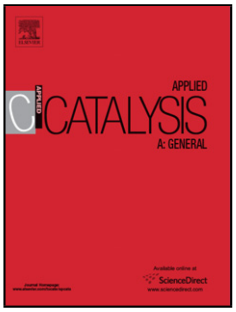

Title: In site preparation of Pd(II)-MoS$_2$ Complex: a new high-efficiency catalyst for alkenylation of heteroaromatics by direct C-H bond activation

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In site preparation of Pd(II)-MoS_2 Complex: a new high-efficiency catalyst for alkenylation of heteroaromatics by direct C-H bond activation

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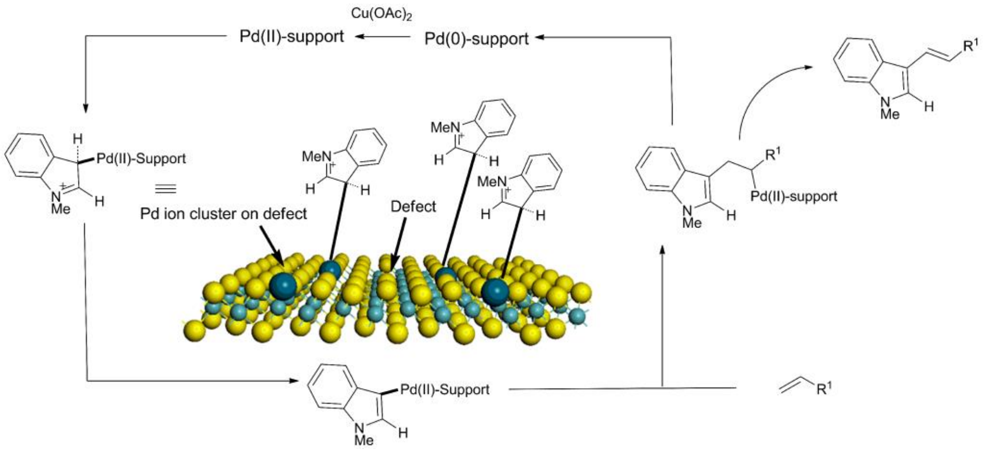
Graphical Abstract



Highlights

1. A Pd catalyst was designed by affording Pd^{2+} salt on the surface of single-layered MoS_2.
2. This metal salt and molybdenum disulfide complex offered several advantages, including easy preparation, low cost, and capability to prepare excellent dispersible metal ion cluster nanostructures with controllable size.
3. Direct C-H activation of indoles, furans and thiophenes was carried out to combine with several kinds of terminal olefins with 0.2% amount of the catalyst.
4. This easy-prepared catalyst also performed high efficiency in several other kinds of C-C coupling reactions.

Abstract

Pd(II)-MoS_2 catalyst was designed by affording Pd^{2+} salt on the surface of single-layered molybdenum disulfide nanosheets. Based on the dispersible template, this metal salt and molybdenum disulfide complex offered several advantages, including easy preparation, low cost, and capability to prepare excellent dispersible metal ion cluster nanostructures. The application of this complex in alkenylation of heteroaromatics was reported. Direct C-H activation of indoles, furans and thiophenes was carried out to combine with several kinds of terminal olefins. This catalyst also performed high efficiency in several other kinds of coupling reactions. Thus, a universal suitable catalyst for C-H activation and C-C bond formation was invented by a convenient in situ preparation.

Keywords: Transition metal dichalcogenides; C-H activation; Heterogeneous catalysis; MoS_2

1. Introduction

In the last decade, tremendous attention has been paid to two-dimensional crystal with exceptional electronic, optical and mechanical properties [1-4]. Although graphene is the most well-known layered material, transition metal dichalcogenides (TMDs) have acquired increasing attention, because of their unique properties and various applications in energy storage, sensing, electronic devices and photo-catalysis [5-11]. Among these TMDs, MoS_2 is a representative example. The monolayer MoS_2 can be applied in the field effect transistor (FET) [12] and NO detection [13]. Moreover, MoS_2 nanosheets are also promising materials for catalytic hydrogenation and potential building blocks for thermoelectric and energy storage devices [11,14,15]. However, application of MoS_2 nanosheets as a catalyst support in chemical catalysis has been rarely studied so far.

With regards to metal catalytic applications in the last decades, palladium catalyzed carbon-carbon bond formations are a powerful set of synthetic tools [16-22]. Normally, aryl halide is catalyzed by palladium(0) in the procedure in which aryl or alkyl palladium(II) intermediates are formed [23-25]. These intermediates can be subsequently functionalized to form carbon-carbon bonds through the reaction with organometallic reagents [26-29]. Due to the need of a more straightforward and economical process to prepare such intermediates, the C-H activation reactions have thus been greatly improved [30-32]. Palladium(II) catalyzed direct C-H activation reactions are now attracting more and more attention [33-38]. Traditional palladium(II) catalysts used in C-H activation is usually palladium salts in a large amount, up to 10%. Therefore, it is significant to find a suitable support for palladium which will bring a remarkable reduce of catalyst amount [39-43].

Herein, a generally applicable catalyst was acquired by in situ preparation of two stable materials, providing a cheap and efficient palladium catalyst for C-H activation. The preparation of single-layer MoS_2 nanosheets could be realized by using n-butyl lithium as the intercalation agent to insert lithium ions into the layered structures, followed by exfoliation in water with ultrasonication [44-46]. After dried through cryodesiccation, the two-dimensional MoS_2 was dispersed in DMF under ultrasonication, which could be used as catalyst carrier by a straightforward mixing with $PdCl_2$ solution [47]. This catalyst could be widely used in alkenylation of heteroaromatics by direct C-H bond activation. In all the examples we had tried, the reactions were carried out with a lower catalyst amount compared to traditional catalysts, and in high yield [48-50]. Meanwhile, Mizoroki-Heck reactions, Suzuki-Miyaura reactions and functionalization reactions of thiophene could also be catalyzed by this complex. By this means, a new generally suitable palladium catalyst had been developed.

2. Experimental details

2.1 Catalyst preparation

To obtain large quantities of MoS_2 nanosheets, solution based exfoliation methods had been used [46,51]. 0.1 ml of $PdCl_2$ solution in DMF (0.01 M) and 0.4 mg of MoS_2 nanosheets dispersed in 2 ml of DMF were directly mixed for just ten minutes at room temperature. Pd(II)-MoS_2 complex could be in situ prepared by this way.

2.2 Catalyst characterization

Fig. 1a showed the chemical exfoliated MoS_2 nanosheets, which were single layered. The ion cluster of palladium was supposed to be formed after the Pd^{2+} depositing onto the surface of the MoS_2 nanosheets (Fig. 1b). Interestingly, the ion cluster was inclined to form on the edge sites of MoS_2 (Fig. 1b insert), which indicated that the edge was more active than the basal plane [52]. As reported, because of the violent nature of chemical exfoliation reaction, the crystal structure of MoS_2 became deformed [53], and the defects could be visible [54]. The MoS_2 nanosheets had been proved to contain negative charge after chemical exfoliation [55]. It was supposed that the negative charge might gather around the defects, where molybdenum atoms were unsaturated. Thus, palladium ion with positive charge would deposit around the defects, especially onto the defect-rich edge sites with high surface energy [44,56]. Meanwhile, as studied before, using DMF as the solvent and capping agent, sulphur atoms had strong interaction with palladium, leading palladium clusters to decorate on the surface of two-dimension nanosheets with well-defined size and shape [57]. The sulphur atoms on the surface of our single-layered MoS_2 might also have strong interaction with palladium ion in DMF, therefore perfect dispersion of palladium ion cluster could also be observed from this image, which might lead to good catalytic performance.

The XPS spectra of Pd doped MoS_2 nanosheets were showed in Fig. 2. The Mo 3d showed two peaks at 228.2 eV and 231.4 eV, respectively, indicating the MoS_2 nanosheets were in 1T phase [51]. The binding energy of Pd 3d peaks at 336.4 eV and 341.8 eV, respectively suggested the successful deposition of palladium(II) onto the surface of the MoS_2. Metallic Pd doublet peaks (at about 335.0eV and 341.0eV) were not observed in the spectra.

The particle size distribution of the Pd(II) ion clusters on the MoS_2 supports was also determined by TEM analysis, and the average particle diameter was 6.28 nm (Fig. 3a). The small size of the Pd ion clusters contributed greatly to the high catalytic activity [58].

After centrifugation of the catalyst suspension in DMF, the Pd(II)-MoS_2 complex was separated. The EDX result of the catalyst showed the palladium content was amounted to 6.07% by weight, which could be converted into 3.19% by number of atom (Fig. 3b, calculation see in ESI). Compared to the amount of $PdCl_2$ added to the MoS_2 suspension, 25% of the Pd(II) ion were deposited onto the surface of the MoS_2 nanosheets.

3. Results and discussion

3.1 Application of catalyst in C-H activation and oxidative Heck reaction

The indole motif is a ubiquitous feature of alkaloid and peptide natural product, and the functionalization of indoles is an important transformation in organic chemistry [59,60]. Meanwhile, other five-membered cycles, especially thiophenes and furans, are common structural motifs found in abroad range of natural products, drug molecules, and industrial materials [61]. They are considered to be important targets [59,62]. Many useful and practical processes exist for the modification of them, and metal-catalyzed coupling reactions are of particular utility [63-66].

Traditional Heck reactions contain an unconquered disadvantage, that is, the overall coupling of the two fragments requires two discrete activation steps: the formation of an aryl or vinyl halide and the palladium(0)-catalyzed union of the reaction partners [27-29,67,68]. A direct oxidative Heck through palladium-catalyzed C-H activation/C-C bond-forming processes would bypass this disadvantage and lead to a more efficient process [69]. Here we applied our in site prepared Pd(II)-MoS_2 complex in the direct C-H activation, to our delight, a high efficiency Heck product was acquired [48,70].

We began to explore the reaction with N-methylindole and n-butyl acrylate by use of DMF as the solvent and $Cu(OAc)_2$ as the oxidant. According to the report, ligand conjugation of chemically exfoliated MoS_2 brought out the thiol functionalization route to modify MoS_2 sheets. Here we prepared MoS_2 decorated by mercaptoethylamine, mercaptoethanol and mercaptoacetic acid using this method. Undecorated MoS_2 and MoS_2 decorated by mercaptoethylamine, mercaptoethanol or mercaptoacetic acid, were dispersed in DMF (2 mL, 0.2 mg/mL) and mixed with $PdCl_2$ (0.1 ml, 0.01 M) solution. Then it was used as the catalyst in the reaction. Beyond our expectation, undecorated MoS_2 performed much better than decorated MoS_2 (Table 1). As MoS_2 could be decorated along with the defects on the surface trapping sulfydryl group, once the MoS2 sheets completely modified, Pd ion would not be concentrated on the surface of MoS_2 thereof. Once the reaction was carried out using only $PdCl_2$ without support, the reaction scarely happened.

Table 2 showed a range of five numbered heterocyclic compounds reacted with alkenes. It could be found that the C-H activation and oxidative coupling reactions were catalyzed by Pd(II)-MoS_2. These reactions were carried out with Pd(II)-MoS_2 (0.1 ml of 0.01M $PdCl_2$ with 2 ml of MoS_2 suspension), hetero cycles (1a~1c) (0.5 mmol, 1 equiv), olefins (2a~2e) (1 mmol, 2 equiv), and $Cu(OAc)_2$ (0.9 mmol, 1.8 equiv). The C-H activation and coupling proceeded smoothly to give the corresponding products at 70 ^{o}C for 18 h.

Compared to traditional palladium catalysts, we reduced the amount of palladium catalyst from 10% to 0.2% of the reactant. To confirm the role of the Pd(II)-complex in catalysis, the in site prepared catalyst was also separated from the solvent with the dissociative $PdCl_2$ removed. After redispersed in DMF, the catalyst was used to the reactions of compound 1a with 2a. The result had none different manifestations with the previous reactions which certified that the Pd(II)-MoS_2, not the dissociated Pd ion played a main role in catalysis.

We proposed a Pd(II) involved C-H activation mechanism (Fig. 4), in relation to a Pd(II)-Pd(0)-Pd(II) catalytic cycle [71]. But since everything has two sides, our convenient and high-efficiency catalyst were not recyclable, because the palladium(II)-MoS_2 could not be easily separated. In the reaction, 165 mg copper salt was used. Although we tried many ways, the only 0.4 mg MoS_2 support in the reaction system could not be separated from the large amount of copper salt.

3.2 Application of catalyst in other C-C bond formation reactions

This catalyst showed not only high efficiency in C-H activation reaction, but also good performance in traditional coupling reaction, such as Suzuki reaction, Heck reaction and functionalization of hetero cycles by aryl halides. The Suzuki reaction between aryl halide (0.50 mmol) and boronic acid (0.55 mmol) proceeded in the presence of Pd(II)-MoS_2 (0.01 ml of 0.01 M $PdCl_2$ with 2 ml of MoS_2 suspension) in EtOH and water, using Na_2CO_3 as the base under atmosphere, to acquire the coupling product with up to 95% yield. The Heck reaction of aryl bromide (0.50 mmol) and olefins (1.0 mmol) was performed with Pd(II)-MoS_2 (0.05 ml of 0.01M $PdCl_2$ with 2 ml MoS_2 suspension), triethylamine and tetrabutylammoniumacetate (TBAA) in DMF at 120 ^{o}C, to acquire the corresponding cinnamates with up to 89% yield. Beside the direct C-H activation and oxidative coupling, hetero cycles could also be functionalized by aryl halide in the reaction catalyzed by palladium catalyst [72,73]. The reactions were carried out with thiophene (1.0 mmol), aryl halide (0.50 mmol), Pd(II)-MoS_2 (0.25 ml of 0.01M $PdCl_2$ with 2 ml of MoS_2 suspension) and CsOAc (2 equiv) in DMF. This reaction proceeded successfully.

4. Conclusions

In summary, Pd^{2+} combined to single layered MoS_2 nanosheets showed favorable catalytic property in several kinds of coupling reactions, including the C-H activation and oxidative functionalization of hetero cycles. Existence form of palladium as a Pd(II) salt brought many benefits, especially, a more straightforward and economical process to prepare intermediates in C-C bond formation. Low cost, simple material, and high stability were also significant advantages. This catalyst could also be widely used in Suzuki-Miyaura reaction, Heck reaction, and C-H bond functionalization reactions of thiophenes. By this means, by the aid of a reliable support, commercial Pd(II) salt could turn to be an efficiency and normal applicable C-C bond catalyst. This new methodology in designing catalyst may promise a broad prospect in virtue of its productiveness, as atom economy is encouraged in current chemistry.

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References

[1] K.S. Novoselov, A.K. Geim, S. Morozov, D. Jiang, Y. Zhang, S. Dubonos, I. Grigorieva, A. Firsov, Science 306 (2004) 666-669.

[2] X. Huang, Z. Yin, S. Wu, X. Qi, Q. He, Q. Zhang, Q. Yan, F. Boey, H. Zhang, Small 7 (2011) 1876-1902.

[3] A.K. Geim, K.S. Novoselov, Nature Mater. 6 (2007) 183-191.

[4] M. Chhowalla, H.S. Shin, G. Eda, L.-J. Li, K.P. Loh, H. Zhang, Nature Chem. 5 (2013) 263-275.

[5] Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman, M.S. Strano, Nature Nanotech. 7 (2012) 699-712.

[6] H. Zeng, J. Dai, W. Yao, D. Xiao, X. Cui, Nature Nanotech. 7 (2012) 490-493.

[7] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, F. Wang, Nano Lett. 10 (2010) 1271-1275.

[8] Z. Yin, H. Li, H. Li, L. Jiang, Y. Shi, Y. Sun, G. Lu, Q. Zhang, X. Chen, H. Zhang, ACS Nano 6 (2011) 74-80.

[9] H. Gao, X. Wu, J. Zhang, Chem. Eur. J. 17 (2011) 2838-2841.

[10]H. Li, G. Lu, Z. Yin, Q. He, H. Li, Q. Zhang, H. Zhang, Small 8 (2012) 682-686.

[11]K. Chang, W. Chen, ACS Nano 5 (2011) 4720-4728.

[12]B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, Nature Nanotech. 6 (2011) 147-150.

[13]H. Li, Z. Yin, Q. He, H. Li, X. Huang, G. Lu, D.W.H. Fam, A.I.Y. Tok, Q. Zhang, H. Zhang, Small 8 (2012) 63-67.

[14]J. Kibsgaard, Z. Chen, B.N. Reinecke, T.F. Jaramillo, Nature Mater. 11 (2012) 963-969.

[15]R.J. Smith, P.J. King, M. Lotya, C. Wirtz, U. Khan, S. De, A. O'Neill, G.S. Duesberg, J.C. Grunlan, G. Moriarty, Adv. Mater. 23 (2011) 3944-3948.

[16]N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457-2483.

[17]L. Yin, J. Liebscher, Chem. Rev. 107 (2007) 133-173.

[18]K. Nicolaou, P.G. Bulger, D. Sarlah, Angew. Chem. Int. Ed. 44 (2005) 4442-4489.

[19] J. P. Corbet, G. Mignani, Chem. Rev. 106 (2006) 2651-2710.

[20] A.B. Dounay, L.E. Overman, Chem. Rev. 103 (2003) 2945-2964.

[21] T.-Y. Luh, M.-k. Leung, K.-T. Wong, Chem. Rev. 100 (2000) 3187-3204.

[22] M. Hosseini-Sarvari, Z. Razmi, M.M. Doroodmand, Appl. Catal. A: Gen. 475 (2014) 477–486.

[23] X. Chen, K.M. Engle, D.H. Wang, J.Q. Yu, Angew. Chem. Int. Ed. 48 (2009) 5094-5115.

[24] A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2879-2932.

[25] R.G. Bergman, Nature 446 (2007) 391-393.

[26] L. Ackermann, R. Vicente, A.R. Kapdi, Angew. Chem. Int. Ed. 48 (2009) 9792-9826.

[27] J.-J. Dong, J. Roger, F. Pozgan, H. Doucet, Green Chem., 11 (2009) 1832-1846.

[28] J. Roger, H. Doucet, Adv. Synth. Catal. 351 (2009) 1977-1990.

[29] J. Roger, H. Doucet, Tetrahedron 65 (2009) 9772-9781.

[30] B.-J. Li, S.-D. Yang, Z.-J. Shi, Synlett 2008 (2008) 949-957.

[31] B.M. Trost, Science 254 (1991) 1471-1477.

[32] B.M. Trost, Acc. Chem. Res. 35 (2002) 695-705.

[33] F. Kakiuchi, S. Murai, Acc. Chem. Res. 35 (2002) 826-834.

[34] K. Godula, D. Sames, Science 312 (2006) 67-72.

[35] F. Kakiuchi, T. Kochi, Synthesis (2008) 3013-3039.

[36] D. Alberico, M.E. Scott, M. Lautens, Chem. Rev. 107 (2007) 174-238.

[37] I. V. Seregin, V. Gevorgyan, Chem. Soc. Rev. 36 (2007) 1173-1193.

[38] I. J. Fairlamb, Chem. Soc. Rev. 36 (2007) 1036-1045.

[39] V.A. Zinovyeva, M.A. Vorotyntsev, I. Bezverkhyy, D. Chaumont, J.-C. Hierso, Adv. Funct. Mater. 21 (2011) 1064-1075.

[40] L. Wang, W.-b. Yi, C. Cai, Chem. Commun. 47 (2010) 806-808.

[41] M.R. Nabid, Y. Bide, S.J.T. Rezaei, Appl. Catal. A: Gen. 406 (2011) 124–132.

[42] S.K. Movahed, M. Dabiri, A. Bazgir, Appl. Catal. A: Gen. 488 (2014) 265–274.

[43] P. Wang, G. Zhang, H. Jiao, L. Liu, X. Deng, C. Yan, X. Zheng, Appl. Catal. A: Gen. 489 (2015) 188–192.

[44]S.S. Chou, M. De, J. Kim, S. Byun, C. Dykstra, J. Yu, J. Huang, V.P. Dravid, J. Am. Chem. Soc. 135 (2013) 4584-4587.

[45]Z. Zeng, Z. Yin, X. Huang, H. Li, Q. He, G. Lu, F. Boey, H. Zhang, Angew. Chem. Int. Ed. 50 (2011) 11093-11097.

[46]P. Joensen, R. Frindt, S.R. Morrison, Mater. Res. Bull. 21 (1986) 457-461.

[47]X. Huang, Z. Zeng, S. Bao, M. Wang, X. Qi, Z. Fan, H. Zhang, Nat. Commun. 4 (2013) 1444.

[48]N. P. Grimster, C. Gauntlett, C.R. Godfrey, M.J. Gaunt, Angew. Chem. Int. Ed. 44 (2005) 3125-3129.

[49] W.-L. Chen, Y.-R. Gao, S. Mao, Y.-L. Wang, Y.-Q. Wang, Org. Lett. 14 (2012) 5920-5923.

[50] H. P. L. Gemoets, V. Hessel, T. Noël, Org. Lett. 16 (2014) 5800-5803.

[51]G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, M. Chhowalla, Nano Lett. 11 (2011) 5111-5116.

[52]Y. Shi, J.K. Huang, L. Jin, Y.T. Hsu, S.F. Yu, L.J. Li, H.Y. Yang, Sci. Rep. 3 (2013) 1839.

[53]K.E. Dungey, M.D. Curtis, J.E. Penner-Hahn, Chem. Mater. 10 (1998) 2152-2161.

[54]G. Eda, T. Fujita, H. Yamaguchi, D. Voiry, M. Chen, M. Chhowalla, ACS Nano 6 (2012) 7311-7317.

[55]W. Divigalpitiya, R. Frindt, S.R. Morrison, Science 246 (1989) 369-371.

[56]D. Kaplan, T. Fujita, M. Chen, T. Asefa, M. Chhowalla, Nature Chem. 7 (2015) 45-49.

[57] E. Gracia-Espino, G. Hu, A. Shchukarev and T. Wågberg, J. Am. Chem. Soc. 136 (2014) 6626-6633.

[58]H. Li, S. Gan, D. Han, W. Ma, B. Cai, W. Zhang, Q. Zhang, L. Niu, J. Mater. Chem. A 2 (2014) 3461-3467.

[59] L.S. Hegedus, Angew. Chem. Int. Ed. 27 (1988) 1113-1126.

[60]M.C. Willis, G.N. Brace, I.P. Holmes, Angew. Chem. Int. Ed. 44 (2005) 403-406.

[61]F.W. Lichtenthaler, Angew. Chem. Int. Ed. 35 (2002) 728-737.

[62] E. Capito, J.M. Brown, A. Ricci, Chem. Commun. (2005) 1854-1856.

[63] S. Cacchi, G. Fabrizi, Chem. Rev. 105 (2005) 2873-2920.

[64] C.G. Hartung, A. Fecher, B. Chapell, V. Snieckus, Org. Lett. 5 (2003) 1899-1902.

[65] X. Cai, V. Snieckus, Org. Lett. 6 (2004) 2293-2295.

[66] Z. Zhao, A. Jaworski, I. Piel, V. Snieckus, Org. Lett.10 (2008) 2617-2620.

[67] I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009-3066.

[68] L.E. Overman, D.J. Poon, Angew. Chem. Int. Ed. 36 (1997) 518-521.

[69] M.S. Sigman, M.J. Schultz, Org. Biomol. Chem. 2 (2004) 2551-2554.

[70] Y. Fujiwara, I. Noritani, S. Danno, R. Asano, S. Teranishi, J. Am. Chem. Soc. 91 (1969) 7166-7169.

[71] M.A. Campo, Q. Huang, T. Yao, Q. Tian, R.C. Larock, J. Am. Chem. Soc. 125 (2003) 11506-11507.

[72] F. Bellina, R. Rossi, Tetrahedron 65 (2009) 10269-10310.

[73] Q. Wang, R. Takita, Y. Kikuzaki, F. Ozawa, J. Am. Chem. Soc. 132 (2010) 11420-111421.

Figure Captions

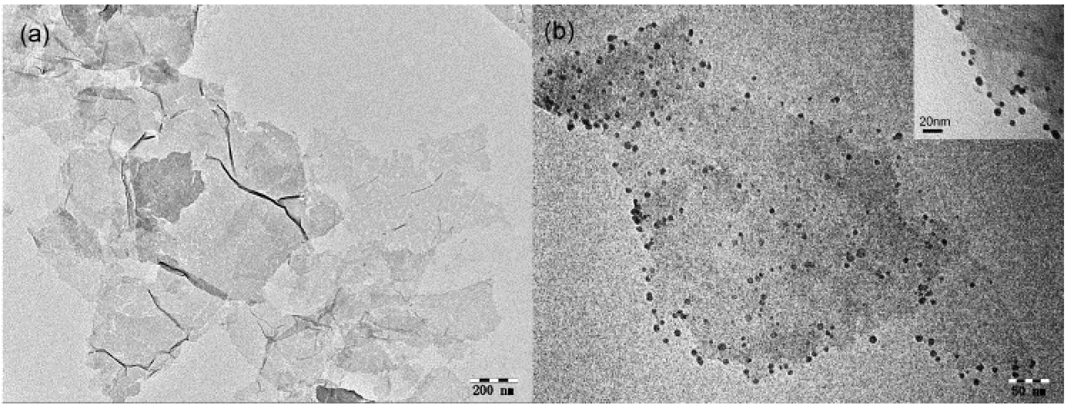


Fig. 1. Characterization of the Pd(II)-MoS_2 catalyst. (a) TEM image of the MoS_2 nanosheets scale. (b) TEM image of the Pd(II)-MoS_2 complex

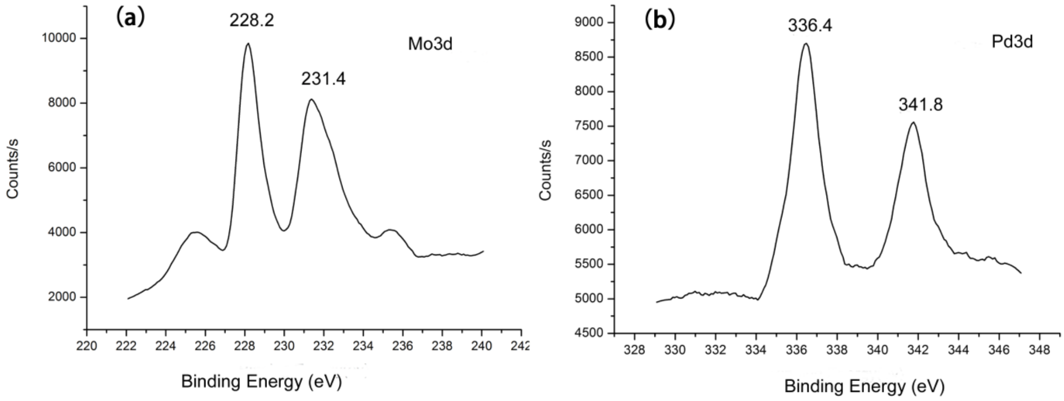
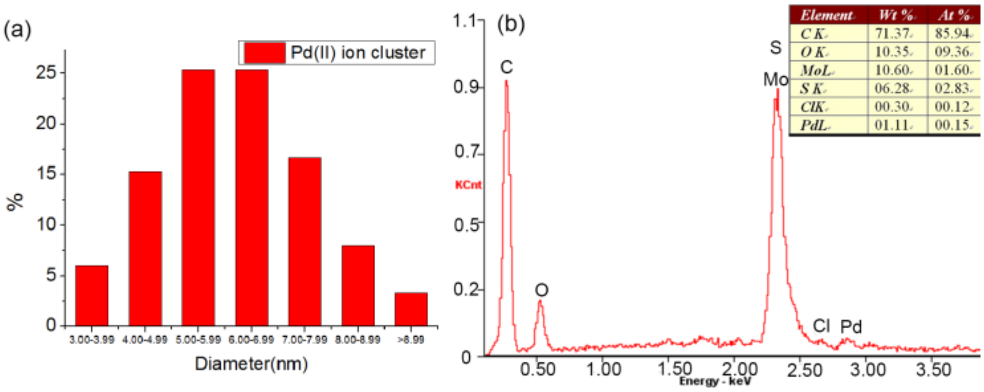


Fig. 2. Characterization of the Pd(II)-MoS_2 catalyst (a) Binding energy of Mo 3d (b) Binding energy of Pd 3d



Element	*Wt %*	*At %*
C K	71.37	85.94
O K	10.35	09.36
MoL	10.60	01.60
S K	06.28	02.83
ClK	00.30	00.12
PdL	01.11	00.15

Fig. 3. (a) Particle size distributions of Pd(II) ion cluster (b) EDX analysis for elements

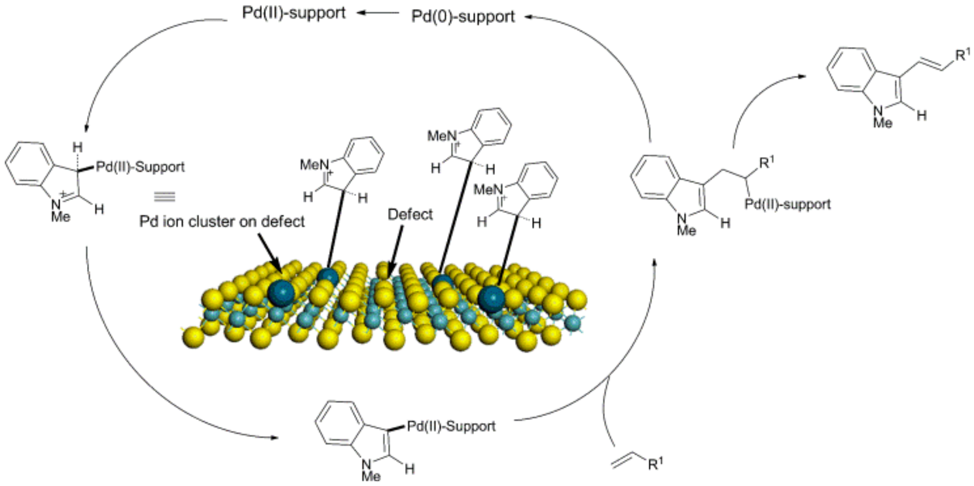
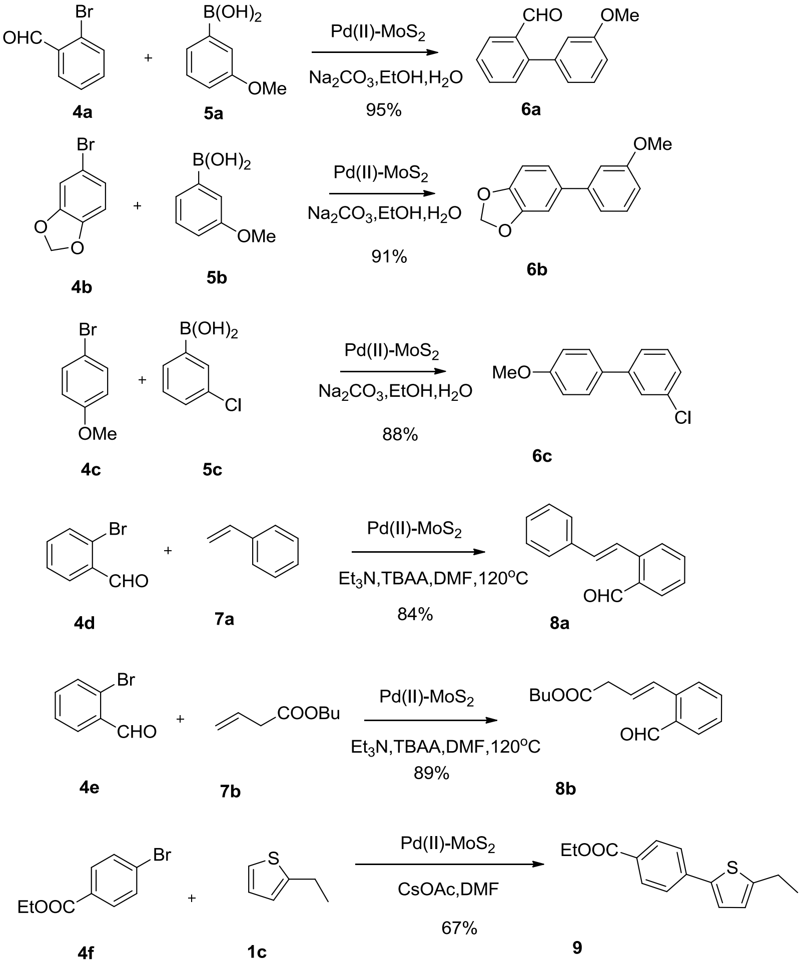


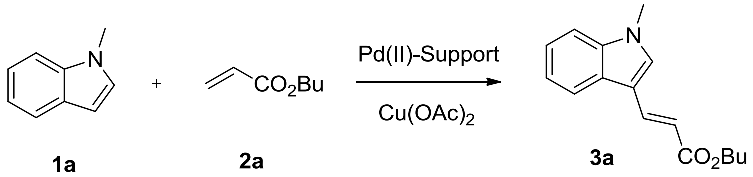
Fig. 4. Supposed mechanism of Pd(II)-MoS$_2$ catalyzed C-H activation



Scheme 1. Application of Pd(II)-MoS2 in coupling reaction

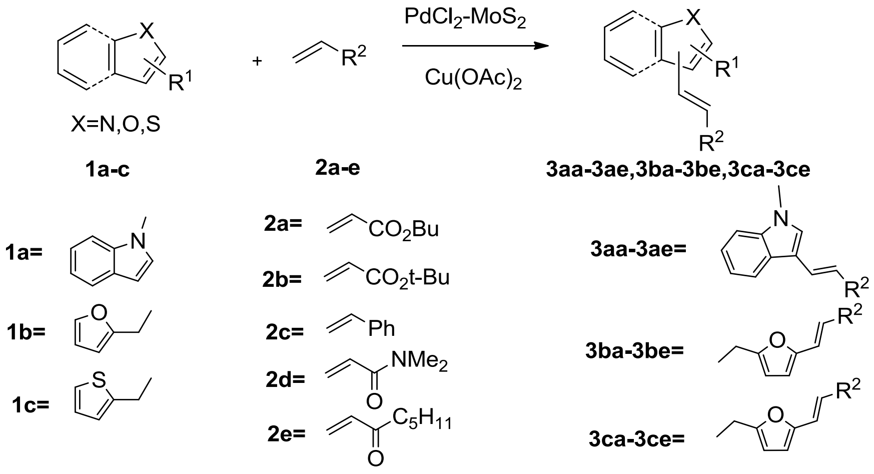
Tables

Table 1. Catalytic activity of Pd(II)-support in C-H activation



Catalyst Support	Conversion（%）
MoS_2	100
MoS_2 decorated by mercaptoethylamine	30
MoS_2 decorated by mercaptoethanol	0
MoS_2 decorated by mercaptoacetic acid	0
None	5

Table 2. System Expansion of C-H activation and oxidative coupling reaction



Entry	Compound 1	Compound 2	Product	Yield（%）
1	1a	2a	3aa	75
2	1a	2b	3ab	86
3	1a	2c	3ac	68
4	1a	2d	3ad	55
5	1a	2e	3ae	84
6	1b	2a	3ba	82
7	1b	2b	3bb	83
8	1b	2c	3bc	71
9	1b	2d	3bd	61
10	1b	2e	3be	89
11	1c	2a	3ca	74
12	1c	2b	3cb	73
13	1c	2c	3cc	67
14	1c	2d	3cd	64
15	1c	2e	3ce	82