

负载型钯催化剂用于氯代芳烃 Suzuki 交叉偶联反应的研究进展

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摘 要: Suzuki 交叉偶联反应是一类典型的形成碳-碳单键的反应, 是以金属钯(Pd)为催化剂, 卤代芳烃与有机硼酸化合物进行的交叉偶联反应. 相对于传统仅用价廉易得的氯代芳烃化合物为反应原料的 Suzuki 交叉偶联反应, 负载型 Pd 催化剂有着催化高效、分离简便、可重复使用等优点. 简述了不同载体负载的 Pd 催化剂对于氯代芳烃的 Suzuki 交叉偶联反应的研究进展.

关键词: 负载型钯(Pd)催化剂; 氯代芳烃; Suzuki 交叉偶联

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Research progress of supported palladium catalysts for Suzuki cross-coupling reaction of aryl chlorides

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Abstract: The palladium(Pd)-catalyzed cross-coupling reaction between organic boronic acids and aryl halides provides a powerful and general method for the formation of carbon-carbon bonds known as the Suzuki cross-coupling. It was found that with the cheap and commercially available aryl chlorides as reactants, the supported Pd catalysts exhibited high efficiency, easy separation, and reusability. This review describes some research progresses of the supported Pd catalysts for Suzuki cross-coupling reaction of aryl chlorides.

Key words: supported palladium(Pd) catalyst; aryl chlorides; Suzuki cross-coupling

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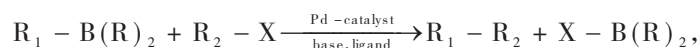
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0 引言

碳-碳偶联反应在有机合成中占有重要的地位,其中Suzuki交叉偶联反应是构建碳-碳单键最有效和最灵活的方法之一^[1-2].1979年,MIYAURA等^[3]报道了钯(Pd)催化剂条件下卤代芳烃与苯硼酸的合成反应^[3].Suzuki交叉偶联反应通常是指卤代芳烃与有机硼酸试剂进行的交叉偶联,芳烃上的取代基通常是卤素,也可以是三氟甲基磺酸基和甲基磺酸基等,有机硼试剂的优点是无毒,对空气稳定而且易得,同时兼容反应物上共存的多种官能团,因此被广泛应用于制药、催化、高分子和先进材料等领域^[4].Suzuki交叉偶联反应的反应通式如下:



其中, R_1 :alkyl, allyl, alkenyl, alkynyl, aryl; R :alkyl, OH, O-alkyl; R_2 :alkenyl, aryl, alkyl; X :Cl, Br, I, OTf, OPO(OR)₂(enol phosphate);base: Na_2CO_3 , $Ba(OH)_2$, K_3PO_4 , Cs_2CO_3 , K_2CO_3 , KF, Bu_4F , NaOH.

尽管具有合成简易和高转化率的特点,但Suzuki交叉偶联反应仍因为使用昂贵的溴代和碘代芳烃而严重受限,从而无法在工业上广泛使用^[5].由于氯代芳烃具有廉价和易得等优点,在过去的十几年中,对Suzuki交叉偶联反应的研究一直集中在使用氯代芳烃作为偶联底物^[6].另一方面,由于氯代芳烃的C-Cl键能比较大,Pd作为催化剂不容易插入C-Cl之间进行氧化加成,这在一定程度上限制了氯代芳烃在Suzuki交叉偶联反应的发展.在这一领域中,均相Pd催化剂已经取得了很大进展,均相催化剂具有分散性好、催化活性高、选择性好等优点,但是存在着均相催化剂难以分离、回收等问题^[7-9],在大规模有机合成中,会对环境 and 经济造成破坏.非均相Pd催化剂因其易分离和可循环利用等优点,成为解决这一问题的有效方法^[10].已知的非均相催化体系有负载的Pd配合物^[11]、负载的Pd纳米颗粒^[12]、没有负载的Pd纳米颗粒^[13]等.因此,研究并开发高效的负载型Pd催化剂用于氯代芳烃的Suzuki交叉偶联反应至关重要,也受到越来越多研究人员的重视.本文作者拟对不同载体负载的Pd催化剂催化氯代芳烃的Suzuki交叉偶联反应进行简单综述.

1 无机载体负载的Pd催化剂在氯代芳烃Suzuki交叉偶联反应中的应用

1.1 含镁材料负载的Pd催化剂

1.1.1 Mg-Al负载的催化剂LDH-Pd⁰

层状二氢氧化物(LDH)在材料、阴离子交换剂以及催化剂上有许多用途^[14],其以LDH为载体,不仅可以稳定纳米Pd颗粒,还可以为Pd⁰提供足够的电子密度,以促进氯代芳烃进行Suzuki偶联反应^[15-16].CHOUDARY等^[17]发现将PdCl₄²⁻交换到用氯化物饱和的LDH上,可得到深棕色的LDH-Pd^{II},然后用水合肼进行还原,得到对空气稳定的黑色纳米Pd催化剂LDH-Pd⁰粉末.用LDH-Pd⁰催化剂进行氯代芳烃和芳硼酸的Suzuki交叉偶联反应,如图1所示.

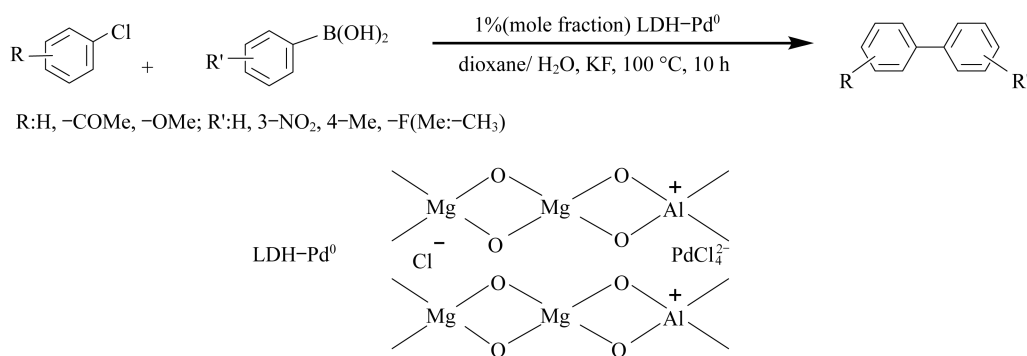


图1 LDH-Pd⁰催化的氯代芳烃的Suzuki交叉偶联反应

在LDH-Pd⁰催化的氯代芳烃的Suzuki交叉偶联反应中,具有极性溶剂、带给电子取代基的氯代芳烃和缺电子的芳硼酸有利于催化剂的反应活性,产物的收率为80%~90%.LDH-Pd⁰纳米催化剂可循环使用5次,催化剂的反应活性和选择性保持不变.

1.1.2 MgO负载的纳米晶体催化剂 NAP-Mg-Pd⁰

由于纳米氧化镁晶体(NAP-MgO)本身具有强碱性和高比表面积,所负载的Pd催化剂在反应中无需额外加入碱,就能表现出很高的催化活性.KANTAM等^[18]通过纳米MgO晶体对PdCl₄²⁻进行反离子稳定化,然后还原制得的NAP-Mg-Pd⁰催化剂在氯代芳烃的Suzuki偶联反应中表现出优异的催化活性,可催化生成不对称的联苯,如图2所示.

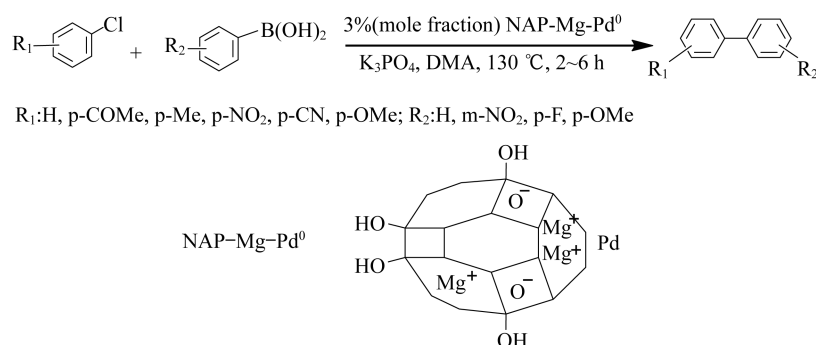


图2 NAP-Mg-Pd⁰催化的氯代芳烃的Suzuki交叉偶联反应(DMA为N,N-二甲基乙酰胺)

在NAP-Mg-Pd⁰催化的氯代芳烃的Suzuki交叉偶联反应中,产物的收率达90%左右,带吸电子基团的氯代芳烃和给电子基团的芳硼酸有利于催化剂的反应活性,该催化剂以平均85%的收率可循环使用4次.

1.2 介孔材料负载的Pd催化剂

1.2.1 中孔方钠石和介孔羧乙酸(NaA)沸石负载的Pd催化剂

将Pd⁰纳米颗粒或Pd²⁺负载在碳、沸石、介孔二氧化硅(SiO₂)等多孔固体材料上的报道已有很多^[19-25].CHOI等^[26-28]通过将有机硅烷表面活性剂添加到常规的方钠石和NaA沸石中,合成介孔方钠石和介孔NaA沸石,然后在Pd²⁺水溶液中进行离子交换,设计了Pd²⁺交换的介孔方钠石和NaA沸石^[29],该催化剂具有很高的热稳定性和催化活性,并且不需要加碱,用于氯代芳基的Suzuki交叉偶联反应,如图3所示.

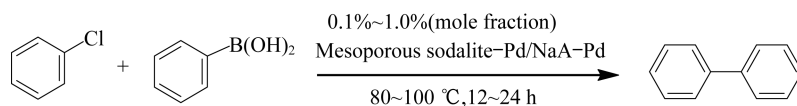


图3 中孔Sodalite-Pd/NaA-Pd催化的氯代芳烃的Suzuki交叉偶联反应

在中孔Sodalite-Pd/NaA-Pd催化剂催化的氯代芳烃的Suzuki交叉偶联反应中,使用体积小的氯代芳烃,产物的收率可达96%左右,使用体积较大的氯代芳烃,产物的收率也可达85%左右,催化剂可循环使用5次,催化反应的收率保持在85%左右.

1.2.2 中孔LTA沸石(MP-LTA)负载的Pd催化剂(Pd@MP-LTA)

LEE等^[30-31]制备了Pd@MP-LTA催化剂用于氯代芳基的Suzuki交叉偶联反应,如图4所示.首先用2,4-戊二酮和3-氨基丙基三乙氧基硅烷反应生成烯弗碱,然后再与Pd₂(μ-Cl)₂Me₂(PPh₃)₂作用形成含硅基的Pd配位化合物,最后将含硅基的Pd配合物水解沉积在中孔结构的LTA沸石上,得到Pd@MP-LTA催化剂.

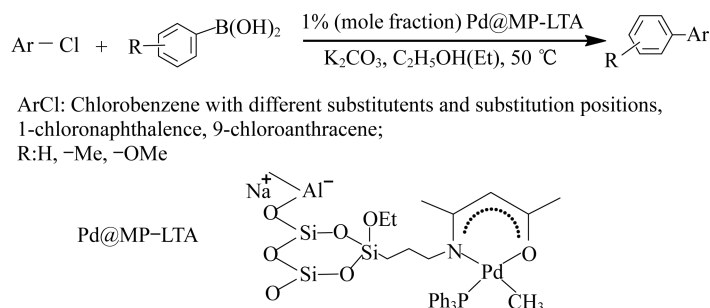


图4 Pd@MP-LTA催化的氯代芳烃的 Suzuki 交叉偶联反应

所制备的 Pd@MP-LTA 催化剂用于氯代芳烃的 Suzuki 交叉偶联反应中,可以在乙醇/水溶液中使用,催化反应活性受底物取代基的影响很小,也可以用氯代杂环化合物进行 Suzuki 交叉偶联反应,产物的收率在 89%~95% 之间,催化剂可循环使用 10 次,未见失活.

1.3 磁性四氧化三铁(Fe_3O_4)纳米复合材料负载的Pd催化剂

1.3.1 磁性 $\text{SiO}_2/\text{Fe}_3\text{O}_4$ 纳米颗粒负载的 $\text{Pd}@\text{SiO}_2/\text{Fe}_3\text{O}_4$ 催化剂

由于 Fe_3O_4 具有磁性,用 Fe_3O_4 作为载体的负载型催化剂可以通过外部永磁体与反应介质分离,磁性 Fe_3O_4 纳米颗粒已成为非常具有应用前景的固载化载体^[32].这避免了费时费力的分离步骤,并可实现连续化的催化反应.包裹有 SiO_2 薄层的 Fe_3O_4 纳米颗粒具有优异的特性,如不变的催化活性和稳定性^[33].JIN等^[34]通过将含三乙氧基硅基的Pd配位化合物水解聚合在 $\text{SiO}_2@\text{Fe}_3\text{O}_4$ 的表面上合成了 $\text{Pd}@\text{SiO}_2@\text{Fe}_3\text{O}_4$ 催化剂.

$\text{Pd}@\text{SiO}_2@\text{Fe}_3\text{O}_4$ 催化剂可在水相中高效催化氯代芳烃的 Suzuki 交叉偶联反应, 如图 5 所示. 产物的收率在 83%~93% 之间. 通常偶联剂中含有氨基供电子体的话很难发生偶联反应^[35]. 但是, 该催化剂在 2-氯苯胺和 3-氯苯胺的 Suzuki 交叉偶联反应中, 产物的收率可达 82%~90%; 在 1-氯萘和 9-氯蒽的偶联反应中, 收率高达 92%~93%; 位阻较大的底物 2-氯-1,3-二甲基苯也能以 71%~73% 良好的收率进行偶联反应. $\text{Pd}@\text{Fe}_3\text{O}_4$ 在循环使用 10 次以后, 催化活性保持不变.

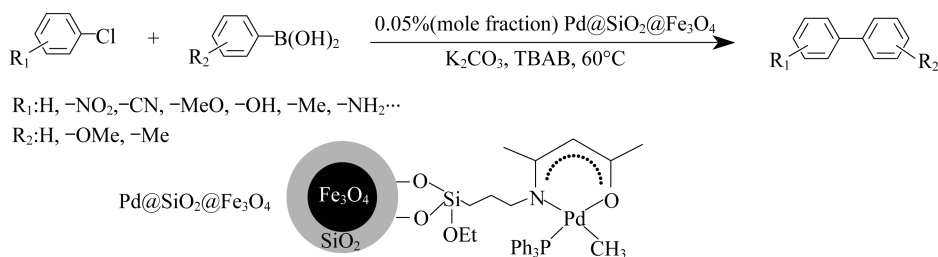


图5 Pd@SiO₂@Fe₃O₄催化的氯代芳烃的 Suzuki 交叉偶联反应(TBAB 为四丁基溴化铵)

1.3.2 磁性 $\text{Fe}_3\text{O}_4@\text{C}(\text{MFC})$ 纳米材料上负载的Pd/MFC催化剂

磁性可分离的纳米催化剂已成为均相和非均相催化剂之间的桥梁^[36].ZHU等^[37]使用沉淀沉积方法将Pd纳米颗粒固定在MFC载体上,制备了一种用碳包裹磁性Fe₃O₄的负载型Pd/MFC催化剂,用于氯代芳烃的Suzuki交叉偶联反应,如图6所示.该磁性纳米材料既充当Pd纳米颗粒的载体又充当稳定剂,防止了Pd粒子的团聚,提高了催化剂的重复使用性能^[38-40].

Pd/MFC 催化剂氯代芳烃的 Suzuki 交叉偶联反应中,反应产物的收率最高可达 95 %,催化剂可循环使用 5 次,催化活性没有降低.

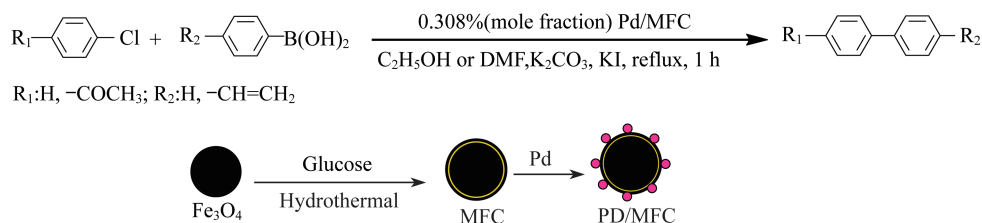


图6 Pd/MFC催化的氯代芳烃的Suzuki交叉偶联反应(DMF为N,N-二甲基甲酰胺)

2 有机载体负载的Pd催化剂在氯代芳烃Suzuki交叉偶联反应中的应用

2.1 聚苯胺纳米纤维(PANI)负载的Pd/PANI催化剂

由于“半均相催化剂”的优势^[41],人们对金属纳米颗粒催化的兴趣急剧增加.半均相催化将非均相催化的特性(可回收性和可循环性)与均相催化的特性(相对较低的催化剂负载量和良好的选择性)结合在一起.聚苯胺(PA)作为一种新型的半均相催化载体,CHOUDARY等^[42-43]对Pd纳米粒子负载在PA上进行了研究.通常这些纳米粒子是通过将Pd(II)盐添加到PANI的水分分散液中制备的^[42].当界面聚合用于合成PANI时,会形成纳米纤维^[44].PANI纳米纤维的高比表面积和孔隙率是制造金属—PA纳米催化剂的理想载体^[45-46].利用这些特性,GALLON等^[47]用硝酸Pd负载在PANI纳米纤维上制备了Pd/PANI催化剂.KANTAM等^[48]利用PA进一步合成了Pd/PANI,PA/Pd1,PA/Pd2,PA/Pd3,PA/Pd4,共5种催化剂.Pd/PANI催化剂对氯代芳烃的Suzuki交叉偶联反应,如图7所示.

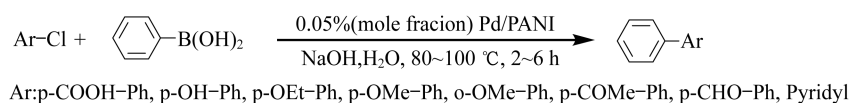


图7 Pd/PANI催化的氯代芳烃的Suzuki交叉偶联反应

在Pd/PANI催化的氯代芳烃的Suzuki交叉偶联反应中,由于PANI可稳定水中的Pd纳米颗粒,该催化反应可以在水相中进行,催化剂使用量非常少,这符合绿色化学的要求;同时偶联反应产物的收率在88%~95%之间,催化剂可循环使用10次,催化活性没有降低,收率在90%左右.

2.2 聚苯乙烯负载的Pd配合物Pd/PS催化剂

SCHWEIZER等^[49]和INADA等^[50-51]报道了利用叔丁基锂、二氯苯基膦、可溶性Pd(PPh₃)₄等物质合成了叔丁基苯基膦甲基聚苯乙烯(PS)负载的Pd催化剂,如图8所示.该催化剂用于代氯代芳烃的Suzuki交叉偶联反应,如图9所示.

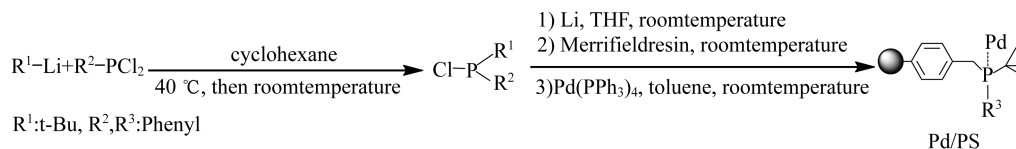


图8 Pd/PS催化剂的合成

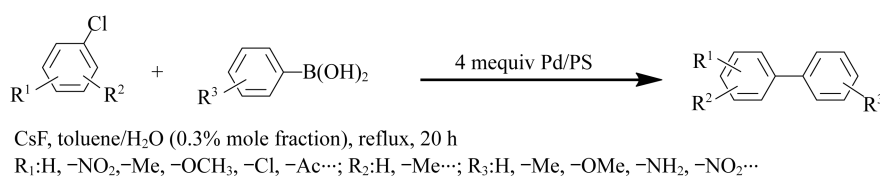


图9 聚苯乙烯负载的Pd催化剂催化的氯代芳烃的Suzuki交叉偶联反应

在Pd/PS催化的氯代芳烃的Suzuki交叉偶联反应中,偶联反应产物的收率在78%~90%之间,催化剂可以用于体积较大的2,6-二取代、2,6,2'-三取代的联苯和氯代杂环化合物的交叉偶联反应.催化剂可循环使用7次以上,催化活性未见降低.

2.3 氮(N)杂环卡宾主链有机金属聚合物负载的Pd(NHC-Pd-MCOPs)催化剂

在Pd催化的Suzuki交叉偶联反应中,用N-杂环卡宾(NHC)替代对空气敏感的膦配体越来越受到关注^[52].与传统的叔膦配体相比,NHC配体具有低毒性、可调节的空间体积、拓扑结构和强供电子等特点,与金属Pd结合牢固,催化剂稳定性好.KHORAMOV等^[53]报道了NHC-MCOPs的制备方法,KARIMI等^[54]在文献[53]的基础上,用Pd(OAc)₂处理二咪唑鎓盐溴化物,再负载在NHC-MCOPs载体上制备NHC-Pd-MCOPs的催化剂,用于氯代芳烃的Suzuki交叉偶联反应,如图10所示.

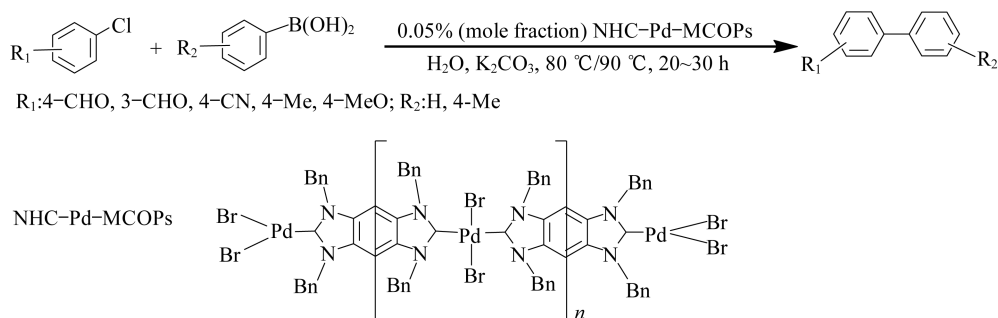


图10 NHC-Pd-MCOPs催化的氯代芳烃的Suzuki交叉偶联反应

在NHC-Pd-MCOPs催化的氯代芳烃的Suzuki交叉偶联反应中,催化反应可以在水相中进行,同时偶联反应产物的收率在88%~94%之间,催化剂可循环使用6次以上,催化活性未见降低,收率在92%左右.

3 其他类型催化剂在氯代芳烃Suzuki交叉偶联反应中的应用

3.1 N-二苯基膦基-2-氨基吡啶的PdCl₂加合物(L1-PdCl₂)催化剂

先前已广泛报道了带有P,N型,或者P,O型半不稳定配体的配合物的合成和催化活性,带有大基团的P-和N-供体配体由于其稳定过渡金属催化剂的能力而受到关注^[55].XU等^[56]利用P,N型双齿配体N-苯基磷烷基甲基-2-氨基吡啶(L1)和PdCl₂成功设计了L1-PdCl₂催化剂,并将其用于氯代芳烃的Suzuki交叉偶联反应中,如图11所示.偶联反应产物的收率在82%~98%之间,该催化体系催化效率更高和适用更多的底物^[57-65].

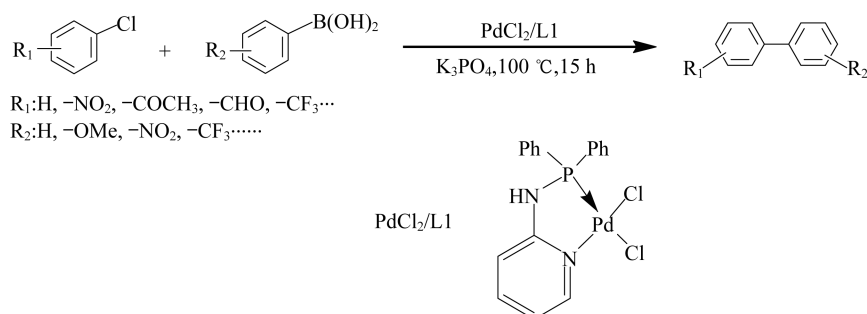


图11 L1-PdCl₂催化的氯代芳烃的Suzuki交叉偶联反应

3.2 在复杂硅材料上负载的Pd催化剂

3.2.1 SiO₂负载的卡宾Pd配合物催化剂P

GURBUZ等^[66]将富电子的氮杂环卡宾Pd配合物嫁接在硅材料的表面,制备出的负载Pd催化剂P应

用于氯代芳烃的 Suzuki 交叉偶联反应中,如图 12 所示.以碳酸铯为碱,二恶烷为溶剂,反应收率大于 85%,催化剂可循环使用 4 次,活性略有降低.

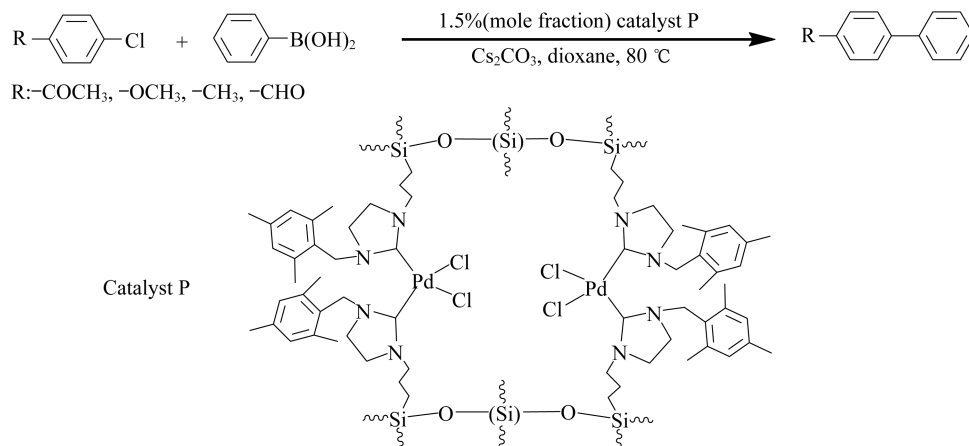


图 12 催化剂 P 催化的氯代芳烃的 Suzuki 交叉偶联反应

3.2.2 空壳结构的 SiO₂ 手性双功能催化剂

SHU 等^[67]利用空壳结构的 SiO₂, 将 Pd 中心固定在纳米笼中, 而将共价键固定的手性 Ru 中心固定在纳米通道中, 从而构建了手性双功能催化剂 Me@IPrPdBF₄@mesityleneRuArDPEN@HSMSNs, 如图 13 所示. 由于空壳 SiO₂ 中 Pd-Ru 活性位点的分离和协同作用^[68], 所制备的手性双功能 Pd-Ru/SiO₂ 催化剂, 实现了氯代苯乙酮的 Suzuki 交叉偶联反应和不对称氢转移 (ATH) 一锅法串联反应, 如图 14 所示, 得到了手性产物.

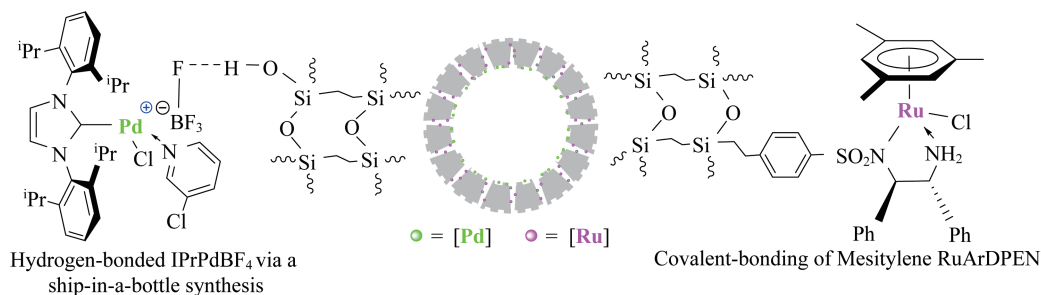


图 13 手性双功能 Me@IPrPdBF₄@mesityleneRuArDPEN@HSMSNs 催化剂

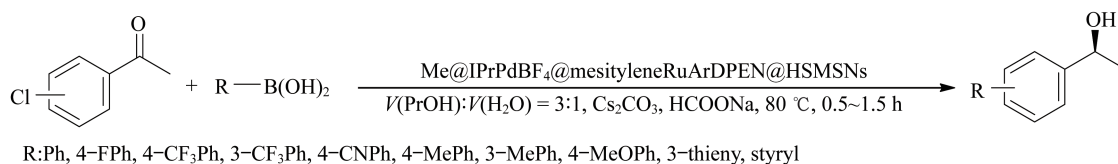


图 14 手性双功能 Me@IPrPdBF₄@mesityleneRuArDPEN@HSMSNs 催化剂催化的氯代苯乙酮的 Suzuki 交叉偶联-ATH 串联反应

手性双功能 Me@IPrPdBF₄@mesityleneRuArDPEN@HSMSNs 催化剂在氯代苯乙酮的 Suzuki 交叉偶联-ATH 串联反应中, 能以高达 97% 收率和 96% 的对映体过量 (ee) 值得到手性联芳醇.

4 展 望

上文简述了一些不同类型载体负载的 Pd 催化剂在氯代芳烃 Suzuki 交叉偶联反应中的研究进展. 虽然氯代芳烃在 Suzuki 交叉偶联反应中 C-C 键更难断开, 但却是廉价易得的化合物, 现已成为热门的研究

课题.由于介孔材料和有机聚合物的独特优势,它们作为负载的载体已经得到了很大的发展.展望未来并希望:1) 制备出更多具有功能化的负载型的Pd非均相催化剂,研究出具有更长寿命的催化剂,提高催化效率,降低催化剂的成本;2) 开发出更多高效环境友好的催化剂,可以在水相进行反应,减少对环境的污染;3) 研制出更多具有手性双功能负载型金属催化剂,进行一锅法偶联——ATH串联反应,利用这些反应合成更多有用的天然有机化合物和药物等,为社会和人类作更多的贡献.

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