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Hydrogen auto-transfer under aerobic oxidative conditions: Efficient synthesis of saturated ketones by aerobic C–C cross-coupling of primary and secondary alcohols catalyzed by a Au₆Pd/resin catalyst

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ABSTRACT

Au and Au-containing bimetallic nanoparticles are promising catalysts for the green synthesis of fine chemicals. Here, we used a Au₆Pd/resin catalyst for the aerobic C–C cross-coupling of primary and secondary alcohols to produce higher ketones under mild conditions. This is of importance to the construction of a C–C bond. Various substrates were used in the reaction system, and moderate to good yields were obtained. The catalysts can be reused at least five times without decrease of yield. The control experiment and XAFS characterization results showed that hydrogen auto-transfer occurred on metallic Pd sites even under oxidative conditions. On alloying with Au, the Pd sites became resistant to oxidation and readily abstracted the β-H of the alcohols and transferred the hydride to the C=C bond in the reaction intermediate to give the saturated product.

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1. Introduction

The construction of complex and diverse molecules from simple substrates by C–C bond forming reactions is a central theme in organic synthesis [1–3]. The traditional synthesis, mainly employing aryl (alkyl) halides as the coupling reagent [4–6], suffers from low atom efficiency due to the large amount of mass loss with the leaving group of the alkylating agent and it also has toxic issues. Efforts have been devoted to developing efficient, mild, and straightforward approaches to achieve the

C–C coupling reaction. Among these, the hydrogen auto-transfer strategy, which uses cheap, stable and readily available alcohols as the alkylation reagent, has attracted increasing attention (Scheme 1(A)) [7]. In this protocol, alcohols undergo sequential dehydrogenation or aldol condensation or transfer hydrogenation to afford higher alcohols or ketones with H₂O and/or H₂ as the only byproduct. Various homogeneous catalysts [8,9] and heterogeneous catalysts such as Pd/C [10], Ag/Al₂O₃ [11] and Au–Pd/HT [12] have been used for this reaction. However, several drawbacks of these catalysts are:

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(A): Previous hydrogen autotransfer process

(B): This study: aerobic C–C cross-coupling strategy

Scheme 1. Different protocols of C–C cross-coupling reaction of primary and secondary alcohols.

first, the homogeneous metal complex and ligands are difficult to recycle and are sensitive to moisture and air; second, due to the sluggish dehydrogenation of alcohols, harsh reaction conditions are employed (temperature usually above 115 °C and an organic solvent is used). For this reason, it is highly desirable to develop an efficient heterogeneous catalyst to accomplish the coupling reactions of alcohols under mild reaction conditions.

Gold and gold-containing bimetallic catalysts have attracted increasing attention for a broad array of organic reactions because of their unique activity and selectivity, as well as the mild conditions needed, especially for aerobic oxidative reactions [13–16]. Recently, our group developed a series of Au-based catalysts for the aerobic oxidation of alcohols and silanes, and the aerobic C–C cross-coupling of alcohols and amines [17–19]. With our ongoing interest in the aerobic oxidative reaction, we turned our attention to an alternative route: an aerobic oxidative strategy to accomplish the direct cross-coupling reactions of secondary and primary alcohols. To our delight, by employing an ion exchange resin supported Au–Pd alloy as catalyst, we succeeded in accomplishing the direct cross-coupling of secondary and primary alcohols to produce higher ketones (Scheme 1(B)) under mild reaction conditions under an O₂ balloon atmosphere. A wide scope of substrates and functional groups can be used in the reaction system, and moderate to good yields of the products were obtained. Furthermore, the catalyst can be recovered and reused for at least 5 times without loss of activity.

2. Experimental

2.1. Catalyst preparation

HAuCl₄·3H₂O and PdCl₂ were purchased from Shanghai Chemical Reagent Co., Ltd., and 717# ion exchange resin was provided by Sinopharm Chemical Reagent Co., Ltd. Other chemicals were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. All chemicals were analytical grade and used as received without further purification. The water used in this study was deionized by a milli-Q Plus system, having 18.2 MΩ electrical resistivity.

An aqueous solution of HAuCl₄ with Au concentration of 9.56 mg/mL was prepared by dissolving 1.0 g of HAuCl₄·3H₂O in 50.0 mL milli-Q water. An aqueous solution of H₂PdCl₄ with Pd concentration of 12.00 mg/mL was prepared by dissolving

1.0 g of PdCl₂ in 1.5 mL HCl (12 mol/L), and then diluted to 50.0 mL with milli-Q water. The 717# resin after anion exchange was washed with water several times until the filtrate became clean. After drying at 60 °C, the resin was crushed with a ball mill at 250 r/min for 1 h and then sieved to 100–180 mesh for use as the catalyst support. The resin support was then soaked sequentially in NaOH (1.0 mol/L), HNO₃ (1.0 mol/L), and NaOH (1.0 mol/L) for 8 h, and finally in K₂CO₃ solution (2.0 mol/L) for 24 h. The resultant ion exchange resin was filtered and washed with water until the filtrate became neutral and then dried under vacuum at 60 °C for 12 h.

Monometallic Au/resin, Pd/resin and bimetallic Au–Pd/resin with different Au/Pd ratios were prepared with the ion exchange–NaBH₄ reduction method reported in the literature [5]. With Au₆Pd/resin as an example, 1.92 mL HAuCl₄ solution (*C*_{Au} = 9.56 mg/mL) and 0.14 mL H₂PdCl₄ (*C*_{Pd} = 12.00 mg/mL) were mixed together in 200 mL H₂O, followed by the addition of 1.0 g 717# resin and stirring for 2 h in dark. The recovered solid was re-dispersed in 30.0 mL water, followed by the addition of 15.0 mL NaBH₄ solution (10.0 equiv.) and stirred for 0.5 h in dark to reduce the metal precursor. After filtration, washing, and drying at 60 °C for 8 h under vacuum, the catalyst was obtained and denoted as Au₆Pd/resin. The other catalysts were prepared with the same method except for a different volume of the precursor solution. The total metal loading was controlled at 2.0 wt% for all the catalysts. All of the catalysts were stored in air before use.

2.2. Catalyst characterizations

X-ray powder diffraction (XRD) analysis was carried out on a PANalytical X'pert diffractometer using nickel-filtered Cu Kα radiation with a scanning angle (2θ) of 10°–80°, operated at 40 kV and 40 mA. High resolution transmission electron microscope (HRTEM) characterization was carried out with a Tecnai G² Spirit (FEI) microscope operating at 200 kV. Prior to observation, a powder sample of the catalyst was ultrasonically dispersed in ethanol and a few droplets of the suspension were put on a copper grid covered with a holey carbon film and dried at room temperature.

X-ray absorption fine structure (XAFS) spectra at the Au L_{III}-edge and Pd K-edge were measured at the 14W beam line of Shanghai Synchrotron Radiation Facility (SSRF) and the insertion-device beamline 10-ID-B of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source at Argonne National Laboratory. The X-ray absorption spectra were recorded at room temperature in the transmission mode. Au foil and Pd foil as references were measured simultaneously using the third ionization chamber so that the energy calibration could be performed scan-by-scan. The X-ray absorption data were processed by the Athena software package.

2.3. Catalyst evaluation

Unless otherwise noted, the reactions were carried out as follows. A mixture of primary alcohol (1.0 mmol), secondary alcohol (0.5 mmol), KOH (2.0 mmol) and catalyst (1.0–3.0

mol%) was added to 2 mL H₂O in a test tube. The tube was sealed before evacuation and purging with O₂ three times. The reaction mixture was vigorously stirred at 60 °C for 6 h under an oxygen balloon. After cooling down to room temperature, the catalyst was separated by filtration and the filtrate was extracted with ethyl acetate (2 × 20.0 mL). The organic layer was dried over anhydrous magnesium sulfate. After adding 100 μL *n*-dodecane as the internal standard, the organic mixture was submitted to GC analysis for conversion and yield determination. The crude product was purified by flash chromatography on a short silica gel (eluent: petroleum ether/ethyl acetate = 10/1, 2/1).

3. Results and discussion

3.1. XRD and STEM characterization results

The Au/resin, Pd/resin and Au-Pd/resin catalysts were prepared with the ion exchange-NaBH₄ reduction method. STEM images (Fig. 1(a)–(c)) showed that nanoparticles with an average size of 2–3 nm were highly dispersed on the support. In agreement with the STEM images, the XRD patterns (Fig. 1(d)) showed broad peaks of the (111) reflection. The size of the nanoparticles in Au/resin and Au₆Pd/resin samples calculated by the Scherrer equation was 2.5 nm, in good agreement with that estimated from the STEM images. On comparing with monometallic Au/resin and Pd/resin catalysts, the (111) reflection of the Au₆Pd/resin was found to be positioned between them, suggesting the formation of a Au-Pd alloy in the Au₆Pd/resin sample [20–22].

3.2. Catalytic performance

To evaluate the catalysts, aerobic C–C cross-coupling of

Fig. 1. STEM images of (a) Au/resin, (b) Au₆Pd/resin, (c) Pd/resin and (d) XRD patterns of the samples.

Table 1

Catalytic performance of Au-Pd/resin for C–C cross-coupling reactions of alcohols. ^a

Entry	Conversion of 1b (%)	Catalyst	Yield (%) ^b		
			1c	1d	1e
1	34	Pd/resin	18	0	16
2	48	Au/resin	11	0	37
3	68	AuPd ₂ /resin	26	13	29
4	62	Au ₄ Pd/resin	28	16	18
5	80	Au ₆ Pd/resin	5	45	30
6 ^c	98	Au ₆ Pd/resin	3	70	25

^a Reaction conditions: 1 mmol **1a**, 0.5 mmol **1b**, 2 mmol KOH, catalyst (1 mol%), 2 mL H₂O, *P*(O₂) = 0.1 MPa, 60 °C, 6 h. ^b Determined by GC using *n*-dodecane as an internal standard and calculated based on **1b**. In all experiments, **1a** were totally converted, and the corresponding by-product was benzoic acid. ^c 3 mol% catalyst, 1.5 mmol **1a**.

benzyl alcohol and 1-phenylethanol was selected as the test reaction. The reaction was first conducted at 60 °C for 6 h under O₂ atmosphere in aqueous media to have an environmentally benign process. As shown in Table 1, monometallic Au/resin and Pd/resin gave poor selectivity for the coupling reaction, giving the unsaturated chalcone with 18% and 11% yield, respectively. The main side products were benzoic acid and hypnone which came from the (over)oxidation of benzyl alcohol and 1-phenylethanol that did

Table 2

Substrate scope of the Au₆Pd/resin catalyst for aerobic C–C cross-coupling of alcohols. ^a

$R^1-CH_2OH + R^2-CH(OH)-CH_3 \xrightarrow[\substack{O_2 \text{ balloon, KOH,} \\ H_2O \text{ 2 mL} \\ 70^\circ C, 6 h}]{Au_6Pd/resin} R^1-CH_2-CH_2-C(=O)-R^2$		
Product	Molecular formula	Isolated yield (%)
1		60
2		71
3		61
4		46
5		18

^a Reaction conditions: primary alcohol 1.0 mmol, secondary alcohol 0.5 mmol, 2 mmol KOH, catalyst 3 mol%, 2 mL H₂O, *P*(O₂) = 0.1 MPa, 60–70 °C, 6 h. The yields refer to the isolated products. In all experiments, the secondary alcohols were totally converted, and the only by-product was hypnone.

not undergo the cross-coupling reaction. In contrast, the bimetallic Au-Pd/resin catalysts gave a significantly increased yield of the product in comparison with the monometallic counterparts. For example, AuPd₂/resin afforded a total yield of the coupling products of 39%, while Au₆Pd/resin gave a total yield of 50%. The yield reached as high as 73% when the amount of catalyst was increased to 3.0 mol% under optimized reaction conditions, demonstrating a strong synergistic effect between Au and Pd.

After establishing the optimum reaction conditions, we addressed the issues of substrate scope and functional group tolerance of the catalytic system. As shown in Table 2, the Au-Pd/resin catalyst exhibited good tolerance for various substrates with different functional groups, and moderate to good yields were obtained. Notably, aliphatic alcohols, e.g., biomass derived 1-butanol that are usually slow to oxidize, was converted readily to the product although relatively low yields were obtained. More importantly, the Au-Pd/resin catalyst can be easily recovered from the reaction system by simple filtration. After washing and drying, the Au₆Pd/resin catalyst was directly submitted to another cycle of reaction. As shown in Table 3, the catalyst could be reused for at least 5 times without significant decrease in product yield, demonstrating the high stability of the Au-Pd/resin catalyst.

3.3. Reaction mechanism

It is interesting to note that the bimetallic Au-Pd/resin catalysts showed a distinct product distribution different from their monometallic counterparts. The main product over the Au-Pd/resin catalysts was the saturated ketones. It is widely accepted that in the coupling reactions of primary and secondary alcohols the substrates are first converted to the aldehyde and ketones, which then undergo aldol condensation reaction under basic conditions to yield the unsaturated ketones. When under inert or reduced conditions, this is followed by hydrogenation to yield the saturated products [12,23]. Based on this reaction mechanism, we envision that in the case of the monometallic Au/resin and Pd/resin, the alcohols underwent sequential aerobic oxidation-aldol

Table 3

Recovery and reuse of Au₆Pd/resin for the C–C cross-coupling of alcohols.^a

Reuse	Yield (%)
1st	70
2nd	54
3rd	68
4th	59
5th	57

^a Reaction conditions: 1.5 mmol **1a**, 0.5 mmol **1b**, 2 mmol KOH, catalyst 3 mol%, 2 mL H₂O, *P*(O₂) = 0.1 MPa, 60 °C, 6 h. Yield was determined by GC using *n*-dodecane as an internal standard and calculated based on **1b**.

Table 4

Control experiment.^a

Entry	Catalyst	Conversion of 1c ^b (%)	Yield of 1d ^b (%)
1	Au/resin	0	0
2	Pd/resin	0	0
3	Au ₆ Pd/resin	100	92.7

^a Reaction conditions: **1a** 1.0 mmol, **1c** 0.5 mmol, KOH 2.0 mmol, H₂O 2 mL, *P*(O₂) = 0.1 MPa, catalyst 1.0 mol%, 60 °C, 6 h. ^b Determined by GC using *n*-dodecane as an internal standard.

condensation to produce α,β -unsaturated ketone, whereas in the bimetallic Au-Pd/resin system, hydrogen auto-transfer occurred after the aldol condensation reaction, thus yielding the saturated product. To show the transfer reduction mechanism, control experiments of coupling of benzyl alcohol and chalcone under the same reaction conditions were conducted (Table 4). It can be seen that over the monometallic Au/resin and Pd/resin, the chalcone remained intact, whereas it was transformed to the corresponding saturated ketone over the bimetallic Au₆Pd/resin catalyst. This confirmed that the hydrogen auto-transferred indeed occurred on the bimetallic Au-Pd/resin system.

To understand how the transferred hydrogenation occurred on the bimetallic Au-Pd/resin catalyst, we then performed XAFS characterizations to determine the valence state of Au and Pd in the catalyst. Fig. 2 shows the XANES spectra at the Pd K-edge of the Au-Pd/resin catalysts as well as of the reference samples. The *E*₀ values of the catalysts, which usually increase with an increase of the oxidation state of Pd [24], followed the order of Pd foil < Au₆Pd/resin < Au₄Pd/resin < AuPd₂/resin < Pd resin $\approx$ PdO (Fig. 2, inset and Fig. 3). This indicated that the Pd component in the Au₆Pd catalyst was mainly in metallic state (Pd⁰). In other words, Pd became more resistant to oxidation when alloyed with Au, which was further demonstrated by the EXAFS fitting results. As shown in Table 5, Pd was totally oxidized to PdO in the Pd/resin sample when it was stored at ambient conditions for a long time. However, the

Fig. 2. Normalized XANES spectra at Pd K-edge for different samples. Inset shows the *E*₀ shift of different samples.

Fig. 3. The XANES spectra at Pd L_{III} -edge of Pd/resin and different Au-Pd/resin.

Table 5

EXAFS data fitting results of Au-Pd/resin, Au/resin and Pd/resin catalysts.^a

Sample	Scatter	<i>N</i>	<i>R</i> /nm	$\Delta\sigma^2$ (10^3)	ΔE_0 (eV)
Au/resin	Au-Au	7.9	0.282	2.0	-0.8
Au ₆ Pd/resin	Au-Au	8.2	0.281	1.0	3.0
	Au-Pd	1.1	0.279	1.15	3.0
	Pd-Au	5.0	0.279	0.88	-4.4
	Pd-O	1.4	0.200	0.15	-4.4
Au ₄ Pd/resin	Au-Au	8.0	0.280	1.5	-1.7
	Au-Pd	1.4	0.272	1.5	3.7
	Pd-Pd	0.9	0.278	2.0	-5.2
	Pd-Au	5.2	0.280	2.0	-3.8
AuPd ₂ /resin	Pd-O	1.8	0.204	3.0	-1.7
	Au-Au	6.0	0.280	1.5	-1.9
	Au-Pd	4.0	0.276	1.5	4.6
Pd/resin	Pd-O	3.7	0.204	3.0	-0.3
	Pd-O	4.0	0.204	3.0	-0.1

^a *N*—the coordination number for the absorber-backscatterer pair. *R*—the average absorber backscatterer distance. σ^2 —the Debye Waller factor. ΔE_0 —the inner potential correction.

proportion of Pd⁰ (coordination number of Pd-Au and Pd-Pd) increased in the bimetallic Au-Pd/resin samples with an increase of Au/Pd ratio. Based on these results, it was concluded that the forming of an alloy with Au prevented the oxidation of Pd and allowed Pd to keep its metallic state. Interestingly, in all of the samples investigated, Au always kept its metallic state. As mentioned before, the products over Au/resin was an unsaturated ketone. Therefore, we can exclude the possibility that the transferred reduction occurred on Au sites. Taken together, the metallic Pd sites on the Au-Pd/resin catalysts were believed to be responsible for the auto-transferred hydrogenation reaction.

It is well known that in the Pd catalysed oxidation reaction of alcohols, the abstraction of β -H, which is usually regarded as the rate determining step in the reaction, can directly occur on

the Pd(0) catalyst [25]. Similarly, the Pd(0) sites in our Au₆Pd/resin catalyst probably can abstract the β -C-H of alcohols to form a Pd-H species, which would be the source of hydrogen in the auto-transferred hydrogenation reaction. However, under our aerobic oxidative conditions, the super-oxo species activated on Au sites can also dissociate the β -C-H bond. Given the similar role of the super-oxo species and Pd(0) sites in the reaction, a contradiction would be: (1) if Pd(0) sites were responsible for the abstraction of the β -C-H of alcohols, the coupling reaction of primary and secondary alcohols would readily occur under inert atmosphere conditions, whereas our control experiment results showed that no any coupling products was detected; (2) if the super-oxo species contributed to the dissociation of β -C-H bond, then the auto-transfer hydrogenation reaction would not occur because of the transformation of the β -H to H₂O.

To gain more insight into the reaction mechanism and discriminate between the role of the super-oxo species and Pd(0) sites in the reaction, another control experiment of Au₆Pd/resin catalysed transformation of benzyl alcohol and 1-phenylethanol under an inert atmosphere condition was performed. Benzyl alcohol was smoothly converted to benzoic acid with a GC yield of 23.1% over Au₆Pd/resin under Ar, whereas 1-phenylethanol remained intact. The results suggested that for primary alcohols that are usually easily oxidised, the Pd(0) sites in Au₆Pd/resin can directly abstract the β -C-H without the assistance of oxygen, whereas for secondary alcohols which are more difficult to transform, oxygen is needed for the dissociation of the β -C-H bond.

Based on the control experiments and characterization results, a reaction mechanism of hydrogen auto-transfer in the coupling reactions of primary and secondary alcohols on the bimetallic Au₆Pd/resin catalyst was proposed (Fig. 4). First, the metallic Pd sites on Au-Pd alloys abstract the β -H in the primary alcohols to form Pd-H species, and the alcohols are converted to the corresponding aldehydes. The super-oxo species on the Au sites readily dissociate the β -C-H bond in the secondary alcohols, and ketone is then produced. Second, the

Fig. 4. Proposed reaction mechanism of hydrogen auto-transfer in the aerobic C-C cross-coupling of alcohols.

aldehyde and ketone undergo aldol condensation catalysed by KOH to yield the α,β -unsaturated ketone. Upon formation, the $-C=C$ in the α,β -unsaturated ketone is hydrogenated by the hydride on Pd sites to give the saturated product.

4. Conclusions

We achieved the coupling of primary and secondary alcohols using Au_6Pd /resin as catalyst and an aerobic oxidative route. The Au_6Pd /resin catalyst showed good tolerance for many substrates and can be reused several times without significant decrease in yield. XAFS characterization results showed that Pd became more resistant to oxidation with an increase of Au/Pd ratio in the Au-Pd/resin and it kept its metallic state. Metallic Pd sites readily abstract the β -H in primary alcohols and transfer the hydride to the reaction intermediate α,β -unsaturated ketone, and were responsible for the transferred hydrogenation reaction. Our results provide an avenue to take advantage of hydrogen auto-transfer to synthesize fine chemicals under mild reaction conditions.

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Graphical Abstract

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Aerobic C–C cross-coupling of primary and secondary alcohols was catalyzed by Au_6Pd /resin under mild conditions.

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Au₆Pd/resin 催化伯醇和仲醇氧化偶联-转移加氢反应制备酮类化合物

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摘要: 由简单小分子通过 C–C 键偶联来构筑复杂多样的大分子是有机合成的重要方向. 传统的 C–C 键偶联反应一般使用卤代烃和金属有机化合物为底物, 具有原子效率低、有害废弃物排放等缺点. 因此, 迫切需要发展一种绿色高效的 C–C 键偶联方法. 其中, 以醇类化合物作为底物通过“氢转移”(脱氢/aldol 缩合/加氢) 实现 C–C 键偶联的途径受到广泛关注. 该方法具有诸多优点: (1) 醇类化合物来源广泛、价格低廉、相对安全; (2) 只产生 H₂ 和 H₂O, 没有其它副产物. 但由于醇类化合物(特别是仲醇) 脱氢困难, 该偶联反应条件一般比较苛刻. 我们使用 O₂ 来辅助仲醇脱氢, 采用离子交换树脂负载的 Au₆Pd 纳米颗粒为催化剂, 实现了温和条件下伯醇和仲醇的偶联反应. 而且发现在氧化气氛下, 反应过程中发生了“氢转移”现象, 产物为饱和酮类化合物. 通过设计对照实验并结合 XAFS(X-射线吸收光谱) 表征结果, 我们揭示了在 Au₆Pd/resin 催化剂上发生“氢转移”反应的机理.

AuPd/resin 催化剂采用离子交换–NaBH₄ 还原法制备. TEM 照片显示 Au, Pd 以及双金属 AuPd 纳米颗粒均匀分散在载体上, 平均粒径为 2–4 nm, 而且随着 Au/Pd 比例减小, AuPd 纳米颗粒的粒径逐渐减小. XRD 谱图显示, 随着 Au/Pd 比例减小, Au(111) 衍射峰逐渐向高角度发生偏移, 说明 AuPd 形成了合金.

我们以苯甲醇和 (±)-1-苯乙醇氧化偶联为探针反应考察了催化剂的催化性能. 结果显示, 以 Au/resin 和 Pd/resin 为催化剂时, 产物为不饱和酮. 而以 AuPd/resin 为催化剂时, 转化率显著提高, 说明 AuPd 之间存在明显的协同作用. 而且随着 Au/Pd 比例增加, 产物逐渐由不饱和酮转变为饱和酮, 当 Au/Pd ≥ 6 时, 产物完全为饱和酮, 说明反应过程中发生了“氢转移”. 为验证这一推测, 我们以苯甲醇和查尔酮为底物在相同条件下反应. 结果显示, 以 Au/resin 和 Pd/resin 为催化剂时, 查尔酮没有转化. 而以 AuPd/resin 为催化剂时, 查尔酮大部分转化为饱和酮 (转化率为 91%), 验证了反应中发生了“氢转移”的推测.

为研究“氢转移”发生的机理, 我们采用 XAFS 对催化剂价态进行了表征. Pd 元素 K 边 X 射线吸收谱图显示, 随着催化剂中 Au/Pd 比例的增加, E₀ 值逐渐减小, 说明 Pd 价态逐渐降低. EXAFS 拟合数据表明, 随催化剂中 Au/Pd 比例增加, Pd–O 配位数逐渐减小. 基于以上结果推断, 在 AuPd/resin 催化剂中, 随着 Au/Pd 比例的增加, Pd 的抗氧化能力显著增强, 更多的 Pd 以 Pd(0) 形式存在. 结合文献报道结果, 我们认为正是催化剂中的 Pd(0) 夺取了醇的 βC–H 后生成了 Pd–H, 而 Pd–H 是“氢转移”反应的催化剂.

另一方面, 有文献报道, 在氧化气氛下, O₂ 也可以辅助脱除醇的 βC–H. 为区分 Pd(0) 和 O₂ 在脱除醇 βC–H 中的作用, 我们对 Au₆Pd/resin 在惰性气氛下对伯醇(苯甲醇) 或仲醇 ((±)-1-苯乙醇) 转化的催化性能进行了考察. 结果显示, 苯甲醇可以转化为苯甲酸 (收率为 23%), 而 (±)-1-苯乙醇则完全没有转化. 这说明伯醇可以直接被催化剂 (Pd(0)) 活化, 而仲醇的活化则必须有 O₂ 参与. 综上, 我们提出伯醇和仲醇氧化偶联反应的机理: Au₆Pd/resin 催化伯醇转化为醛 (同时产生 Pd–H 物种), 而 O₂ 辅助活化仲醇转化为酮. 醛和酮发生 aldol 缩合生成 α,β-不饱和酮, 该中间物种被 Pd–H 加氢生成饱和产物.

关键词: 金钯合金; C–C 键偶联; 醇氧化; 转移加氢; 抗氧化

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