

PS-HQ: More convenient *in situ* polymeric cocatalyst for the PdCl₂-catalyzed acetalization in supercritical carbon dioxide

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Abstract

Polystyrene-supported hydroquinone (PS-HQ) is presented as an *in situ* polymeric cocatalyst to replace polystyrene-supported benzoquinone (PS-BQ) in the PdCl₂-catalyzed acetalization of methyl acrylate with methanol in supercritical carbon dioxide (scCO₂) under oxygen atmosphere. Due to deletion of H₂O₂ oxidation step, PS-HQ is more convenient and relatively inexpensive.

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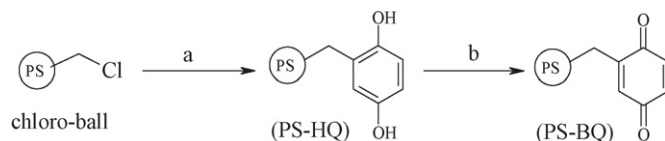
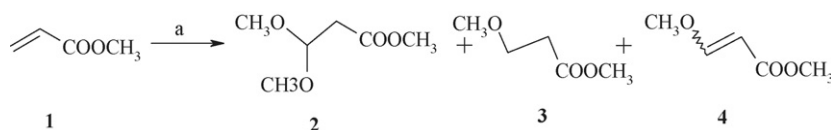
Wacker reaction is extensively applied in organic synthesis [1]. In order to improve the activity of the catalyst system in Wacker reaction, many efforts have been made [1,2]. Recently, our group has been successfully developed Wacker reaction in two fields: (1) using supercritical carbon dioxide (scCO₂) [3–5] as an alternative green solvent [6]; (2) using polystyrene-supported benzoquinone (PS-BQ) as an easily separated and recyclable cocatalyst instead of the traditional copper salts [2,5].

Lately, because of PS-BQ is easily separated, recovered and recycled, environment-friendly and markedly superior to the small molecular catalysts, more and more importance has been attached to polymer-supported catalysts [7,8]. In addition, polystyrene-supported hydroquinone (PS-HQ) is the intermediate of PS-BQ and the latter could be obtained *via* the H₂O₂ oxidation step (Scheme 1) [2,5]. Thus, it is interesting and necessary to make clear if PS-HQ could be oxidized *in situ* under oxygen atmosphere to give PS-BQ in the acetalization system.

As expected, using PS-HQ as cocatalyst with palladium chloride, the acetalization of methyl acrylate was carried out smoothly in scCO₂ under oxygen atmosphere with the similar excellent yield and selectivity as PS-BQ does (Scheme 2).

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Scheme 1. (a) HQ/ZnCl₂; (b) H₂O₂.Scheme 2. (a) CH₃OH/O₂, PdCl₂/PS-HQ (or PS-BQ), scCO₂.

1. PdCl₂/PS-HQ -catalyzed acetalization

Alkyl 3,3-dialkoxypropanoates is a kind of important intermediates for organic synthesis [9–11]. The Pd^{II}-catalyzed reaction between terminal olefins with electron-withdrawing groups and alcohols is the simplest one among the methods to prepare these 3,3-dialkoxy acetals [11–13].

In our previous research on polymer-supported cocatalyst PS-BQ, various kinds of terminal olefins with electron-withdrawing groups, including acrylate esters (CH₂=CH-COOR), acrylonitrile (CH₂=CH-CN), and methyl vinyl ketone (CH₂=CH-CO-CH₃), have been investigated, and the results are satisfactory [2,5].

When PdCl₂/PS-HQ was used as the catalyst, the acetalization of terminal olefins with electron-withdrawing groups, *e.g.* methyl acrylate (CH₂=CH-COOCH₃, **1**) with methanol was investigated under oxygen atmosphere (Scheme 2 and Table 1) [14].

The yields of the main product methyl 3,3-dimethoxypropanoate **2** were obtained from 88.2 to 92.2% (Table 1, entries 1–3), which were even higher than the results when cocatalyst CuCl₂ was employed [2,3]. Compared with PdCl₂/CuCl₂ catalyst system, the selectivity of PdCl₂/PS-HQ for **2** is on a similar level.

The experimental results also showed that the higher total pressure was advantageous to the reaction due to a better solvent power of the reaction medium (Table 1, entries 1–3). The availability of the reactants is thereby increased.

Under a higher total pressure, the reaction time could be shortened from 24 to 6 h, the reaction still gave the satisfactory result and the efficiency was remarkably improved (Table 1, entry 2).

2. Possible catalytic mechanism for PS-HQ

The IR analyses of fresh and recovered PS-HQ showed that, the absorption of phenolic hydroxyl near 1201 cm⁻¹ was greatly weakened, and even the absorption near 3512 cm⁻¹ nearly disappeared. At the same time, the absorption of carbonyl in quinone structure near 1706 cm⁻¹ was observed. This indicated that PS-HQ was used as *in situ* cocatalyst in the presence of oxygen.

Table 1
Acetalization of methyl acrylate and MeOH using PS-HQ as cocatalyst in scCO₂

Entry ^a	Time (h)	Total system pressure ^b (MPa)	Conversion (%)	GC yield (%)			Selectivity for 2 ^c (%)
				2	3	4	
1	12	9	100	88.2	6.1	5.0	88.8
2	6	16	99.8	92.2	0	4.3	95.6
3	24	15	98.5	90.1	0	5.2	94.6

^a Reaction conditions: 5 mmol methyl acrylate **1**, 0.15 mmol (3 mol%) PdCl₂, and 2 mmol PS-HQ; the molar ratio of methanol to methyl acrylate 4.94:1; reaction temperature 50 °C.

^b The initial O₂ pressure was all controlled at 0.5 MPa.

^c Selectivity = [2/(2 + 3 + 4)] × 100.

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