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水相中交联型聚合物负载的 Pd 催化氨基醇氧化羰化反应

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摘要: 在水相无助剂条件下, 将含有离子液基团的聚合物负载的 Pd 催化剂用于催化氨基醇氧化羰化反应高效合成噁唑烷酮. 催化剂能够重复使用 5 次而活性没有明显降低.

关键词: 钯; 负载型催化剂; 氨基醇; 氧化羰化; 水相; 重复使用

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Oxidative Carbonylation of 2-Amino-1-alkanols Catalyzed by Cross-Linked Polymer Supported Palladium in Water

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Abstract: Employing palladium supported on polymeric monolith containing ionic liquid as an efficient heterogeneous catalyst, the oxidative carbonylation of 2-amino-1-alkanols could be successfully carried out, affording the corresponding 2-oxazolidinones in good to excellent yields in pure water without excessive iodine-containing promoter. The catalyst was reused up to five cycles without significant loss of its catalytic activity.

Key words: palladium; supported catalyst; 2-amino-1-alkanol; oxidative carbonylation; water phase; recovery

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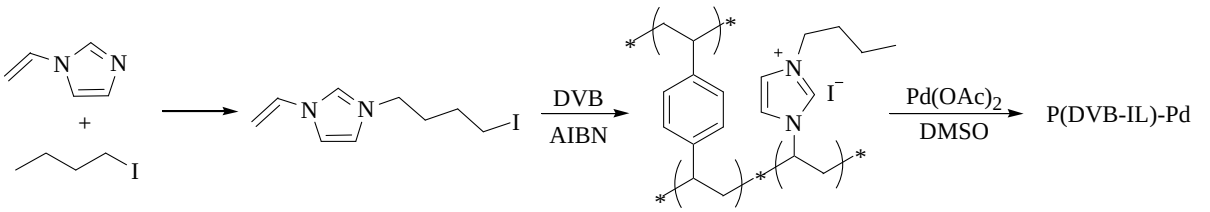
作为一类很重要的杂环化合物, 2-噁唑烷酮及其衍生物在有机化学和药物化学中有着重要的应用. 特别是手性的 2-噁唑烷酮作为手性单元广泛应用于不对称反应[1~3], 并且有些含有 2-噁唑烷酮基团的化合物表现出很好的抗菌活性[4~6]. 在制备 2-噁唑烷酮及其衍生物的各种方法中[7], 过渡金属 (或非金属) 在以 CO 为羰基源的条件下催化氨基醇的氧化羰化是一类高效的原子经济的合成路线[8,9], 如 S[10], Se[11]和 Pd[12~15]. 目前相关研究已取得很大进展, 但反应多是在含有机溶剂的均相体系中进行, 催化剂分离困难, 不便于重复使用, 同时还采用过量的腐蚀性含碘化合物 (如 I_2, KI) 作为反应的促进剂.

本课题组[16~19]研究了一些过渡金属催化的均相体系, 并首次将 Pd/C 多相催化体系[20]用于该反应, 虽然实现了贵金属的重复使用, 但仍需加入促进剂 I_2 才能使催化反应高效进行. 因此, 有必要发展高效、简单、催化剂可回收利用的、环境友好的催化体系.

近几年来, 不同载体负载的金属催化剂成为研究的热点, 其中含有离子液基团的聚合物负载的催化剂广受关注[21~23]. 本课题组[24]成功地将含离子液片断的交联型聚合物负载的 Pd 催化剂 P(DVB-IL)-Pd (图式 1) 用于水相中 Sonogashira 羰化偶联反应. 本文进一步将该催化剂用于水相中氨基醇氧化羰化合成 2-噁唑烷酮反应中.



图式 1 催化剂 P(DVB-IL)-Pd 的合成

Scheme 1. Synthesis of the P(DVB-IL)-Pd catalyst.

将氨基醇 (1.0 mmol), P(DVB-IL)-Pd, 5 ml 蒸馏水加入带有磁子的不锈钢反应釜中, 用 O_2 置换 3 次后充入 0.5 MPa 的 O_2, 再充入 2.0 MPa 的 CO, 然后放入 140 °C 的油浴中反应 6 h. 反应结束后冷却至室温, 放空未反应完的气体. 加入丙酮将反应液完全取出, 离心得催化剂, 干燥后用于下次循环. 反应液经过柱层析得到目标产物. 产物的核磁分析数据如下.

2-噁唑烷酮 (表2, 反应1). 无色固体, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (r, s, 1H), 4.45–4.09 (m, 2H), 3.68–3.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 64.9, 40.6.

5-甲基-2-噁唑烷酮 (表2, 反应2). 淡黄色油状物, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (r, s, 1H), 4.76–4.67 (m, 2H), 3.67–3.63 (m, 1H), 3.17–3.13 (m, 2H), 1.38 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 73.4, 47.4, 20.4.

4-甲基-2-噁唑烷酮 (表2, 反应3). 淡黄色油状物, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (br, s, 1H), 4.46 (t, J = 8.3 Hz, 1H), 4.01–3.90 (m, 1H), 3.89 (dd, J = 6.3 Hz, J = 8.3 Hz, 1H), 1.29 (d, J = 5.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 71.5, 48.2, 20.7.

4-乙基-2-噁唑烷酮 (表2, 反应4). 淡黄色油状物, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (r, s, 1H), 4.44–4.12 (m, 2H), 3.98–3.80 (m, 1H), 3.78–3.71 (m, 1H), 1.60–1.49 (m, 2H), 0.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 70.0, 53.8, 28.0, 9.2.

4-异丙基-2-噁唑烷酮 (表2, 反应5). 无色固体, ^{1}H NMR (400 Hz, $CDCl_3$) δ 7.24 (br, s, 1H), 4.44 (t, J = 8.0 Hz, 1H), 4.10 (dd, J = 4.4 Hz, J = 6.8 Hz, 1H), 3.61–3.56 (m, 1H), 1.76 (m, 1H), 0.95 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 135.9, 130.0, 128.9, 127.2, 69.5, 53.7, 41.3.

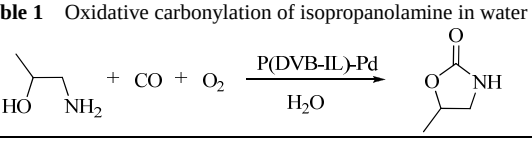
4,4-二甲基-2-噁唑烷酮 (表2, 反应6). 淡黄色油状物, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (br, s, 1H), 4.02 (s, 2H), 1.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 76.9, 55.2, 27.4.

3-(2-羟乙基)-2-噁唑烷酮 (表2, 反应7). 无色油状物, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35–4.31 (m, 2H), 3.78–3.76 (m, 2H), 3.70–3.66 (m, 2H), 3.39–3.36 (m, H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 62.1, 60.3, 46.8, 45.6.

以异丙醇胺的氧化羰化作为探针反应考察 P(DVB-IL)-Pd 在水相体系中的催化性能, 以优化反

表 1 异丙醇胺氧化羰基化反应条件筛选

Table 1 Oxidative carbonylation of isopropanolamine in water



Entry	T/°C	p(CO/O_2)/MPa	t/h	Isolated yield (%)
1	120	2.0/0.5	3	51
2	140	2.0/0.5	3	84
3	120	4.8/0.2	3	40
4	140	2.0/0.5	6	90
5[a]	140	2.0/0.5	6	86

Reaction conditions: isopropanolamine 1 mmol, P(DVB-IL)-Pd 20 mg (0.005 mmol Pd), distilled water 5 ml.

[a]P(DVB-IL)-Pd 10 mg (0.0025 mmol Pd) was used.

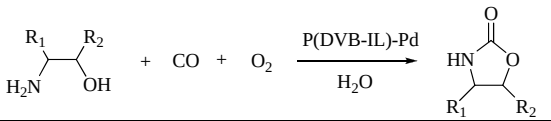
应条件, 结果见表 1. 可以看出, 当反应温度从 120 °C 升高到 140 °C 时, 产物收率从 51% 提高到 84%; 当反应时间从 3 h 增至 6 h, 2-噁唑烷酮收率从 84% 提高到 90%. 另外, 当催化剂量从 0.25% 增加到 0.5% 时收率也有所增加. 因此适宜的反应条件为: 催化剂用量 0.5%, 140 °C, 压力 CO/O_2 = 4, 水为溶剂, 反应 6 h.

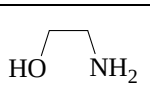
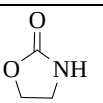
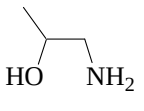
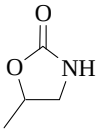
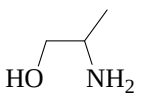
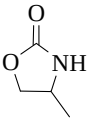
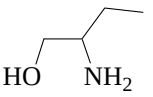
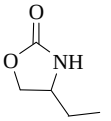
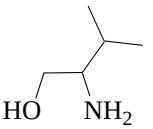
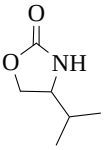
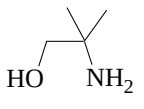
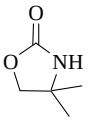
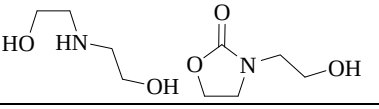
在上述优化反应条件下, 本文将 P(DVB-IL)-Pd 体系用于各类氨基醇的氧化羰化反应, 结果见表 2. 可以看出, 该催化体系对烷基取代的氨基醇类化合物氧化羰化反应具有较高的活性和选择性, 表明该催化剂具有良好的底物适应性. 另外, 对于氮上带有取代基的氨基醇类化合物, 产物收率为 92%.

本文进一步以异丙醇胺的氧化羰化反应考察

表 2 氨基醇氧化羰化底物适应性

Table 2 Oxidative carbonylation of 2-amino-1-alkanols in water



Entry	Substrate	Product	Isolated yield (%)
1			70
2			90
3			84
4			88
5			89
6			82
7			92

Reaction conditions: 1 mmol 2-amino-1-alkanols, 20 mg (0.005 mmol Pd) P(DVB-IL)-Pd, 5 ml distilled water, 140 °C, 6 h, CO 2.0 MPa, O_2 0.5 MPa.

P(DVB-IL)-Pd 催化剂的稳定性, 结果见图 1. 反应结束后, 催化剂经过简单离心分离后用于下一次反应. 由图 1 可见, 该催化剂循环使用 5 次后, 催化活性没有明显降低, 产物收率仍达 82%. 图 2 为反应前后 P(DVB-IL)-Pd 催化剂的 TEM 照片, 可以看出催化剂使用 5 次后 Pd 颗粒没有明显的团聚, 表明聚合物载体对 Pd 颗粒有很好的稳定作用.

综上所述, 聚合物负载的 Pd 催化剂在水相催化氨基醇的氧化羰化反应中表现出较高的催化活性, 该含离子液片断的聚合物载体很好地稳定了 Pd, 实

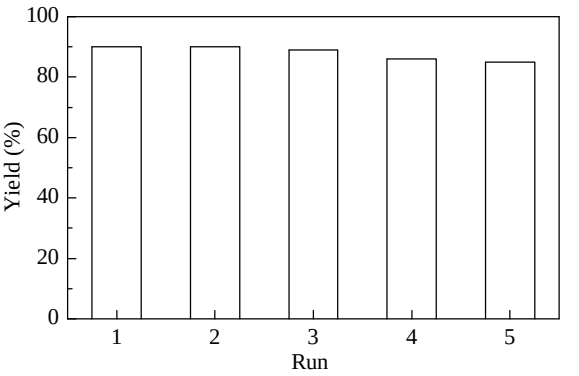


图 1 P(DVB-IL)-Pd 催化剂的重复使用性能

Fig. 1. The recycling testing of P(DVB-IL)-Pd for oxidative carbonylation of isopropanolamine in water.

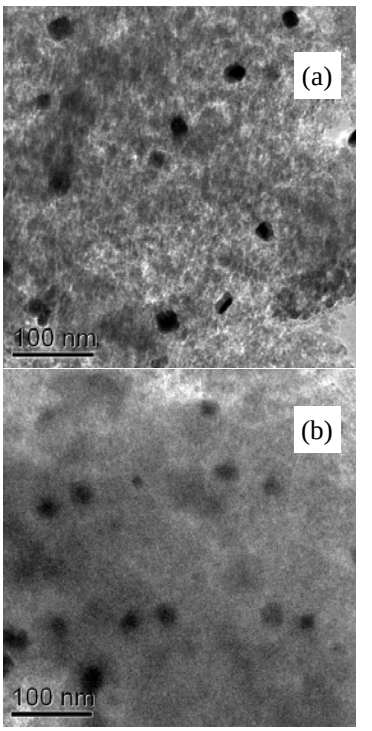


图 2 反应前后催化剂 TEM 照片

Fig. 2. TEM images of the fresh (a) and used (b) P(DVB-IL)-Pd.

现了催化剂循环使用且催化活性没有明显的降低. 本文提供了一种高效绿色合成 2-噁唑烷酮的途径.

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英 译 文

English Text

The 2-oxazolidinone nucleus is a very popular heterocycle framework in both organic as well as medicinal chemistry. The chiral analogues, 2-oxazolidinones in particular, have been used as chiral auxiliaries (Evans' chiral auxiliaries) in a wide range of asymmetric reactions [1–3], and some molecules containing the 2-oxazolidinone moiety have also shown antibacterial activity [4–6]. Intramolecular oxidative carbonylation of 2-amino-1-alkanols catalyzed by transition metals using carbon monoxide as the carbonyl source is better compared with other pathways to build this cottage-like molecule [7]. This scheme represents an attractive and effective way to construct oxazolidinone [8,9]. Many efforts have been devoted to the field, and several catalytic systems including S [10], Se [11], and Pd [12–15] have been reported. Although some advancements have been made, there are two obvious limitations of these studies. The present systems are often carried out using organic solvents under homogeneous conditions, wherein the catalysts are difficult to isolate and reuse, and excessive iodine-containing compounds are mostly employed as promoters (e.g. iodine, potassium iodide). These are known to be very corrosive in the reaction system and therefore alternative frameworks are required. Thus, we are reporting our newly developed transition metal catalyzed homogeneous systems [16–19] as well as the first heterogeneous catalyst based on palladium on charcoal (Pd/C) that provide good catalytic efficiency for the oxidative carbonylation reaction [20]. Although the recycle of expensive transition metal catalyst was achieved in these reaction mechanisms, the catalytic efficiency still needed some improvements. Therefore the aim of the current work is to investigate another versatile and efficient recyclable, and environmentally benign catalyst system for the reaction.

In recent years, immobilization of catalysts on suitable supports has been a topic of interest [21–23]. Especially polymers containing ionic liquids that share the same properties of such liquids could be used for immobilization of catalyst. We have reported the synthesis of cross-linked polymer supported palladium catalyst P(DVB-IL)-Pd and its application in carbonylative Sonogashira coupling reaction in water [24] (Scheme 1). Herein we illustrate P(DVB-IL)-Pd serving as catalyst in oxidative carbonylation of 2-amino-1-alkanols to synthesize oxazolidin-2-ones in water.

All solvents were purified and degassed according to standard procedures before use. The carbonylated products were purified by flash chromatography on silica gel and characterized by comparison of their spectra with authenticated samples. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer (400 and 100 MHz, respectively) with reference to tetramethylsilane (TMS) as internal standard in $CDCl_3$. The catalyst was prepared utilizing established procedures [24].

All oxidative carbonylation experiments were carried out in a 75 ml autoclave equipped with magnetic stirring and

automatic temperature control. The reactor was charged with 2-amino-alkahols (1.0 mmol), catalyst P(DVB-IL)-Pd (20 mg, 0.5 mol%), and distilled water (5.0 ml), and then pressurized with oxygen/carbon monoxide (0.5 MPa/2.0 MPa). The reactor was heated to 140 ^{o}C for 6 h. After the reaction was completed , the reaction mixture was allowed to cool to room temperature. The reaction mixture was analyzed by GC-MS and the water was removed under vacuum. The residue was purified by chromatography on silica gel (acetone:petroleum ether = 1:1). After each experiment, the catalyst was separated by centrifugation and then washed with acetone and dried under vacuum to remove the residual solvent before the next cycle.

Oxazolidin-2-one (Table 2, entry 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (r, s, 1H), 4.45–4.09 (m, 2H), 3.68–3.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 64.9, 40.6

5-Methyloxazolidin-2-one (Table 2, entry 2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (r, s, 1H), 4.76–4.67 (m, 2H), 3.67–3.63 (m, 1H), 3.17–3.13 (m, 2H), 1.38 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 73.4, 47.4, 20.4.

4-Methyloxazolidin-2-one (Table 2, entry 3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (br, s, 1H), 4.46 (t, J = 8.3 Hz, 1H), 4.01–3.90 (m, 1H), 3.89 (dd, J = 6.3 Hz, J = 8.3 Hz, 1H), 1.29 (d, J = 5.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 71.5, 48.2, 20.7.

4-Ethyloxazolidin-2-one (Table 2, entry 4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (r, s, 1H), 4.44–4.12 (m, 2H), 3.98–3.80 (m, 1H), 3.78–3.71 (m, 1H), 1.60–1.49 (m, 2H), 0.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 70.0, 53.8, 28.0, 9.2.

4-Isopropyloxazolidin-2-one (Table 2, entry 5). ^{1}H NMR (400 Hz, $CDCl_3$) δ 7.24 (br, s, 1H), 4.44 (t, J = 8.0 Hz, 1H), 4.10 (dd, J = 4.4 Hz, J = 6.8 Hz, 1H), 3.61–3.56 (m, 1H),1.76 (m, 1H), 0.95 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 135.9, 130.0, 128.9, 127.2, 69.5, 53.7, 41.3.

4,4-Dimethyloxazolidin-2-one (Table 2, entry 6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (br, s, 1H), 4.02 (s, 2H), 1.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 76.9, 55.2, 27.4.

3-(2-Hydroxyethyl) oxazolidin-2-one (Table 2, entry 7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35–4.31 (m, 2H), 3.78–3.76 (m, 2H), 3.70–3.66 (m, 2H), 3.39–3.36 (m, H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 62.1, 60.3, 46.8, 45.6.

The catalytic activity of P(DVB-IL)-Pd was examined for its ability to catalyze the oxidative carbonylation reaction of 2-amino-1-alkanols to oxazolidin-2-ones in water. In order to optimize the reaction conditions, the oxidative carbonylation of isopropanolamine as a model reaction was carried out using P(DVB-IL)-Pd. Different reaction temperatures, reaction times, catalyst amounts, and CO/O_2 pressures were uesd to examine the effects on the oxidative carbonylation in water. As shown in Table 1, the reaction temperature plays an important role in the reaction rate. The yield of oxazolidin-2-one was increased from 51% to 84% when the temperature was elevated from 120 ^{o}C to 140 ^{o}C (Table 1, entries 1 and 2). Of note is that when the CO/O_2 ratio was increased, the yield of the desired product decreased significantly (Table 1, entry 3). Increasing the reaction time had a positive effect on the catalytic activity (Table 1, entries 2, 4, and 5). When the Pd loading was decreased to 0.0025 mmol, the oxazolidin-2-one yield was 86% under the same reaction conditions (Table 1, entry 5). Therefore, the best results were obtained by stirring at 140 ^{o}C for 6 h with 20 mg (0.5 mol %) Pd catalyst loading in distilled water.

In order to expand the scope of the 2-amino-1-alkanols in the oxidative carbonylation, different 2-amino-1-alkanols were employed in the reaction under optimal reaction conditions, and the results are summarized in Table 2. Clearly, the heterogeneous system (polymer supported palladium complex catalyzed reaction in water) shows high catalytic activity in the oxidative carbonylation reaction by producing the oxazolidin-2-ones in good to excellent yields (70%–92%).

The key property of heterogeneous catalysts is their recovery and reuse, which is an essential attribute for green chemistry. To test the stability and deactivation of P(DVB-IL)-Pd, a series of continuous runs of the oxidative carbonylation of isopropanolamine in water were carried out (Fig. 1). In each cycle, the catalyst was separated by centrifugation. Obviously, the catalyst could be reused five times only with a slight loss of activity for the oxidative carbonylation of isopropanolamine (the 5th reuse still can produce more than 80%). The TEM image of the catalyst after five times usage is shown in Fig. 2(b). It is obvious that the palladium particle on the polymer still disperses well without clear aggregation.

In summary, the ionic liquid composite material proved to be an effective support for immobilizing palladium complex. The polymer supported palladium catalyst P(DVB-IL)-Pd exhibited high efficiency for oxidative carbonylation of 2-amino-alkahols when water was used as solvent. In addition, the catalyst offered practical advantages such as easy separation from the products and reuse without activity loss. This heterogeneous carbonyaltion reaction in water provides a practical and environmentally friendly procedure for the synthesis of oxazolidin-2-ones.

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