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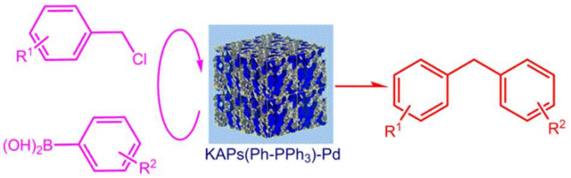

Microporous polymers with built-in triphenylphosphine palladium exhibit highly efficient catalytic activity for cross-coupling reactions of benzyl chloride under mild conditions.

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A highly efficient catalyst for Suzuki–Miyaura Coupling Reaction of Benzyl chloride under mild conditions

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Diarylmethane derivatives, essential building blocks in organic synthesis, are usually synthesized through the traditional electrophilic substitution reaction i.e., Friedel-Crafts reaction, which suffers from the rearrangement and weak reactivity of aromatic compounds with deactivating/electron-withdrawing groups. The Suzuki–Miyaura coupling reaction of low-cost benzyl chloride as an alternative method overcomes these defects. Pd(II) organometallic catalysts immobilized on the triphenylphosphine-functionalized microporous knitting aryl polymer (KAPs(Ph-PPh_3)-Pd) as a novel heterogeneous catalyst was employed in Suzuki–Miyaura coupling reaction of benzyl chloride and exhibited excellent catalytic activity under mild conditions with a turnover frequency (TOF) up to 76 min^{-1} (4569 h^{-1}). This work enlightens that the microporous structure of catalyst can rapidly adsorb substrates, consequently facilitate their interaction, and eventually promote the catalytic efficiency.

Introduction

Diarylmethane derivatives are fundamental building blocks in organic synthesis and their preparation is an important industrial goal. They have been exploited to produce biologically active compounds,[1, 2] polybenzyls[3, 4] as well as build blocks in organic synthesis,[5-7] and usually can be obtained through the traditional electrophilic substitution reaction, i.e., Friedel-Crafts reaction. But the weak reactivity of the aromatic compounds containing electron-withdrawing groups and the tendency of alkyl/aryl halides to rearrange seriously limit industrial applications.[6, 8, 9] Hence, the replacement of this method by so-call Suzuki-Miyaura cross-coupling reaction employing a benzyl halide could be highly beneficial to overcome these problems, benefitting from the use of less toxic materials, boronic acids and esters, mild and operationally easy reaction conditions, tolerance to many functional groups and its suitability for sterically hindered substrates, especially high efficiency and selectivity of Suzuki-Miyaura cross-coupling reaction with palladium catalysts.

Up to now, many types of homogeneous catalysts have been used for coupling reactions of benzyl halides, including palladium chloride[10] and palladium complexes with phosphine,[11-19] N-heterocyclic carbene,[20-23] oxime,[24-26] acetonitrile,[27] N-based ligands[28-31] and Nickel complex[32] etc. These reactions were carried out in a mixture of an organic solvent and an aqueous inorganic base at room temperature to 130 °C, with Pd loading of 0.1-10 mol%, frequently in the presence of substoichiometric amounts of TBAB and good to excellent yields were obtained. Monteiro and co-workers[12] demonstrated that $Pd(PPh_3)(OAc)_2$ showed high activity for the coupling of benzyl bromides and chlorides with aryl boronic acids, at low catalyst loading (1 mol%) and mild conditions (80 °C) for 19 h (not optimized) furnishing diarylmethane derivatives in high yields (86-99%). More recently, Lo and Lam[25] developed a new strategy to enhance the efficiency of coupling reaction by microwave irradiation using a fluoro oxime-based palladacycle catalyst. The catalyst gave 92% yield of diphenylmethane within 3.5 min at 140 °C in the coupling of benzyl chloride and phenylboronic acid, and its polymer-supported analogue showed a low yield (86%) at 100 °C, thus necessitating longer time to get the high product yield. The heterogeneous catalytic systems for this reaction were, however, not much demonstrated yet.[12-16] Corma and co-workers[33] anchored the oxime carbapalladacycle complex on SiO_2, polystyrene (PS), poly ethylene glycol bis(methacrylate) (PEA) and MCM-41, and PdL@SiO_2 gave 99% yield of product in the presence of 5 mol % Pd, in water at reflux temperature. Reusability of the PdL@SiO_2 catalyst was investigated using 4-chloroacetophenone and phenylboronic acid as substrates without any significant change in the reactivity and selectivity after 7 cycles. Later, Nájera[34] performed the reaction using a polymer-bound palladacycle derived from Kaiser oxime resin as a pre-catalyst and the catalyst was recovered by filtration and reused for 3-9 cycles with up to 5% of Pd leaching in each run. Yang synthesized bulky N-heterocyclic carbene (NHC) precursor in the framework of several hybrid materials: SBA-

16,[35] mesoporous ethane-silica[36] and core-shell-structured nanoporous organosilica microspheres.[37] Apparently, in these catalysis systems, to obtain a high yield, a relatively long time and high temperature were required. The low dispersion and protection for palladium by meso- or macro-pores were believed to be one of the reasons for low reaction rate. For this reason, there is still a need to find a method and strategy to prepare a new solid catalyst so as to overcome these limitations. Zeolites, silicas, and activated carbon have been extensively employed as heterogeneous catalysts given their high surface areas and substantial porous structure, however, there still are limits due to their inorganic chemical structure. Zeolites, silicas, activated carbon with monotonous micropore (pore sizes <2 nm) are not suitable for free diffusion of reaction substrate and product.[38] Their inorganic crystal structures rigidify the micropore size and pore volume, and stop the solvent swell the materials. Although mesoporous or macroporous aluminosilicate and zeolites are developed to settle the diffusion puzzle of microporous analogue, they tend to decompose in acidic and basic circumstance, especially for long reaction time or under hydrothermal condition. The post-modification of porous inorganic materials as universal method to graft ligand tend to block pores and the low ligand loading is another defect. Besides, most porous inorganic materials are used in organic catalysis system, result in weak affinity in the interface between catalyst and reaction substrate.[39] Comparing to inorganic porous materials, porous organic polymers (POPs)[40, 41] with high surface area have several merits. (i) Most of MOPs are stable in acidic and basic environment.[42, 43] (ii) The porous size of POPs is adjustable[44, 45] and amorphous POPs can swell in solvent,[43, 46] which are favourable for mass transfer. (iii) The particular advantage of POPs is to introduce a broad range of useful chemical functionalities within the porous framework by one-step.[47] The introduction of Tröger's base into conjugated microporous polymers (CMPs) for heterogeneous catalysis is an early example in this regard.[48] The use of metal-organic CMPs has been demonstrated for heterogeneous catalysis,[49] and highly stable and porous cross-linked polymers are reported as efficient photocatalysts.[50] In addition, microporous phthalocyanine polymer with metal ions[51-53] and covalent organic frameworks (COFs) with palladium catalyst[54] have also been studied for heterogeneous catalysis reactions. Previously, we have proposed a low-cost strategy to synthesize high surface area microporous knitting aryl network polymers (KAPs) via one-step 'knitting' of rigid aromatic compounds with an external crosslinker.[55] Successively, we have knitted PPh_3 with benzene to get functionalized KAPs(Ph-PPh_3) and bonded Pd with PPh_3 groups to form KAPs(Ph-PPh_3)-Pd which exhibited excellent catalyst activity in Suzuki-Miyaura coupling reactions of aryl chlorides in aqueous media. It illuminated that microporous polymers could not only play the role of support materials, but also protect the metal catalyst and positively affect the catalytic activity.[56] Herein, aiming to obtain highly reactive activity toward the Suzuki-Miyaura coupling of the challenging benzyl chlorides and overcome the negative effect of electron-withdrawing groups, KAPs(Ph-PPh_3)-Pd was employed as heterogeneous catalyst in this work. Strikingly, it enables cross-coupling reactions of benzyl chloride in an ethanol solution quickly (5 min) under mild conditions (80 °C) with a turnover frequency (TOF) of up to 76 min^{-1}.

Experimental Section

Materials. Benzene, triphenylphosphine, $PdCl_2$, $FeCl_3$ (anhydrous), methanol 1,2-dichloroethane (DCE), and acetonitrile were obtained from National Medicines Corporation Ltd. of China, all of which were of analytical grade and were used as received. Formaldehyde dimethyl acetal (FDA, Alfa Aesar, 98 %) was also used as received.

Synthesis of KAPs(Ph-PPh_3).[56] $FeCl_3$ (anhydrous 9.75 g, 0.06 mol) was added to a solution of benzene (1.56 g, 0.02 mol), triphenylphosphine (5.25 g, 0.02 mol) and FDA (4.56 g, 0.06 mol) in 20 ml DCE. The resulting mixture was efficiently stirred initially at room temperature and then at 45 °C for 5 h to form original network, and then heated at 80 °C for 67 h to react completely. The resulting precipitates were washed 3 times with methanol, then washed with methanol in a Soxhlet for 24 h, and finally dried under reduced pressure at 60 °C for 24 h. Elemental analysis: C, 82.75; H, 5.67; P, 1.90.

Preparation of KAPs(Ph-PPh_3)-Pd catalyst.[56] The Pd (II) organometallic catalyst immobilized on the KAPs(Ph-PPh_3) support was prepared by coordinating Pd (II) ions with the PPh_3 ligand. Briefly, 1.0 g KAPs(Ph-PPh_3) was added to 20 ml acetonitrile solution containing 0.10 g $PdCl_2$ and stirred under reflux at 80 °C for 12 h. The solid was separated by centrifugation, washed repeatedly with acetone, followed by Soxhlet-extraction with acetone to remove physisorbed Pd (II) species. The final catalyst was dried at 60 °C under vacuum and the as-prepared catalysts were denoted as KAPs(Ph-PPh_3)-Pd. Pd, 0.7 wt% (0.066 mmol/g).

Preparation of MCM-41-PPh_2.[57] The mesoporous material MCM-41 (0.5 g) was treated with ligand $(EtO)_3SiCH_2CH_2CH_2PPh_2$ (0.5 g) in toluene (20 mL) in the presence of pyridine (0.5 mL) at reflux under N_2 atmosphere for 24 h. The mixture was slowly cooled to room temperature, and then the precipitated white solid was isolated by a filtration, washed with methanol and acetone successively, and dried at 80 °C under vacuum for 8 h. The mesoporous material MCM-PPh_2 was eventually obtained as white solid powders.

Preparation of MCM-41-PPh_2-Pd.[57] 1.0 g MCM-PPh_2 was added to 20 ml acetonitrile solution containing 0.10 g $PdCl_2$ and stirred under reflux at 80 °C for 12 h. The solid was separated by centrifugation, washed repeatedly with acetone, followed by Soxhlet-extraction with acetone to remove physisorbed Pd (II) species. The final catalyst was dried at 60 °C under vacuum and the as-prepared catalysts were denoted as MCM-PPh_2-Pd. Pd, 0.5 wt% (0.047 mmol/g).

Typical procedure for the coupling reaction. The coupling reactions were carried out at 80 °C in a 10 ml reactor under air or nitrogen atmosphere. In a typical run, a catalyst containing 0.26 mol % Pd, 0.5 mmol benzyl chloride, 0.75 mmol phenylboronic acid and 1.5 mmol base were added to 2 ml solvent and allowed to react for a definite time. Then the mixture was separated quickly by centrifugation. The solid was extracted with copious ethyl acetate and the liquid was concentrated. The product was obtained by preparative TLC. Purity of products was checked by NMR and yields are based on benzyl chlorides.

Catalyst durability. The KAPs(Ph-PPh_3)-Pd catalyst was allowed to settle down after each run of reactions and the clear supernatant liquid was decanted slowly. After washing with acetone as well as water, and drying under vacuum at 60 °C, the catalyst was re-used with fresh charge of solvent and reactant for subsequent reaction under the same conditions. The content of Pd species leached off from the heterogeneous catalyst was determined by AAS analysis.

Characterization. Polymer surface areas, N_2 adsorption isotherm (77.3 K) and pore size distributions were measured using Micromeritics ASAP 2020M surface area and porosity analyzer. Before analysis, the samples were degassed at 110 °C for 8 h under vacuum (10^{-5} bar). Elemental analyses (EA) were performed on a Vario Micro cube Elemental Analyzer (Elementar, Germany). Pd content data were obtained on Perkin Elmer AA-800 (USA). The XPS analysis was carried out with a VG Multilab 2000 spectrometer using Al Kα radiation at a power of 300 W. The pass energy was set at 100 eV, and C_{1s} line at 284.6 eV was used as a reference. Adsorption capacities of benzyl chloride and phenyl boronic acid were calculated by UV data (SHIMADZU UV-2550 spectrophotometer, Japan).

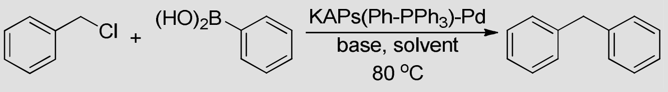
Results and Discussion

KAPs(Ph-PPh_3) and KAPs(Ph-PPh_3)-Pd were synthesized as previous method. [56] The BET surface area of KAPs(Ph-PPh_3) is 1036 m^2/g, while that of KAPs(Ph-PPh_3)-Pd is 1025 m^2/g. As shown in Figure S1 and S3, the adsorption and desorption isotherms of KAPs(Ph-PPh_3) and KAPs(Ph-PPh_3)-Pd are similar. The adsorption isotherms present a steep nitrogen gas uptake at low relative pressure ($P/P_0 < 0.001$) reflecting abundant micropore structure, a slight hysteresis loop implying a spot of mesopore and a sharp rise at medium and high pressure regions (P/P_0 = 0.8-1.0) indicating the presence of macropores in these materials. The pore size distribution of KAPs(Ph-PPh_3) and KAPs(Ph-PPh_3)-Pd (Figure S2 and S4) also confirms the presence of such heterogeneous porous structure which is favourable for catalysis process, as the macroporous structure accelerates the mass diffusion of reactants and products, and micropore of suitable size is beneficial for anchoring and protecting metal catalysts. XPS spectroscopy was employed to analyze the elemental compositions of the surface and coordination states of Pd species. In Figure S5, an XPS study of KAPs(Ph-PPh_3)-Pd derived from $PdCl_2$ reveals that C, P, Cl and Pd elements exist in the KAPs(Ph-PPh_3)-Pd. The XPS spectra in Figure S6 reveals that Pd species in the KAPs(Ph-PPh_3)-Pd are in +2 oxidation state rather than in metallic state, corresponding to the binding energy (B.E.) of 337.7 eV and 342.8 eV in the Pd $3d_{5/2}$ and $3d_{3/2}$ levels respectively. In comparison with the $PdCl_2$ (338.0 and 343.2 eV), the Pd^{II} binding energy in the KAPs(Ph-PPh_3)-Pd shifts negatively by 0.3 eV, because of the strong electron-donation of the Ph-PPh_3 network. These results demonstrate that the Pd^{II} is successfully immobilized on the KAPs(Ph-PPh_3) by coordination to PPh_3 functional groups rather than by physical adsorption of $PdCl_2$ on the surface.

In initial catalytic reaction attempt, a set of experiments were carried out in order to establish the best reaction conditions: solvent, base and temperature for the Suzuki-Miyaura cross-coupling of benzyl chloride and phenylboronic acid as a reaction model (Table 1). Our preliminary screening of solvent revealed that the presence of alcohol could efficiently promote the reaction, and in our previous study in Suzuki-Miyaura cross-coupling reaction of various aryl halides and arylboronic acids, the addition of water to the solvent could speed up the conversion of the substrate to some extent[58]. Thus, we tried mixture of water and ethanol in different ratio and ultimately, the best optimal conditions were achieved using K_2CO_3 as a base and ethanol as the reaction medium (Entries 1-10). Further studies indicated that Cs_2CO_3, Na_2CO_3, $NaOAc{\cdot}3H_2O$, KOAc, NaOH, KOH and $Na_3PO_4{\cdot}12H_2O$ were poor bases for this reaction (Entries 10-17). NaOH and KOH gave extremely poor yields, because of the dehalogenation of benzyl chloride under basic condition. Remarkably, when $K_3PO_4{\cdot}3H_2O$ was used (Entry 18), excellent yield (99%) of diphenylmethane was obtained within 5 min at 80 °C. Besides, when reducing the reaction temperature to 60 °C, yield (91%) was obtained, but the reaction took a bit longer i.e., 15 min (Entry 19). Lowering the reaction temperature to room temperature, the catalyst activity was reduced accordingly leading to lesser products yield (33%), even after letting the reaction to proceed for 30 min (Entry 20). A reaction in 10 mmol scale was also carried out, and it was found that the reaction proceeded successfully, indicating the effectiveness of this catalyst for large-scale synthesis (Entry 21). Thus, reaction conditions (ethanol as solvent, $K_3PO_4{\cdot}3H_2O$ as base, 80 °C, 5 min in air, without any additives) were defined as the optimal set of conditions for the reaction. In several mesoporous materials supported NHC-Pd catalyst,[35-37] using isopropyl alcohol as solvent and KO*t*-Bu as base, 75-88% yields were obtained within 8-12 h. Our catalyst, however, resulted in rapid reaction under mild conditions.

Under optimized conditions, we investigated the activity of KAPs(Ph-PPh_3)-Pd for various substrates. The corresponding results are summarized in Table 2. The coupling of benzyl chloride and arylboronic acid were first examined. It is worth to note that the turnover frequency (TOF) reached *ca.* 76 min^{-1} in the case of benzyl chloride and phenyl boronic acid, which is much higher than the highest TOF (17 min^{-1}) for heterogeneous catalytic system reported so far.[34] This solid catalyst yielded 4-methyl (99%), 2-methyl (80%) and 4-methoxyl (93%) diphenylmethane within 10 min, with a TOF of 38 min^{-1}, 31 min^{-1} and 36 min^{-1}, respectively (Entries 2-4). To our delight, even deactivated arylboronic acids i.e., 2,6-dimethylphenylboronic acid and 2-naphthalenylboronic acid with sterically hindered groups resulted in product yields of 73% and 80% respectively (Entry 5 and 6). For arylboronic acid bearing an electron-withdrawing group, good to excellent yields were obtained. As high as about 90% yields were obtained for para $-COOCH_3$ and $-OCF_3$ substituted phenylboronic acid (Entries 7 and 8). Remarkably, substrate with the strong electron-withdrawing group, i.e., 4-trifluoromethylphenylboronic acid and 3,5-difluorophenylboronic acid also gave near quantitative yield (90% and 92%) within 10 min and 20 min (Entry 9 and 10), which was impossible by Friedel-Crafts reaction of aromatic substrates with benzyl chloride. Obviously, KAPs(Ph-PPh_3)-Pd had a good tolerance toward the substituents on arylboronic acids under these conditions. We further tested the catalytic performance for the couplings of various benzylic chlorides with phenylboronic acid (Entry 11-14). For benzylic chlorides bearing electron donating groups $-CH_3$ (Entry 11) and $-CH(C_2H_6)$ (Entry 12), the catalyst afforded fast conversion in 10 min and 94% and 99% yields were obtained, respectively. Otherwise, when using a weak electron-withdrawing group substituted benzyl chloride (Entry 13), reactions proceeded slowly (60 min), but very smoothly and 90% yield was obtained under these conditions. Under the optimised conditions, the recycling ability of the catalyst was also studied. As shown in Table S1, the catalyst showed a good recyclibilty in the first run to the third run, up to 95%. In the fourth run, the catalyst activity was reduced to 84 % by increasing the reaction time to 20 min. 4.86 % of Pd leaching was observed after the fourth run.

Table 1. Optimization of reaction conditions[a]

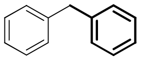
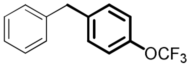
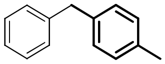
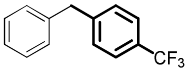
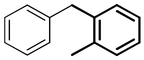
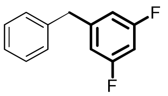
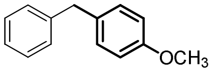
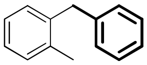
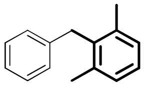
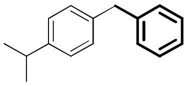
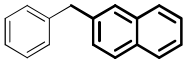
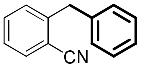
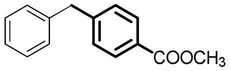
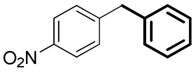


Entry	Solvent	Base	Yield[%][b]
1	1,4-dioxane	K_2CO_3	22
2	PhMe	K_2CO_3	29
3	H_2O	K_2CO_3	49
4	MeOH	K_2CO_3	74
5	i-PrOH	K_2CO_3	62
6	EtOH	K_2CO_3	90
7	EtOH:H_2O =1:4	K_2CO_3	76
8	EtOH:H_2O =2:3	K_2CO_3	85
9	EtOH:H_2O =3:2	K_2CO_3	78
10	EtOH:H_2O =4:1	K_2CO_3	74
11	EtOH	Cs_2CO_3	30
12	EtOH	Na_2CO_3	45
13	EtOH	$NaOAc\cdot 3H_2O$	12
14	EtOH	KOAc	21
15	EtOH	NaOH	46
16	EtOH	KOH	67
17	EtOH	$Na_3PO_4\cdot 12H_2O$	74
18	EtOH	$K_3PO_4\cdot 3H_2O$	>99
19	EtOH	$K_3PO_4\cdot 3H_2O$	91[c]
20	EtOH	$K_3PO_4\cdot 3H_2O$	33[d]
21	EtOH	$K_3PO_4\cdot 3H_2O$	92[e]

[a] Reaction conditions: 0.26 mol% of Pd, 0.5 mmol of benzyl chloride, 0.75 mmol of phenyl boronic acid, 1 mmol of base, 2 ml of solvent (*v*/*v*), 80 °C, 5 min, in air. [b] Isolated yield. [c] 60 °C, 15 min. [d] Room temperature, 30 min. [e] 10 mmol scale.

For the substrate with a strong electron-withdrawing group substituted 4-nitrobenzyl chloride (Entry 14), the catalyst gave trace of the target product, which aroused our great interest. In Suzuki-Miyaura coupling reaction,[59-61] the rate determining step is the oxidative addition of benzyl chloride. Electron donating groups in benzyl chlorides can promote the oxidative addition and consequently accelerate the reaction rate. When the benzyl chlorides contain electron-withdrawing groups, the rate of reaction become slower, which implies that the oxidative addition is no longer the rate determing step,[62, 63] and meanwhile the dehalogenation reaction become dominant competitive reaction. Ethanol as a hydrogen donor tends to aggravate the dehalogenation reaction under this situation.[64, 65] Therefore, we considered non-protic solvent instead of protic solvent to inhibit the dehalogenation reaction. The solvents were screened for the model reaction of 4-nitrobenzyl chloride with phenylboronic acid under inert atmosphere to avoid phenylboronic acid deboronation homocoupling reaction in presence of oxygen under this condition,[66] the results of which are shown in Table 3. Solvent effect on the activity of KAPs(Ph-PPh$_3$)-Pd was initially examined with different ether solvents and similar results were obtained under the same conditions (Entries 1-4). Reactions in anisole, 1,4-dioxane, furanidine and glycol dimethyl ether gave 35%, 77%, 46% and 27% yields respectively. Then the reaction was conducted in acetonitrile and 50% yield was obtained (Entry 5). Toluene was found to be the best solvent and complete conversion to 4-nitrobenzylbenzene was achieved within 30 min (Entry 6 and 7). Impressively, substrate with stronger electron-withdrawing group –F which gave trace of the coupling product also proceeded smoothly (Figure 1, 94%), indicating the effectiveness of this strategy for such substrates.

Table 2. Suzuki–Miyaura cross-coupling reaction catalyzed by KAPs(Ph-PPh$_3$)-Pd[a]

Entry	Product	Entry	Product
1	 5 min, yield 99%, TOF 76 min^{-1}	8	 15 min, yield 84%, TOF 22 min^{-1}
2	 10 min, yield 99%, TOF 38 min^{-1}	9	 10 min, yield 90%, TOF 35 min^{-1}
3	 10 min, yield 80%, TOF 31 min^{-1}	10	 20 min, yield 92%, TOF 18 min^{-1}
4	 10 min, yield 93%, TOF 36 min^{-1}	11	 10 min, yield 94%, TOF 36 min^{-1}
5	 15 min, yield 73%, TOF 19 min^{-1}	12	 10 min, yield 99%, TOF 38 min^{-1}
6	 10 min, yield 80%, TOF 31 min^{-1}	13	 60 min, yield 90%, TOF 6 min^{-1}
7[b]	 30 min, yield 89%, TOF 11 min^{-1}	14	 trace

[a] Reaction conditions: 0.26 mol% of Pd, 0.5 mmol of benzylic chloride, 0.75 mmol of arylboronic acid, 1 mmol of $K_3PO_4\cdot 3H_2O$, 2 ml of EtOH, 80 °C, in air; Isolated yield; mol product/mol Pd·min. [b] Methanol as the solvent.

To understand the reason for the high activity of this catalyst in such reactions and the role of porous polymer supported in catalysis, we measured the catalytic reaction activity, adsorption kinetics of benzyl chloride and phenyl boronic acid on KAPs(Ph-PPh$_3$)-Pd, as well as MCM-41 loaded PPh$_2$-Pd (MCM-41-PPh$_2$-Pd) for comparison (Figure 2). The surface area of these two kinds of materials were similar, while material were different, for MCM-41-PPh$_2$-Pd (996 m^2/g) possessed regular mesoporous structure and uniform pore diameter (3.9 nm), and KAPs(Ph-PPh$_3$)-Pd (1025 m^2/g) was comprised of abundant micropores. MCM-41-PPh$_2$-Pd which had excellent catalytic activity in Suzuki-Miyaura cross-coupling reaction of iodobenzene or bromobenzene with phenyl boronic acid (yields are 99% and 98%, respectively) afforded only 7% yields of diphenylmethane under the optimised condition when employing benzyl chloride. Under the similar conditions, we found that benzyl chloride in the reaction can be rapidly adsorbed on KAPs(Ph-PPh$_3$)-Pd and adsorption content reached 2.8 g/g within 2 min because of its high surface area and greater affinity for the substrate. Although MCM-41-PPh$_2$-Pd had similar surface area, the adsorption capacity was only 1.5 g/g. Evidently, in adsorption kinetics of benzyl chloride both the two catalysts gave the similar adsorption rate and reached saturation within 1 min, but with different adsorption capacity. These two kinds of catalyst exhibited discrepancy in the Suzuki-Miyaura cross-coupling of benzyl chloride and phenyl boronic acid under the similar conditions, and the product yield was in accordance to their adsorption characters.[67] Reactants in these coupling reactions can be remarkably adsorbed on KAP(Ph-PPh$_3$)-Pd because of their better affinity with the organic framework of the catalyst. The increase of the reactant concentration in the catalyst leads to an enhancement of the activity, which is in good agreement with the reactant enrichment and their improved rate of reaction in carbon nanotube catalysts.[68]

Table 3. The effect of solvents for nitrobenzyl chloride and phenyl boronic acid.[a]

Entry	Solvent	Time [min]	Yield [%][b]
1	Anisole	60	35
2	1,4-Dioxane	60	77
3	Furanidine	60	46
4	Glycol dimethyl ether	60	27
5	Acetonitrile	60	50
6	Toluene	60	99(65)[c]
7	Toluene	30	99

[a] Reaction conditions: 0.26 mol% of Pd, 0.5 mmol of 4-nitrobenzyl chloride, 0.75 mmol of phenyl boronic acid, 1 mmol of $K_3PO_4 \cdot 3H_2O$, 2 ml of solvent, 80 °C, under N_2 atmosphere. [b] Isolated yield. [c] The result in air in parenthesis.

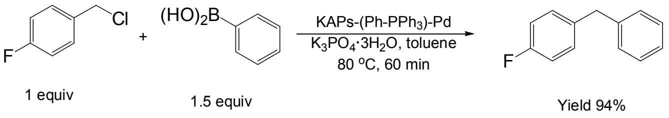


Figure 1. Suzuki–Miyaura cross-coupling under new conditions.

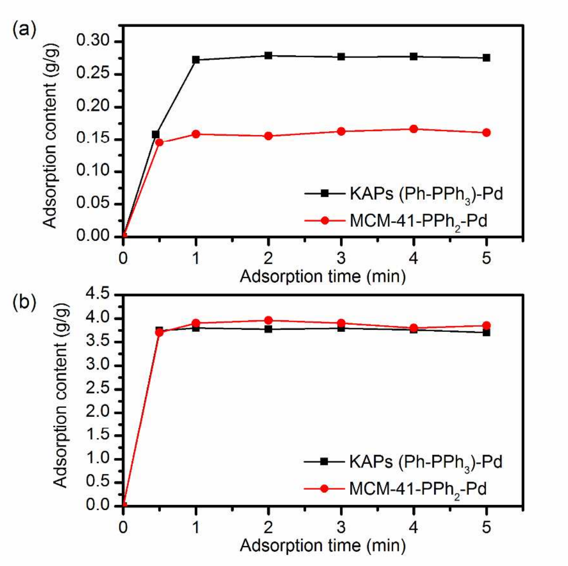


Figure 2. Adsorption kinetics of benzyl chloride (a) and phenyl boronic acid (b) on KAPs(Ph-PPh$_3$)-Pd and MCM-41-PPh$_2$-Pd.

Conclusion

To summarise, we report Pd(II) organometallic catalysts immobilized on the triphenylphosphine functionalized KAPs(Ph-PPh$_3$) as a highly efficient catalyst which enables cross-coupling reactions of benzyl chloride in an ethanol with a turnover frequency (TOF) of up to 76 min^{-1} and highly tolerance towards electrophilic substituted substrates. This work also demonstrates that the microporous polymers possess higher affinity with organic reactants compared to traditional inorganic porous materials, which positively affect their catalytic activity. We expect that this low-cost heterogeneous catalyst can be eventually useful for Suzuki-Miyaura cross-coupling reactions of benzyl chloride at industrial scale.

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