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Dual-functional click-triazole: a metal chelator and immobilization linker for the construction of a heterogeneous palladium catalyst and its application for the aerobic oxidation of alcohols†

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A novel SBA-15 supported catalyst PdL$_n$@SBA-15 containing a 2-pyridyl-1,2,3-triazole ligand framework was prepared *via* a "click" route, in which the click-triazole acted as both a stable linker and a good chelator. The catalyst was characterized and applied for the aerobic oxidation of alcohols, and the product was obtained in up to 98% yield.

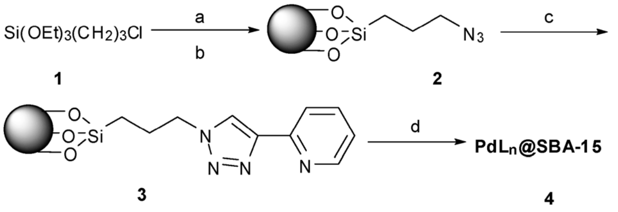
During the past decades, palladium-mediated catalysis has been recognized as one of the most powerful synthetic tools and as a fascinating area in organic transformations for both academic research and industrial processes.[1] Various palladium complexes with original ligand frameworks have been well designed and successfully applied in organic reactions. However, these homogeneous catalysts often suffer from catalyst separation and catalyst recycling. To overcome these problems, palladium complexes have been subsequently immobilized onto various inorganic or organic supports to provide heterogeneous catalysts which are easier for product isolation and catalyst recycling. However, in most cases, the special section that connects the catalysts and supports in these solid palladium catalysts acts only as a linker, and its effects on the catalytic reaction are often negligible. In these regards, we believe that the design of a novel, facile grafting approach to generate heterogeneous catalysts with a multifunctional linker is still desirable in heterogeneous catalysis.

Copper-catalyzed Huigen-type [3+2] azide–alkyne cycloaddition (CuAAC) known as the "click reaction",[2] because of its high efficiency, simple procedure, absence of side products and mild reaction conditions, has shown promising applications in drug discovery, biochemistry, dendrimers, material and polymer science during the past decade. In addition, the 1,2,3-triazoles generated in the CuAAC reaction as a high stable linker have also drawn much attention for catalyst immobilization.[3] Recently, the "1,2,3-triazole" unit has also emerged as a chelator showing great potential for metal coordination,[4] and many metal ions like Cu,[4e,k] Ru,[4c,j,i] Pd,[4b,h] *etc.* have been successively explored. Inspired by its attractive features, we were intrigued to design solid catalysts based on the utilization of the versatile click-triazole, not only as a stable linker to graft catalysts onto the supports but also as a good chelator to participate in the catalytic reactions.[5]

Herein, we report a novel SBA-15 supported catalyst PdL$_n$@SBA-15 containing a "2,2′-bipyridine analogue" ligand framework *via* the copper-catalyzed ligation of 2-ethynylpyridine with azide functionalized SBA-15, and its application for the aerobic oxidation of alcohols.

Our investigation began with the preparation of PdL$_n$@SBA-15 **4** by immobilizing the palladium(II) acetate into mesoporous silica SBA-15, which was modified with bidentate 2-pyridyl-1,2,3-triazole ligand in advance. The detailed route is shown in Scheme 1. The azide group was first introduced into SBA-15 through a simple procedure and verified by the appearance of the N_3 band at 2112 cm^{-1} in FT-IR spectra. Then it underwent a "click" process with commercially available 2-ethynylpyridine in the presence of copper sulfate and sodium ascorbate in aqueous methanol. The resulting functionalized SBA-15 **3** was further treated with Pd(OAc)$_2$ in toluene to provide the desired solid catalyst PdL$_n$@SBA-15 **4**, the palladium amount of which measured by inductively coupled plasma atomic emission spectrometry (ICP-MS) was 0.138 mmol g^{-1}.

X-Ray reflective diffraction (XRD), transmission electron microscopy (TEM) and nitrogen sorption measurements were carried out to get detailed information about the architecture of the novel catalyst. The small-angle XRD (Fig. S10, ESI†) and TEM images (Fig. S12a–c, ESI†) have shown that the structure of the well-ordered mesoporous SBA-15 remained



Scheme 1 Synthesis of PdL$_n$@SBA-15 **4**. *Reaction conditions*: (a) NaN_3, CH_3CN, TBAB, reflux, 24 h; (b) SBA-15, toluene, reflux, 24 h; (c) 2-ethynylpyridine, $CuSO_4$/NaASc, MeOH/H_2O, rt, 3 d; (d) Pd(OAc)$_2$, toluene, rt, 2 h.

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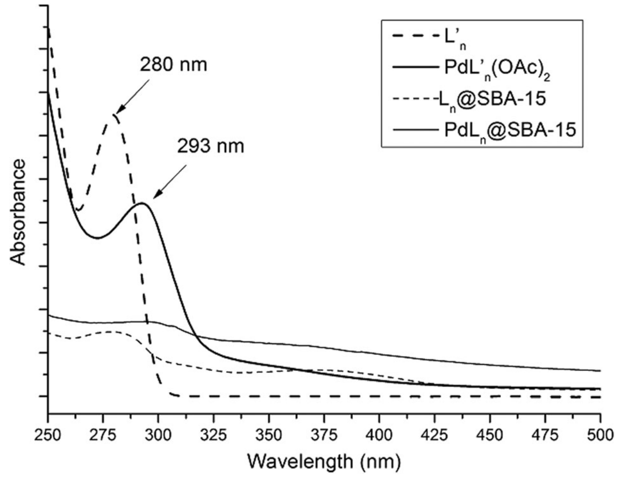


Fig. 1 UV-Vis spectra of L'_n (in methanol), PdL'_n (in methanol), L_n@SBA-15 and PdL_n@SBA-15.

intact after the immobilization process. The TEM images also suggested that no palladium clusters were formed during the preparation. While the PdL_n@SBA-15 material analyzed by nitrogen sorption isotherm measurements (Fig. S11, ESI†) showed less surface area, pore volume and nanopore size compared with starting material SBA-15, which might be ascribed to the occupation of the "2,2′-bipyridine analogue" ligand and palladium that blocked a part of pores of the material.

To further investigate the coordination state of the catalyst **4**, UV-Vis, ^{1}H NMR and FT-IR were performed, meanwhile, its homogeneous ligand counterpart 1-methyl-4-(2′-pyridyl)-1,2,3-triazole (L'_n) and corresponding Pd complex ($PdL'_n(OAc)_2$) were also designed and synthesized for easy comparison (see ESI† for details). From the UV-Vis spectra (Fig. 1), it was found that the ligands in solution (L'_n) and on the solid surface (L_n@SBA-15) showed a distinct π–π* transition around 280 nm. After coordination, a slight red shift from 280 nm to 293 nm was observed from the spectra of the palladium complexes ($PdL'_n(OAc)_2$ and PdL_n@SBA-15), which was probably assigned to the ligand to metal charge transfer transition (LMCT).[6] And the similar absorption bands of the palladium complexes might suggest that palladium existing on the solid surface was in a coordinated fashion. To further test if either the triazole or the pyridine or both units would coordinate to palladium cations, we have carefully examined the ^{1}H NMR, COSY spectra (d^6-DMSO, 298K) of the ligand (L'_n) and those of the palladium complex ($PdL'_n(OAc)_2$). It was clear that the proton signals on pyridine and triazole rings of $PdL'_n(OAc)_2$ in general were shifted downfield apparently (Fig. 2), which indicated that the palladium ion was coordinated with both units of the ligand and the triazole unit worked as a part of the bidentate chelator. Meanwhile, because the triazole ligand could bind with the palladium metal through either N2 or N3 atom, the spectra of $PdL'_n(OAc)_2$ showed two sets of proton signals, the ratio of which was around 1 : 3. To the best of our knowledge, the formation of five-membered chelate rings by binding with the N3 atom and the nitrogen atom of pyridine is considered to be the predominant structure.

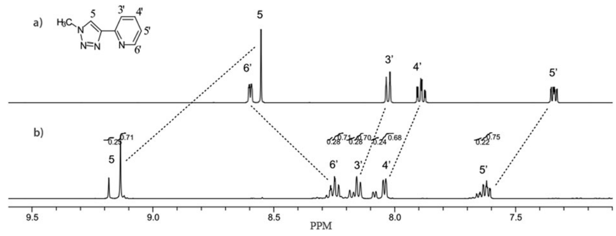
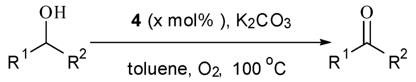


Fig. 2 Partial ^{1}H NMR spectra (500 MHz, d^6-DMSO, 298 K) of the ligand L'_n (a) and the palladium complex $PdL'_n(OAc)_2$ (b).

The selective oxidation of alcohols, especially utilizing oxygen as the terminal oxidant, has been considered one of the most important transformations in organic synthesis.[7] With the SBA-15 supported palladium catalyst in hand, we attempted to evaluate its catalytic activity for the aerobic oxidation of alcohols, and the selected examples are summarized in Table 1. Initially, the benzyl alcohol was chosen as the model substrate, and the oxidation reaction was conducted in toluene at 100 °C using K_2CO_3 as the base. Within 4 h, 95% isolated yield of the benzaldehyde was obtained and the selectivity was more than 99% (Table 1, entry 1). Notably, the starting material could also completely transform either under air atmosphere or at a low temperature (80 °C) although the reaction was prolonged slightly (Table 1, entries 2 and 3). In addition, the catalyst PdL_n@SBA-15 **4** showed good activity in the oxidation of other primary benzyl alcohols containing substituents such as 4-Me, 4-MeO, 4-F and 4-NO_2 groups (Table 1, entries 4–8). No carboxylic acids or esters were detected for all substrates investigated. The oxidation of 2-substitute benzyl alcohol was achieved in a moderate yield (Table 1, entry 9), which may be ascribed to the steric hindrance by the quasi-two-dimensional surface of the palladium sites. For heterocyclic and secondary alcohols, the catalyst also showed satisfactory performances, and the desired products were isolated in moderate to excellent yields (Table 1, entries 10–15).

Table 1 The aerobic oxidation of alcohols with PdL_n@SBA-15 **4** as the catalyst[a]



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Entry	R^1	R^2	*x*	*t*/h	Yield[b] (%)	Selec.[c] (%)
1	Ph	H	0.5	4	95	>99
2[d]	Ph	H	0.5	6.5	94	>99
3[e]	Ph	H	0.5	8	94	>99
4	4-MePh	H	0.5	3	95	>99
5	4-MeOPh	H	0.5	2.5	97	>99
6	3,4,5-triMeOPh	H	0.5	4	96	>99
7	4-FPh	H	0.5	9	94	>99
8	4-NO_2Ph	H	0.5	10	98	>99
9	2-OMePh	H	1	24	65	>99
10	3-Pyridine	H	1	20	65	>99
11	Ph	Me	1	18	96	>99
12	Ph	Et	1	21	95	>99
13	Ph	Ph	1	24	92	>99
14	4-MeOPh	Me	1	12	96	>99
15	PhCO	Ph	0.5	10	98	>99

[a] All the reactions were conducted with substrate/K_2CO_3/PdL_n@SBA-15 **4** (the molar ratios of substrate/K_2CO_3/Pd were 1 : 1 : x%) at 100 °C in toluene (3.0 mL) under an oxygen atmosphere unless otherwise noted. [b] Isolated yield. [c] The selectivity was detected by GC-MS. [d] Air was used instead of oxygen. [e] Under O_2 at 80 °C.

Further experiments were performed to verify the catalyst recyclability. After the first use, the catalyst was recovered by simple filtration and reused in the next run after a simple workup. We were pleased to find that the recovered catalyst was successfully reused in the subsequent seven cycles with a consistent catalytic activity, giving the products in excellent yields (92–95%, Fig. S13, ESI†). To further rule out the contribution of the homogeneous catalysis to the results, the solid catalyst was hot-filtered off from the benzyl alcohol oxidation system after reacting for 0.5 h and the conversion was found to be 22%. Then the liquid filtration was performed for reaction under the same conditions for 3.5 h, however no further reaction was observed. Meanwhile, the ICP-MS analysis of the palladium metal in the filtration showed that the amount of palladium leaching in solution was 0.043 ppm. Moreover, it was noteworthy to mention that no formation of apparent agglomerated palladium was detected after the first cycle from the TEM image (Fig. S12d, ESI†). But we did notice a slight decline in the quality of ordered channel frameworks of SBA-15, which might be attributed to its poor hydrothermal stability under the basic conditions.[8]

In conclusion, we have prepared a new mesoporous SBA-15 supported catalyst PdL_n@SBA-15 **4** *via* a "click" route, in which the click-triazole acts as a stable linker as well as a good chelator to participate in the catalytic reactions. The obtained solid catalyst has demonstrated a promising catalytic activity for the aerobic oxidation of benzyl alcohols. The novel design and facile synthesis of the supported metal catalyst described here might be widely applied to derive diverse catalysts based on the dual-functional click-triazole. Currently, we are investigating more active "2,2′-bipyridine analogue" ligands grafting on other supports such as amphiphilic resins, dendrimers for aqueous alcohol oxidation and other palladium-based reactions.

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