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Mesoporous soot-supported palladium as a heterogeneous catalyst for the Heck reaction in ionic liquids

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The Heck reaction between bromobenzene and styrene in the ionic liquid catalyzed by ultrafine particles of palladium metal supported onto hydrophylized mesoporous soot follows a true heterogeneous mechanism.

The C-C coupling of an aryl halide with an olefin (the Heck reaction) mediated by supported metal Pd is commonly believed to proceed as a quasi-homogeneous process.^{1–7} This mechanism suggests that the thermodynamically non-stable Pd nanoclusters immobilized onto a porous solid play only a role of precursors of active species, which result from the interaction between reaction media and metal nanophase. Once formed, these active Pd-containing species (small clusters or metal complexes) are transferred to the liquid phase where they perform homogeneous catalytic cycles. This suggestion implicates that at the end of reaction the palladuim species return to the support pores and re-precipitate onto Pd particles larger than 'mother' ones.⁵ This re-precipitation accounts for the Ostwald aging of metal nanophase and, as a consequence, results in an irreversible loss in the catalytic efficiency, which makes it impossible to reuse a catalytic material. There are a few papers on the possibility of the direct involvement of Pd atoms located at the vertexes and edges of nanocrystals into catalytic cycles.8

The problem of whether the Heck reaction in the presence of supported Pd is heterogeneous or quasi-homogeneous exhibits a clear practical bearing connected with the not easy separation of leached Pd from the reaction mixture and almost inevitable losses of the precious metal.

The multistage catalytic cycle of the Heck reaction is highly susceptible not only to the properties of both reagents and a catalyst but also to the reaction medium. Hence, very thorough adjustment of reaction conditions, and essentially of a solvent, is required for every particular Heck arylation.⁹ In this connection, ionic liquids (ILs) have evident advantages over commonly used polar solvents not only because of being 'green solvents' but also as exhibiting rather unique combination of physico-chemical characteristics (melting point, viscosity, polarity *etc.*). These important characteristics of ILs as solvents can be readily 'task-specified' by combining the cation and anion constituents of an ionic liquid.¹⁰

Here, we report on the catalytic properties of Pd nanoclusters immobilized onto mesoporous acetylene soot using a tetraalkyl-ammonium-based IL as a solvent.^{\dagger}

After thermooxidative and acid hydrophilisation of starting soot, its surface exhibits a mosaic structure consisted of spatially separated graphite-like domains (nanographenes) over an amorphous carbon substrate. Metallic palladium presents in Pd/C as nanocrystals with an average diameter of 4–5 nm. Note that the size distributions of both Pd particles and support mesopores are similar, which is indicative of predominant location of Pd nanocrystals inside of the support pores.

The comparison of turnover frequencies (TOF) obtained using NaOAc and Bu₂NH bases showed that amine added is about twice as efficient as additive than acetate. This result is in contrast to the data of Köhler et al.7 where the Heck reaction performed in N-methylpyrrolidone showed quite opposite efficiency for these bases. Such a different behaviour of ionic and molecular solvent in the biphase system composed of a liquid with dissolved reagents and a solid containing the active moiety can be attributed to the different properties of these two media. First, effective diffusion coefficients in ILs are lower by 1.5-2 orders of magnitude than that in both polar and apolar solvents.¹⁰ In addition, the ILs exhibit medium range ordering that has dramatic consequence for the diffusion mechanism in these solvents.¹¹ Therefore, ILs act as low-polarity media with non-polar compounds, while the transport of polar and ionic species is strongly hampered. Second, of great importance is the non-polarity of tetraalkylammonium ILs, even more so for those ILs with bistriflimide anions bearing two electron acceptor Me groups.¹⁰ These ILs cannot, in principle, act as ligands to stabilize small metal nanoclusters or complexes by this way preventing them from aggregation. As to molecular solvents, their polarity is the key factor for stabilization of colloid Pd nanoparticles, clusters etc.9 Note that the Pd/C catalyst displays no activity in the Heck reaction when using an apolar molecular solvent.⁵ A poor solvation ability, if any, of the IL used in our study strongly prevents the leaching of Pd from the supported catalytic material upon reaction. This makes it next to impossible for the Heck reaction to proceed via a quasihomogeneous mechanism and vice versa favours the classical Langmuir-Hinshelwood to be operative.

 $^{^\}dagger$ The 5 wt% Pd/C was prepared by the reduction of Pd^{II} hydroxide freshly precipitated upon the hydrophilized acetylene soot A100 (200 m² g⁻¹). The catalytic reaction between bromobenzene (PhBr) and styrene (PhC₂H₃) giving stilbene (Ph₂C₂H₂) was carried out at 140 °C under Ar using NaOAc, Bu₂NH or Bu₃N as bases and tributylhexyl-ammonuim bistriflimide IL (mp 19 °C) as a solvent. The starting carbon support, as well as the Pd/C catalyst, was characterized by AAS, N₂ BET, TEM, HEED, SAXS and ¹H NMR. The qualitative and quantitative analysis of reactants and products was performed by GLC and MALDI-TOF MS.



Figure 1 (1) Conversion of bromobenzene, yields of (2) stilbene and (3) biphenyl vs. reaction time; reaction conditions: (a) $0.1 \mod Pd/C$ catalyst (not preactivated, see the text); (b) $0.1 \mod Pd/C$ catalyst (preactivated, see the text).

The assumption that the Heck reaction catalyzed by supported Pd using a finely 'tuned' IL as a reaction medium may proceed as a true heterogeneous one is supported, though indirectly, by the results of a kinetic study. The typical kinetic curves are given in Figure 1(a). On the one hand, the reaction starts with no visible induction period that would be characteristic of quasihomogeneous process,¹² provided the accumulation of the active Pd-containing species in a liquid phase. On the other hand, the kinetic curves obtained in tetraalkylammonium IL exhibit the well-pronounced reflection points, which are typical of an autoacceleration accompanying the main reaction regardless the progressive reagent consumption. If the fresh sample Pd/C is first heated at 140 °C for 10 h in the presence of dibutylamine using the tetraalkylammonium IL as a solvent and then the starting PhBr, PhC₂H₃ and Bu₂NH (1:1:1.2 molar ratio) are introduced in the reaction system, the value of TOF increases by a factor of 2, the reflection point on the kinetic curve disappears and the reaction rate decreases gradually on the consumption of PhBr [Figure 1(b)]. A blank experiment on heating Pd/C in IL in the absence of Bu₂NH showed no catalyst activation.

Therefore, the slow stage of metal Pd activation initiated by an amine base that occurs in parallel with the main C–C crosscoupling is likely to explain an unusual profile of kinetic curve [Figure 1(*a*)] resulted from the experiment omitting the step of preliminary catalyst activation. Note that such an effect of supported Pd activation in the presence of amine base was not reported earlier. In this connection, the question arises whether the same activation mechanism as was shown for the quasihomogeneous mechanism is taking place with amine base. Significantly, neither NaOAc nor Bu₃N activate the supported Pd/C catalyst but Bu₂NH only.

Supposing the low-coordinated palladium atoms to operate as active centers staying bonded to the nanocrystal surface, the mechanism of palladuim activation by Bu_2NH can be depicted in the following way. First, these reactive Pd(0) atoms undergo oxidative addition to dibutylamine N–H bond and then by surface migration shift to more stable positions on the face of nanocrystal. It is easy to ascertain using a 3D model of the FCC metal Pd framework that such a migration results in an increase in the nanocrystal deficiency, *i.e.*, the generation of new active centers until the steady state is established. The steady-state concentration of these centers may be substantially different from the initial one according to the auto adjustment theory in heterogeneous catalysis.¹³

On addressing the mechanism of Pd nanocrystal activation, it should be taken into account that the efficiency of a catalytic system preactivated in the presence of Bu_2NH is retained after the first catalytic cycle provided that the second reaction cycle starts immediately after the first one. On adding a new portion of reagents to a mixture of IL + Pd/C, in which the complete conversion of PhBr is attained, the reaction does restart with the same rate.

Meanwhile, the 24 h time gap between the first and second catalysis cycles, as well as the lowering of temperature down to 25 °C, reduces noticeably the preactivation effect. This result is consistent with the catalyst autoadjustment mechanism mentioned above. Indeed, on changing the conditions of interaction between catalysts and reaction media, the steady-state concentration of active sites also shifts to its initial value.

The above results point out that performing the Heck reaction in the tetraalkylammonium IL affords the re-use of catalytic system with no significant loss in its efficiency.

The Heck reaction mediated by Pd supported on mesoporous soot as a classical heterogeneous process by no means excludes the sintering of catalyst active component *via* the surface diffusion of metal atoms from small clusters to larger particles enhanced by the presence of Bu_2NH . Here, the features of sootbased support are very likely the key factor hampering this diffusional transport of Pd within its pores. In contrast to an activated carbon support, the mosaic surface of which exhibits high interdomain barriers, the mesoporous acetylene soot displays almost 'metallic' conductivity. Such a peculiarity of soot-based support equalizes the electrochemical potential of spatially separated Pd nanoclusters and in this way it endows their assembly with the property of bulk metal. The lack of chemical potential gradient explains why there is no palladuim transfer between the particles of different sizes.

Two important results obtained in this investigation provide the plain evidence of a true heterogeneous mechanism of the Heck reaction in the presence of soot-supported palladium. First, after preactivation of Pd/C in IL at 140 °C for 5 h and separation of solid catalytic material from the liquid phase this latter does not catalyze the Heck arylation and there is no palladium traces in this liquid. Second, the Heck reaction completed, both the morphology and average diameter of palladium particles were found to be quite similar to those in the asprepared Pd/C sample. We believe that this finding could be considered as providing a strong evidence for the lack of solvation–reprecipitation and hence the metal loss effects that were well documented⁵ on using molecular NMP solvent.

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References

- 1 S. S. Pröckl, W. Kleist and K. Köhler, Tetrahedron, 2005, 61, 9855.
- 2 A. Bifis, M. Zecca and M. Basato, J. Mol. Catal. A: Chem., 2001, 173, 249.
- 3 C. R. LeBlond, A. T. Andrews, Y. Sun and J. R. Sowa, *Org. Lett.*, 2001, **3**, 1555.
- 4 M. T. Reetz and E. Westerman, Angew. Chem., 2000, 112, 165.
- 5 R. G. Heidenreich, J. G. E. Krauter, J. Pietsch and K. Köhler, J. Mol. Catal. A: Chem., 2002, 182–183, 499.
- 6 K. Köhler, R. G. Heidenreich, J. G. E. Krauter and J. Pietsch, *Chem. Eur. J.*, 2002, **8**, 622.
- 7 F. Zhao, K. Kuracami, M. Shirami and M. Arai, J. Catal., 2000, 194, 479.
- 8 J. Le Bars, U. Sprecht, J. S. Bradley and D. G. Blackmond, *Langmuir*, 1999, **15**, 7621.
- 9 I. P. Beletskaya and A. V. Cheprakov, Chem. Rev., 2000, 100, 3009.
- 10 L. A. Aslanov, M. A. Zakharov and N. L. Abramycheva, *Ionnye zhidkosti v ryadu rastvoritelei (Ionic Liquids as Solvents)*, Izdatel'stvo Moskovskogo Universiteta, Moscow, 2005, p. 271 (in Russian).
- 11 C. Chiappe, Monatsch. Chem., 2007, 138, 1035.
- 12 V. Părvulescu and J. Hardacre, Chem. Rev., 2007, 107, 2615.
- 13 G. K. Boreskov, Geterogennyi kataliz (Heterogeneous Catalysis), Nauka, Moscow, 1988 (in Russian).

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