

Metal catalyzed Sonogashira coupling reaction is a heterogeneous process: a study by model and practical catalysts

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Introduction

C-C coupling reactions are of paramount importance in many applications^[1,2]. They represent an important strategy in synthetic organic chemistry, yet the fundamental mechanism remains highly controversial. The key issue is whether the catalysis occurs *heterogeneously* at the surface of transition metal nanoparticles (Pd, Rh, Au...) or whether it occurs *homogeneously*, induced by transition metal complexes in solution, derived from the metal nanoparticles^[1,2]. Despite the number of attempts to resolve the issue but insufficiently rigorous control of various reaction variables hinders the understanding.

In this study we have followed a dual approach in order to address this problem. Firstly by studying Sonogashira coupling of phenyl iodide and phenyl acetylene catalyzed by rhodium nano clusters as a function of reaction variables such as particle size, base, solvent and extent of metal leaching. Secondly, by investigating the same reaction on Au (111) surface under ultra high vacuum conditions where any possibility of homogenous catalysis is totally excluded, thus providing an unambiguous test.

The data obtained using Rh nanoparticles to catalyze the reaction in the liquid phase show that the reaction occurs heterogeneously, and not homogeneously. Even more strikingly, in ultra high vacuum on gold single crystal surfaces, where homogeneous catalysis is precluded, efficient Sonogashira coupling is found. This represents the clearest ever demonstration of the heterogeneous mechanism. Moreover, the observation that extended gold surfaces are effective catalyst for such reaction is unprecedented.

Materials and Methods

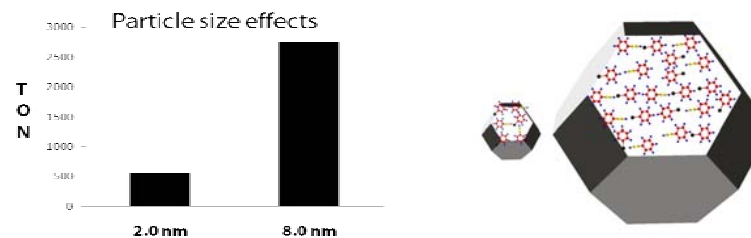
Rhodium nitrate precursor was procured from Chempur Germany. Phenyl acetylene, Iodobenzene and TBAA, superhydride was procured from Sigma Aldrich. Rhodium nanoclusters were synthesized by super hydride^[3] and Polyol-PVP reduction^[3] methods. Rhodium nano particle catalyzed Sonogashira reaction was performed in a carausel reactor and products were analyzed by Gas Chromatography coupled with Mass Spectrometer. Temperature desorption reactions experiments of Sonogashira reactions were performed on Au (111) single crystal under UHV conditions with base pressure 1×10^{-11} mbar equipped with

Low Energy Electron Diffractions (LEED), Auger Electron Spectroscopy (AES) and Quadrupole Mass Spectrometer. Molecules were dosed by means leak valve in to the UHV chamber.

Results and Discussion^[4]

Using rhodium nanoparticles in solution we show that over a wide range of conditions essentially all the observed catalytic activity can be ascribed to the Rh particles with a negligible contribution from Rh species in solution.

Moreover, we find a clear particle size effect—bigger particles are more effective than small ones, the opposite of what is usually reported. This dependence of particle size reinforces our principal conclusion, namely that the catalytic reaction is heterogeneous.



Schematic illustrative size effects

We may rationalize since it is apparent that the reactants may be readily accommodated on a single facet of the large NP, but not on the small NP. Moreover, in the case of the small NP, there is a higher probability of adsorption at a facet edge, where bond-breaking may lead to molecular decomposition. The supported NPs reflect their improved spatial distribution which would act to reduce or eliminate the adverse effect of mass transfer limitations on reaction rates, especially in the case of small NPs.

The observation of Au (111)-catalyzed Sonogashira coupling under UHV conditions is unprecedented; the reaction follows zero order kinetics implying that the reactants form islands on the surface. It is found that both Sonogashira cross-coupling and homocoupling of phenylacetylene are highly sensitive to the details of the surface structure: smooth Au(111) is effective whereas the roughened surface is no. This is entirely in keeping with our finding that the nanoparticle-catalyzed reaction shows a pronounced particle size effect, big particles being more efficient than small.

In summary, we have demonstrated that at 25° C the rhodium-catalyzed Sonogashira coupling of phenylacetylene with phenyl iodide is overwhelmingly a heterogeneous process that occurs on the surfaces of Rh nanoparticles. Under any given conditions, large nanoparticles are better catalysts than small ones, consistent with the hypothesis that steric limitations adversely affect the efficiency of the latter and in accord with our principal conclusion that the catalytic reaction occurs heterogeneously. The mechanisms of metal nanoparticle catalyzed C-C cross coupling reactions are highly controversial. By using model systems under ultra high vacuum conditions, we demonstrate this chemistry does indeed occur heterogeneously on Au(111) metal surface beyond doubt. The observation that gold is an effective catalyst is unprecedented.

References

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