0 or Pd^{II} catalysts using molecular oxygen as the sole oxidant. Although the reaction exhibited low selectivity for the transformation of cyclohexanone to cyclohexenone, 4,4-dimethylcyclohexenone could be obtained in 81% yield from the corresponding cyclohexanone. For the synthesis of phenols, ZrO_2 supported Pd^0 catalyst showed better catalytic activity than other supported Pd^{II} catalysts, and the corresponding phenols were obtained in moderate to excellent yields. Notably, two novel catalytic protocols were proposed for the preparation of aryl ethers from cyclohexanones with ZrO_2 supported $Pd(OH)_2$ as

catalyst. Cyclohexanones could be converted to aryl ethers in the presence of the corresponding orthoesters, which act as nucleophilic and dehydrating reagents. In the direct reaction with alcohols, the orthoesters (TIPOF) only acted as an efficient

dehydrating reagent. In contrast with previous works, both these processes provide synthetically useful and convenient methods to prepare simple aryl ethers, such as anisole, ethoxybenzene, and propoxybenzene.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [Catalysts preparation method, experimental procedures, reaction conditions for synthesis of phenol and cychohexenone, characterization of catalysts by HAADF-STEM, XAFS, XRD, and MP-AES, characterization of isolated compounds, spectra of ¹H and ¹³C NMR]. See DOI: 10.1039/b000000x/

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