

New directions in organic synthesis: silver-catalyzed Sonogashira cross-coupling of chlorobenzene and phenylacetylene

Noe Orozco Corrales, Carlos Sanchez Sanchez, Agustin Rodriguez Gonzalez-Elipe, Lety Feria, Javier Fernandez Sanz and Richard M. Lambert

Instituto de Ciencias de Materiales de Sevilla (CSIC), C/ Américo Vespucio 49, Sevilla, Spain
noe.orozco@icmse.csic.es

Abstract

Metal-catalyzed Sonogashira coupling reactions that lead to the formation of new C-C bonds are of strategic importance in synthetic organic chemistry [1]. They provide a powerful and flexible method for systematically and efficiently constructing complex molecular architectures from suitably tailored building blocks. This chemistry is almost always carried out *homogeneously* using expensive organometallic complexes of palladium as catalysts. It is now the most important method for preparing arylalkynes and conjugated enynes, which are key precursors in the synthesis of natural products, pharmaceuticals, and molecular organic materials. The ability to carry out such reactions *heterogeneously* by means of suitable *low cost* nanoparticle catalysis is a highly desirable goal because of the well-known operational advantages of heterogeneous over homogeneous methodology. Moreover, the availability of inexpensive and air-stable nanoparticle catalysts capable of carrying out Sonogashira coupling with *low-cost aryl chlorides* (as opposed to expensive aryl iodides) would greatly expand the possibilities for scale-up and technological implementation of Sonogashira coupling [2]. Here, by means of single crystal experiments involving STM and temperature programmed reaction (TPR) supported by DFT calculations, we show that the Ag(100) surface catalyzes Sonogashira coupling of chlorobenzene (ClBz) and phenyl acetylene (PA), thus meeting both the above stated objectives. It is found that both reactants show a pronounced tendency to form islands on extended terraces, thus inhibiting cross-coupling activity which is thought to occur where island boundaries are proximate (Figure 1A and B). Consistent with this view, deliberately roughening the surface so as to limit island size results in the onset of Sonogashira coupling. In this way, simultaneous co-adsorption of PA and ClBz from an approximately equimolar vapour under UHV conditions followed by TPR measurements showed that homocoupling of PA to diphenyldiacetylene (DPDA) and of Chlorobenzene to biphenyl (BP) occurred. Most importantly, Sonogashira cross coupling of the two reactants to yield diphenylacetylene (DPA) was also observed (Figure 1C). These findings open the door to the design and development of optimized Ag nanoparticle catalyst systems.

References

- [1] Rafael Chinchilla and Carmen Najera, Chemical Reviews, Vol. 107 Issue 3 (2007) 874.
- [2] Robin B. Bedford, Catherine S.J. Cazin, Debbie Holder, Coordination Chemistry Reviews, 248 (2004) 2283.

Figures

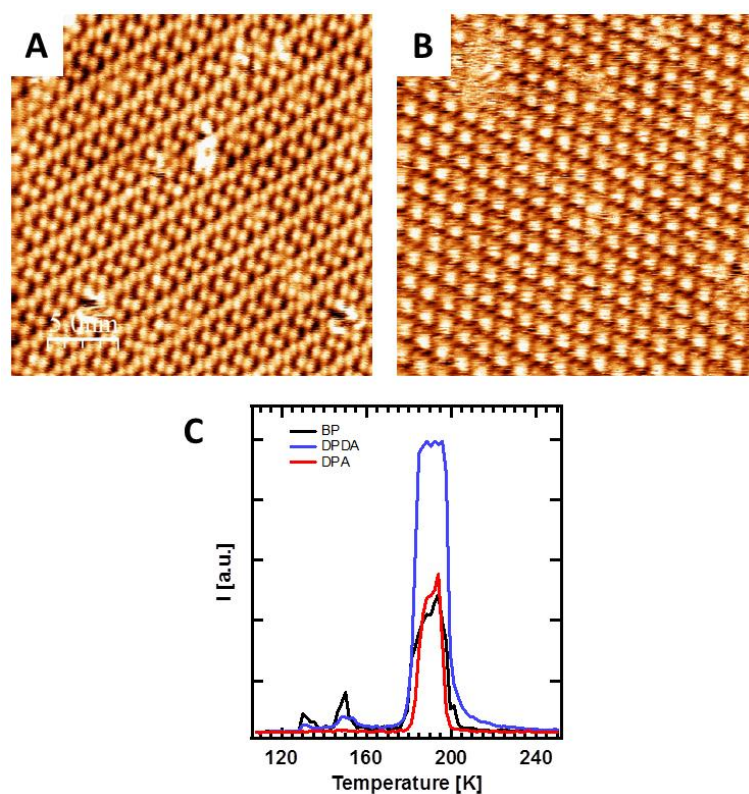


Figure 1.- **A.** STM image of PA structures on clean Ag(100) surface after annealing at 200K for 10 minutes. $T = 115\text{K}$, $(15\text{nm} \times 15\text{nm})$ $I = 0.40\text{nA}$, $V = 2.3\text{V}$. **B.** STM image of CIBz hexagonal structure obtained after annealing at 240K for 10 minutes. $T = 115\text{K}$, $(25\text{nm} \times 25\text{nm})$ $I = 0.44\text{nA}$, $V = 1.9\text{V}$. **C.** TPR spectra for the reaction products obtained after co-adsorption of CIBz and PA.

