Pergamon

Tetrahedron Letters 43 (2002) 5653–5655

TETRAHEDRON
LETTERS

Suzuki cross-coupling reaction catalyzed by palladium-supported sepiolite

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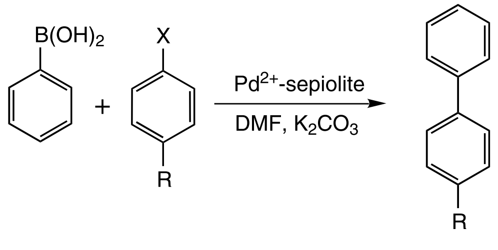
Received 2 May 2002; accepted 7 June 2002

Abstract—Palladium-supported sepiolite clay has effectively catalyzed the Suzuki cross-coupling reaction of phenylboronic acid with aryl halide including less reactive electron-rich aryl bromides. © 2002 Elsevier Science Ltd. All rights reserved.

The palladium-catalyzed cross-coupling reaction of aryl halides and arylboronic acids (Suzuki reaction) represents one of the most important methods for forming sp^2–sp^2 carbon–carbon bonds both in modern synthetic chemistry and in industrial application.[1] In the past few years, attempts have been devoted to the development of new soluble Pd complexes as highly active catalyst for this reaction.[2] In general, the presence of specific ligands, such as electron-rich and sterically-demanding phosphines, are necessary to promote the reaction with the less reactive aryl chlorides and electron-rich aryl bromides.[2] Regarding industrial applications, however, these ligands and Pd precursors are expensive. Homogeneous catalyst is generally connected with the problem of separation and wasted inorganics which are too difficult to reuse. In addition, deactivation of the soluble palladium complex catalysts by forming inactive metal particles is often encountered at high reaction temperature. These problems could be principally minimized by a heterogeneously catalyzed Suzuki reaction. To overcome these problems, heterogeneous palladium catalysts such as palladium complexes immobilized on polymer[3] or inorganic supports[4] have been developed. However, a large amount of the catalysts were required for these heterogeneous catalytic systems, whose turnover numbers were several orders of magnitude lower than those of the homogeneous catalysts, and these aspects limit industrial application of Suzuki reaction.

Sepiolite is a fibrous natural clay mineral with ideal formula of $Mg_8Si_{12}O_{30}(OH)_4 \cdot 4H_2O \cdot nH_2O$. Its structure is formed of talc-like ribbons arranged in such a way that tetrahedral sheet is continuous but inverts in apical directions in adjacent ribbons, generating uniform size parallel-piped intracrystalline tunnels (10.8×4.0 Å) along the fibre.[5] The magnesium ion on the tunnel wall can be substituted with various transition metal ions[6] which can act as the catalytic active site.[7] Here, we report a novel heterogeneous palladium catalyst, palladium(II) supported on the sepiolite clay, as a highly active and stable catalyst for Suzuki cross-coupling reaction of aryl bromides (Scheme 1).

The preparation method of the catalyst is simple. According to our previous report,[8] natural sepiolite (Konan, China) was treated with dilute HCl aqueous solution (0.59 mol dm^{-3}) to eliminate impurities (calcite and dolomite) without a decomposition of sepiolite itself. The Pd^{2+}-complex immobilized catalyst (Pd^{2+}-sepiolite) was prepared by exchanging the sepiolite with aqueous solution of $[Pd(NH_3)_4]Cl_2$ at 298 K for 48 h,



Scheme 1.

Keywords: Suzuki reaction; palladium catalysts; sepiolite.

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PII: S0040-4039(02)01132-2

followed by centrifuging and washing with deionized water, and subsequently drying in vacuo at 298 K. The metal content of the catalyst (0.18 wt%) was determined using ICP. XRD patterns of the catalysts were essentially the same as that of sepiolite. The surface area of Pd^{2+}-sepiolite (240 m^2 g^{-1} by BET method) was very close to that of the original sepiolite (248 m^2 g^{-1}). These results suggest that the palladium complex is immobilized on the surface of sepiolite, without changing tunnel structure of sepiolite.

The catalyst was tested for the cross-coupling between aryl halide and phenylboronic acid (Scheme 1). Typically, the reaction was carried out by stirring the reaction mixture containing aryl halide (2.5 mmol), phenylboronic acid (3.7 mmol), potassium carbonate (5 mmol) and the catalyst (0.5 μmol of Pd) in DMF (5 cm^3) at 100°C under N_2. As shown in Table 1, the Pd^{2+}-sepiolite catalyzed the Suzuki cross-coupling reaction of an aryl iodide or aryl bromides with various substituents and provided the corresponding coupling products in excellent yields using a small amount of the catalyst (0.02 mol%). As expected, aryl chloride was most inactive (entry 8). Variation of the substituents in the aryl bromides was also tested. Electron-donating and electron-withdrawing substituents were both well tolerated by the catalytic system and the coupling products were obtained in excellent yields. However, the initial rate of the reaction depended on the substituents; the 'non-activated' substrate (entry 2) and 'deactivated' (electron-rich) substrates, such as 4-bromoaniline and 4-bromoanisole (entries 3–5) gave better initial rates than the 'activated' (electron-poor) substrates (entries 6 and 7). This reactivity tendency is in contrast to that generally observed for palladium-catalyzed cross-coupling reactions,[9] which suggests that the rate-determining step in the Suzuki reaction of aryl bromides on Pd^{2+}-sepiolite is not the oxidative addition of aryl halides to the palladium catalyst.

We performed the leaching test for the reaction of 4-bromoanisole at 100°C; when the solid catalyst was removed before a completion of the reaction (reaction time = 1 h), the reaction did not proceed any further. This proves heterogeneous catalytic activity of Pd^{2+}-sepiolite and no contribution from homogenous catalysis. The catalyst could be easily separated from the reaction mixture by simple filtration and recycled without loosing its activity in the reaction of 4-bromoanisole (entry 4). For a comparison, commercially available palladium catalyst (Pd/C) was also tested for this reaction. Compared to Pd^{2+}-sepiolite (entry 4), Pd/C showed lower yield and significantly lower TOF (entry 12). Palladium acetate in bulk solution (entry 13), i.e. homogeneous catalysis, gave higher initial rate (TOF) than Pd^{2+}-sepiolite, but resulted in a lower yield after 24 h than that of Pd^{2+}-sepiolite.

To evaluate the durability of the Pd^{2+}-sepiolite catalyst, we have examined the Suzuki reaction of several aryl bromides with low catalysts concentration (entries 9–11). In the cross-coupling of bromobenzene at 130°C, a yield of 39% was obtained after 1 h with 0.001 mol% of palladium, corresponding to TOF value of 39000 h^{-1}. After 24 h, the reaction proceeded in 65% yield (TON = 65000). As for 4-bromoanisole and 4-bromoacetophenone, under the same reaction conditions, the products were obtained after 24 h in yields of 56 and 94%, respectively, corresponding to TONs of 56000 and 94000, respectively. To the best of our knowledge, these are the highest activities for the heterogeneously catalyzed Suzuki cross-coupling of aryl bromides.

Table 1. Reactions of aryl halides with phenylboronic acid over Pd^{2+}-sepiolite catalyst[a]

Entry	Substrate	T (°C)	Yield (%)[b]	TON[c]	TOF[d] (h^{-1})
1	C_6H_5I	100	80	4000	1595
2	C_6H_5Br	100	81	4050	2098
3	4-$NH_2C_6H_4Br$	100	77	3850	2380
4	4-$MeOC_6H_4Br$	100	85 (84)[e]	4250	1633
5	3-ClC_6H_4Br	100	91	4550	1532
6	4-$CH_3COC_6H_4Br$	100	83	4150	819
7	4-$NO_2C_6H_4Br$	100	91	4550	1033
8[f]	4-$CH_3COC_6H_4Cl$	100	23	230	63
9[g]	C_6H_5Br	130	65	65000	39000
10[g]	4-$MeOC_6H_4Br$	130	56	56000	9292
11[g]	4-$CH_3COC_6H_4Br$	130	94	94000	7163
12 (Pd/C)[h]	4-$MeOC_6H_4Br$	100	40	2000	74
13 ($Pd(OAc)_2$)[i]	4-$MeOC_6H_4Br$	100	44	2200	1987

[a] *Reaction conditions*: aryl halide (2.5 mmol), phenylboronic acid (3.7 mmol), K_2CO_3 (5 mmol), catalyst (0.5 μmol of Pd), DMF (5 cm^3).

[b] GC yield using benzonitrile as internal standard after 20–24 h.

[c] TON = (mol of product/mol of catalyst).

[d] Turnover-frequency calculated at reaction time of 1 h.

[e] Cycle 2.

[f] Amount of the catalyst was 2.5 μmol of Pd.

[g] *Reaction conditions*: aryl halide (25 mmol), phenylboronic acid (37 mmol), K_2CO_3 (50 mmol), catalyst (0.25 μmol of Pd), DMF (25 cm^3).

[h] Pd/C catalyst (Pd = 0.5 wt%) was used.

[i] Palladium(II) acetate was used as homogeneous catalyst.

In conclusion, the cross-coupling of aryl bromides with phenylboronic acid are efficiently catalyzed by Pd^{2+}-sepiolite prepared by simple ion-exchanging. This novel catalyst provides clean and convenient alternative for Suzuki reaction in view of the following advantages: (1) higher TON than previously reported heterogeneous Pd catalysts, (2) simple reaction procedures and (3) low-cost, waste-minimizing and recyclable catalyst.

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