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From Alkyl Aromatics to Aromatic Esters: Efficient and Selective C–H Activation Promoted by a Bimetallic Heterogeneous Catalyst

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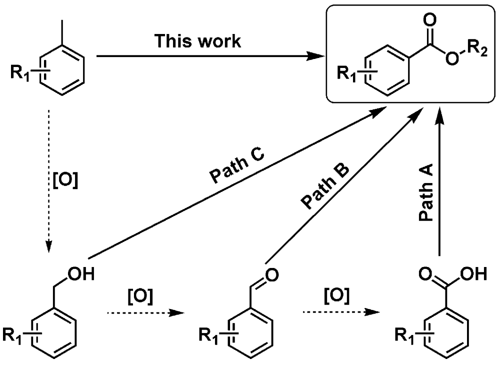
Esters (e.g., aromatic carboxylates) are an important class of chemicals, widely utilized in fine chemicals, natural products, pharmaceuticals, agrochemicals, and food additives.[1] , Esters are traditionally prepared by reacting carboxylic acids or activated carboxylic-acid derivatives (e.g., acid anhydrides, acyl chlorides) with alcohols (Scheme 1, path A). The synthetic procedure involves multiple steps, and suffers from inherent problems such as the formation of undesired byproduct and time- and resource-consuming steps to isolate or separate catalysts and/or products.[2] The oxidative esterification of aldehydes with alcohols (path B) has recently attracted much attention as alternative for traditional protocols.[3] However, such methodologies generally require stoichiometric amounts of transition-metal oxidants or peroxy salts (e.g., $KMnO_4$, CrO_3, Oxone, and sodium perborate). Further research efforts have been devoted to the direct synthesis of esters from alcohols (path C),[4] in which a stoichiometric amount (or excess) of base additives is generally required to achieve high ester yields.[4a–f]



Scheme 1. Esterification methodologies for the synthesis of aromatic-derived methyl esters from various aromatic compounds with alcohols.

In view of these settings, the development of a suitable, more efficient, and environmentally sound alternative catalytic methodology for the direct oxidative synthesis of esters from inexpensive and abundant feedstocks can offer a number of advantages to produce and market high-added-value aromatic esters. Such a method should avoid the use of environmentally unfriendly catalysts and oxidants as well as basic promoters.

Alkanes (as bulk chemicals) are a highly attractive type of esterification reagent because of their availability and low cost compared to their oxidation products, including alcohols, aldehydes, and acids. However, alkanes are rarely utilized as oxidative esterification agents owing to the low reactivity of sp^3 C–H bonds.[5] Aromatic carboxylates are mostly prepared by the oxidative esterification of aromatic acids, aldehydes, or alcohols.[2–4] To date, only two very recent reports describe the selective oxidative esterification of methyl aromatics with alcohols to yield aromatic methyl esters, employing homogeneous organophotocatalysis (CBr_4 or anthraquinone-2,3-dicarboxylic acid) under light irradiation.[6] Nevertheless, the reported protocols have a relatively restricted scope of substrates as well as low efficiencies [with turnover numbers (TONs) <10] related to the inherent drawbacks of photocatalysis. The homogeneous system is not particularly environmentally friendly or cheap, which significantly limits its application to more useful and broad catalytic processes.

As a continuation of our recent development of useful and environmentally sound alternative methodologies in oxidation chemistries, we report here an operationally simple and greener catalytic oxidative esterification approach that efficiently converts methyl aromatics to aromatic carboxylates utilizing a highly stable, active, and reusable heterogeneous bimetallic Au–Pd catalyst and molecular oxygen as benign oxidant (Scheme 1). The proposed catalytic system features a broad substrate scope for both methyl aromatics and alcohols, providing a high selectivity to target products under mild solvent-free conditions without the addition of any base additives.

Au–Pd bimetallic nanoparticles have attracted considerable interest due to their high activities and selectivities in a range of oxidation reactions.[7] Bimetallic Au–Pd nanoparticles on carbon or TiO_2 have been recently shown to be an efficient system in the selective oxidation of toluene to symmetric esters (e.g., benzyl benzoate).[8] Benzyl alcohol and benzaldehyde were detected as intermediates for the formation of esters.[8] Based on these precedents, Au–Pd nanoparticles could possibly be active in the oxidative esterification of toluene with alcohols to synthesize unsymmetric aromatic esters. We selected MIL-101 (a representative metal–organic framework) as support for Au–Pd nanoparticles owing to its high surface area and large pore size. MIL-101 proved to be an excellent support for the preparation of highly dispersed metal nanoparticles as well as in a range of catalytic applications.[9]

MIL-101 supported Au–Pd catalysts were prepared by using a simple colloidal deposition method with poly(vinyl alcohol)

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(PVA) as protecting agent (for experimental details, see the Supporting Information). Different Au–Pd molar ratios were utilized for the preparation of a series of Au–Pd/MIL-101 materials. After the incorporation of metal nanoparticles, the framework of MIL-101 was well preserved, as confirmed by powder X-ray diffraction (XRD) and N_2 adsorption measurements (Supporting Information, Table S1 and Figure S1). Pd and Au/MIL-101 analogous systems were also synthesized and characterized accordingly. XPS results showed that the Pd^0 3d and Au^0 4f peaks for the Au–Pd/MIL-101 were shifted to lower binding energies by approximately 0.5 eV and 0.3 eV, respectively, compared to the monometallic Pd/MIL-101 and Au/MIL-101 samples (Supporting Information, Figures S2 and S3). This effect is particularly noticeable in the Pd XPS (Figure S3) in which peaks intensities are also different. Such observed shifts for both Pd 3d and Au 4f may be attributed to the flow of electron density into Au (higher Au s or p electron densities) and Pd (gaining d electrons from Au), and could be indicative of the formation of Au–Pd bimetallic alloys, in good agreement with previous reports.[10]

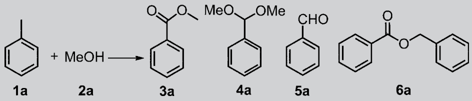
Initially, we chose toluene and methanol as model substrates, with molecular oxygen as oxidant, to screen reaction parameters. Reactions in the absence of catalyst or using the parent MIL-101 as catalyst gave no activity in the systems after 48 h (Table 1, entries 1 and 2). Interestingly, Au/MIL-101 exhibited a very low activity for the oxidative esterification of toluene (entry 3), despite previously reported high activities and selectivities in the aerobic oxidation of alcohols under base-free conditions.[9h]

Conversions were remarkably improved by the addition of Pd (Table 1, entries 4–6), and no CO_2 was observed for all reactions. Methyl benzoate was obtained as main oxidation product, with small quantities of benzaldehyde, benzaldehyde dimethyl acetal, and benzylbenzoate being co-generated in the reaction. We also detected small amounts of formaldehyde and formic acid produced from the oxidation of methanol. Results of the oxidation esterification pointed to an optimized performance of Au–Pd/MIL-101 with a Pd/Au 1.5:1 molar ratio in terms of activity and selectivity (entry 5). A further increase in Pd content led to reduced conversions and selectivities to methyl benzoate (entries 6 and 7). These results indicate a remarkable synergistic effect of the Au–Pd catalysts in the conducted oxidative esterification reactions.

A further optimization of reaction parameters was subsequently conducted. The temperature and pressure of O_2 in the reaction were found to strongly influence activities of the bimetallic systems in the proposed reaction. An increase in O_2 pressure resulted in remarkably reduced selectivities to methyl benzoate (Table 1, entry 8). However, increasing the temperature to 120 °C improved toluene conversions while maintaining high selectivities to methyl benzoate (entry 9). We also increased the amount of methanol and found that the reaction proceeded with enhanced activity and selectivity when 5 mL of methanol were added in the system (entries 5 and 10). The effects of substrate/metal molar ratio were further investigated (entries 11–13), and a maximum of 96.9 % conversion of toluene could be achieved with a 96.6 % selectivity to methyl benzoate at a lower substrate/metal ratio and 120 °C within 48 h (entry 12). The oxidative esterification reaction also proceeded well at a high substrate/metal molar ratio (6000:1), giving a TON of 1386 with a good selectivity to methyl benzoate (entry 13).

The scope of aromatic hydrocarbons amenable to be converted into esters via the proposed Au–Pd/MIL-101 catalyzed aerobic oxidative esterification protocol was also investigated. As shown in Table 2, all reactions proceeded smoothly with excellent selectivities to the desired methyl aromatic esters under optimized reaction conditions. The electronic and steric factors of the substituents played an important role in determining the reactivity of the aromatic substance. In general, electron-deficient aromatic hydrocarbons provided the corresponding ester products in lower yields (e.g., entries 2 vs. 7). An increase in steric hindrance led to a slight decrease in product yields (entries 3–5).

Table 1. Results of the direct oxidative esterification of toluene with methanol.[a]

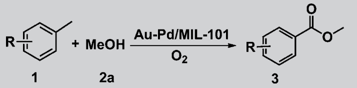


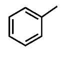
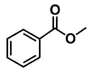
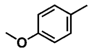
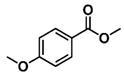
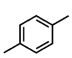
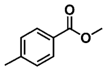
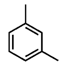
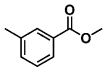
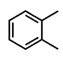
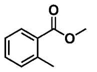
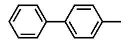
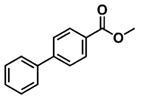
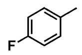
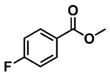
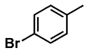
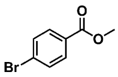
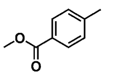
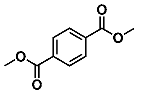
Entry	Pd/Au molar ratio	T [°C]	P_{O_2} [MP]	Conv. [%]	Selectivity to products [%]			
					3a	**4a**	**5a**	**6a**
1[b]	–	100	1	–	–	–	–	–
2[c]	–	100	1	–	–	–	–	–
3	0:1	100	1	1.4	17.2	46.0	36.8	–
4	1:3	100	1	24.7	77.1	4.9	18.0	–
5	1.5:1	100	1	34.3	87.8	1.8	6.2	4.2
6	3:1	100	1	33.8	71.9	2.9	13.2	12.0
7	1:0	100	1	1.5	13.4	62.6	24.0	–
8	1.5:1	100	2	50.5	71.5	9.3	7.1	12.1
9	1.5:1	120	1	50.3	84.2	3.6	6.0	6.2
10[d]	1.5:1	100	1	43.6	96.4	1.4	1.1	0.7
11[d]	1.5:1	120	1	62.6	94.7	1.9	1.8	1.6
12[d,e]	**1.5:1**	**120**	**1**	**96.9**	**96.6**	**1.4**	**1.2**	**0.8**
13[d,f]	1.5:1	120	1	23.1	80.1	6.2	8.6	5.1
14[g]	1.5:1	100	1	35.2	88.5	1.7	5.8	4.0

[a] Reaction conditions: toluene (1 mL), methanol (3 mL), 1 wt % Au–Pd/MIL-101, substrate/metal = 2000, 48 h. [b] No catalyst used. [c] Catalyst: MIL-101. [d] Methanol (5 mL). [e] Substrate/metal = 1000. [f] Substrate/metal = 6000. [g] Third run to test the reusability of Au–Pd/MIL-101 under the conditions of entry 5.

The application of the newly developed oxidative esterification protocol was then extended to the use of various alcohols. Various aliphatic alcohols including methanol, ethanol, *n*-propa-

Table 2. Oxidative esterification of various methyl aromatics with methanol.[a]

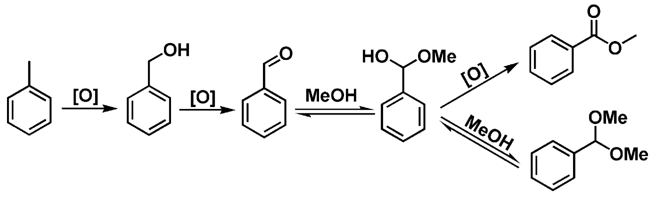


Entry	Substrate		Product		Conv.[b] [%]	Sel.[b] [%]	Yield[c] [%]
1		**1a**		**3a**	96.9	96.6	94 (90)
2		**1b**		**3b**	93.9	98.0	92 (90)
3[d]		**1c**		**3c**	92.4	90.6	84 (80)
4[d]		**1d**		**3d**	88.4	90.0	80 (75)
5[d]		**1e**		**3e**	80.2	87.3	70 (66)
6[d]		**1f**		**3f**	73.3	85.5	63 (58)
7[e]		**1g**		**3g**	75.3	88.2	66 (60)
8		**1h**		**3h**	22.9	80.0	18 (12)
9[e]		**1i**		**3i**	78.6	89.5	70 (65)

[a] Reaction conditions: methyl aromatic (10 mmol), methanol (5 mL), 1 wt% Au–Pd/MIL-101, substrate/metal = 1000, 120 °C, 1.0 MPa O_2, 48 h. [b] Determined by GC-MS analysis. [c] GC yield (isolated yield in parenthesis). [d] 72 h. [e] 140 °C.

nol, and isopropyl alcohol smoothly underwent esterification with toluene and provided excellent selectivities to the desired methyl aromatic esters under optimized conditions using Au–Pd/MIL-101 (Table 3, entries 1–4). A remarkable reduction in product yield was observed as the carbon chain length and steric hindrance of the alcohol increased (e.g., *tert*-butanol). The reaction results of different aromatic hydrocarbons with alcohols (Tables 2 and 3) demonstrated the general applicability of this catalytic system in the proposed selective oxidative esterification.

To ascertain the potential presence of radical intermediates, we added a typical radical scavenger (*p*-benzoquinone) to a reaction run. The addition of *p*-benzoquinone did not significantly affect the reactivity of the oxidative esterification of toluene with methanol (Supporting Information, Table S2), which indicates a rather improbable radical intermediate formation in this transformation using Au–Pd catalysts and under the investigated conditions. In view of these findings, we propose a possible pathway for the one-pot aerobic conversion of aromatic hydrocarbons into methyl aromatic esters, which principally involves four steps (Scheme 2). Firstly, toluene is oxidized to benzyl alcohol via primary C–H bond activation over the bimetallic Au–Pd nanoparticles.[8] In this process, the synergistic effect in Au–Pd nanoparticles is suggested to be responsible for the improved activity and selectivity compared to monometallic catalysts. Such a molecular-scale synergy of Au–Pd alloys has also been observed in a range of other oxidation reactions.[8,10b,11] The enhanced surface electron density of the bimetallic Au–Pd catalyst (see XPS data, Supporting Information) would be favorable for the activation of O_2 to generate oxygen species, probably in a superoxo-like form.[12] Subsequently, the C–H bond in toluene could be oxidized to form benzyl alcohol by the active oxygen species. The formed benzyl alcohol then undergoes a β-hydride elimination to generate benzaldehyde, which directly reacts with methanol to form the corresponding hemiacetal species.[13] Ester products are believed to be finally formed by the direct oxidation of hemiacetals.[13] A proof that supports the proposed mechanism is the observation of benzaldehyde dimethyl acetal as product in the reaction (Table 1).

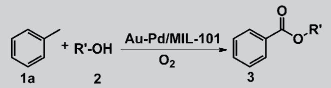


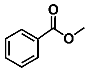
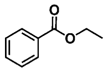
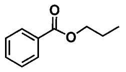
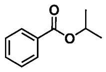
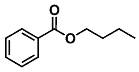
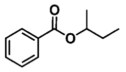
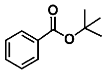
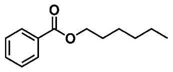
Scheme 2. Possible pathway for the oxidative esterification reaction.

Kinetic studies revealed that the amount of benzaldehyde dimethyl acetal decreased with time, accompanied by a gradual increase in the quantity of methyl benzoate in the course of reaction (Supporting Information, Figure S4). On the basis of these results, it might be speculated that a dynamic equilibrium between the hemiacetal species and benzaldehyde dimethyl acetal is likely to be present in the system under the investigated reaction conditions.[13f] The equilibrium may be driven to the production of hemiacetal species from benzaldehyde dimethyl acetal, which undergo oxidation to form methyl benzoate.

Reusability studies of Au–Pd/MIL-101 indicate that the catalyst can be reused upon simple separation without a significant loss of efficiency (Table 1, entry 14). The crystalline structure of

Table 3. Oxidative esterification of toluene with various aliphatic alcohols.[a]



Entry	Product		Conv.[b] [%]	Sel.[b] [%]	Yield[c] [%]
1		**3a**	96.9	96.6	94 (90)
2		**3j**	99.0	95.6	95 (90)
3		**3k**	94.5	89.3	84 (80)
4		**3l**	92.8	84.6	79 (73)
5[d]		**3m**	80.2	80.0	64 (60)
6[e]		**3n**	71.9	70.1	50 (45)
7[e]		**3o**	69.0	86.9	60 (56)
8[d]		**3p**	45.2	70.3	32 (25)

[a] Reaction conditions: toluene (10 mmol), aliphatic alcohol (0.13 mol), 1 wt% Au–Pd/MIL-101, substrate/metal = 1000, 120 °C, 1.0 MPa O_2, 48 h. [b] Determined by GC-MS analysis. [c] GC yield (isolated yield in parenthesis). [d] 72 h. [e] 96 h.

the catalyst also remained mostly unchanged after three catalytic cycles (Supporting Information, Figure S1). No metal was detected in the filtered reaction solution (after 9 h reaction), and the liquid phase did not exhibit any further reactivity (Supporting Information, Figure S5). In good agreement with these findings, transmission electron microscopy (TEM) images of the reused catalysts did not reveal any appreciable changes in nanoparticle size (average particle size around 3.0 nm) in the materials as compared to the fresh catalysts prior to reaction (Figure 1). These results confirm the stability of the described heterogeneous system under the investigated conditions.

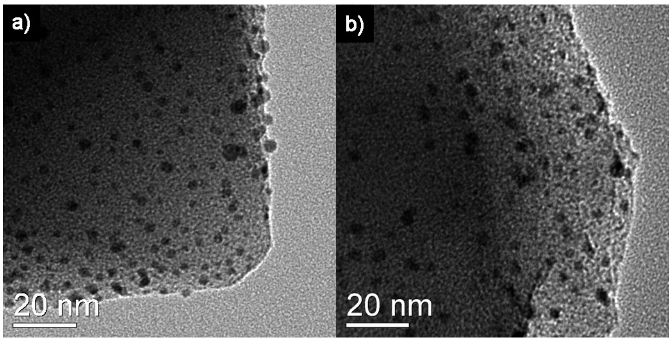


Figure 1. HRTEM images of 1 wt% Au–Pd/MIL-101 a) before, and b) after reaction.

In conclusion, we have developed an innovative, highly efficient, and reusable heterogeneous catalyst system for the direct esterification of alkyl aromatics with alcohols catalyzed by porous MOF-supported Au–Pd bimetallic nanoparticles and molecular oxygen as the oxidant. Our catalytic oxidative esterification method exhibits a broad substrate scope, as well as a high selectivity to target products without requiring any co-catalysts or additives. The use of less-expensive and readily available methyl aromatics as starting materials and O_2 as benign oxidant as well as a recyclable catalyst in the absence of solvents constitutes a significant step towards the development of novel and more efficient industrially relevant and applicable green and sustainable catalytic processes. Studies aimed at understanding the reaction mechanism and further improvements and optimization of the catalytic system are currently underway in our laboratories.

Acknowledgements

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Keywords: C–H activation · esters · heterogeneous catalysis · metal–organic frameworks · oxidation

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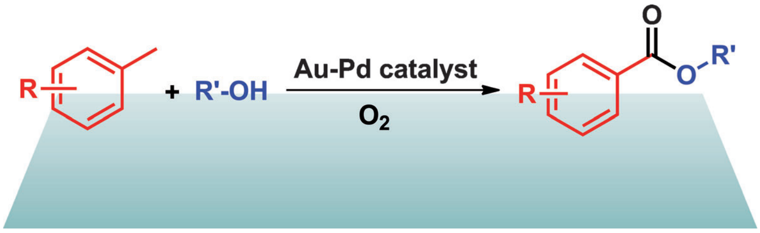
From Alkyl Aromatics to Aromatic Esters: Efficient and Selective C–H Activation Promoted by a Bimetallic Heterogeneous Catalyst



Oxidizing aromatics: We report an operationally simple and green catalytic oxidative esterification approach that selectively converts methyl aromatics to aromatic carboxylates utilizing a highly stable, active, and reusable heterogeneous bimetallic Au–Pd catalyst and molecular oxygen as benign oxidant without requiring any additives.