Angewandte Chemie

Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Pd nanoclusters in Cross−Coupling reactions: A proof of leaching

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Experimental Section

Materials and instrumentation. GC analysis was performed using an Interscience Trace GC-8000 gas chromatograph with a 100% dimethylpolysiloxane capillary column (VB-1, 30 m × 0.325 mm). GC/MS analysis was performed using a Hewlett-Packard 5890/5971 GC/MS equipped with a ZB-5 (zebron) column (15 m × 0.25 mm). All products are known compounds and were identified by comparison of their GC retention times to those of authentic samples and by MS analysis. Samples for GC were added in equivalent amount of water, extracted with hexanes prior to injection. GC conditions: isotherm at 80 ℃ (1 min); ramp at 30 ℃ min^{-1} to 280 ℃; isotherm at 280 ℃ (3 min). Solutions were dispensed using a micropipette. Unless noted otherwise, chemicals were purchased from commercial firms and were used as received. TEM images were obtained with a JEOL-100 CXII instrument, operated at an accelerating voltage of 80 kV. At least four images were taken for each sample. X-ray Photoelectron Spectroscopy (XPS) was performed using a PHI Quantera Scanning ESCA Microprobe.

Synthesis of Pd clusters. A Schlenk-type vessel equipped with a rubber septum and a magnetic stirrer was evacuated and refilled with N_2. The vessel was then charged with Pd precursor salt solution in DMF (20 mL, 10 mM) and 2.5 mL of a 0.2 M TOAG solution in DMF was then added in one portion

at 65 ℃. The mixture was stirred for 6 h under a slight N_2 overpressure. The color of the mixture changed from dark orange to black. The resulting Pd cluster suspension was then used as a catalyst for the Sonogashira and Heck reactions.

Transmission electron microscopy (TEM) analysis. Samples were prepared by placing 150 µL of 1 mM Pd cluster suspension on the carbon-coated copper grids. The solvent was evaporated at 50 ℃ at 250 mm of Hg. The cluster size distribution was determined by counting the size of 85 particles.

Membrane analysis. The γ-alumina membrane was characterized by permporometry. The pore size (d, in nm) is defined by $d = 2·(r_K + t)$, where r_K is the Kelvin radius, and t the layer thickness of the t-layer (~0.3 nm).
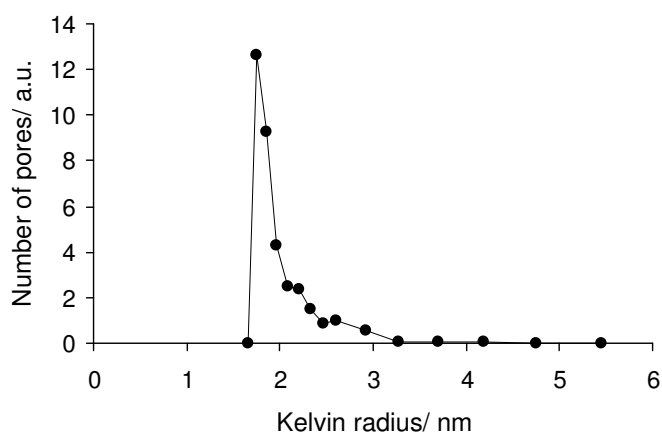
Figure S1. Pore size distribution found using permporometry method.

Description of the membrane reactor. The stainless steel membrane reactor consists of two compartments (referred as side **A** and side **B**) divided by an γ-alumina membrane. Each compartment can handle 75 ml of liquid. The o-ring made of Buna-n tightens the membrane and also make the installation free of leaks. The reactor also has the connections for applying inert atmosphere. The reactor equipped with two magnetic stirrers (one in each compartment) was placed in the oil bath and the reactions were performed under N_2 atmosphere.

Sonogashira coupling of phenylacetylene with iodobenzene using the Pd clusters in the membrane reactor. The phenylacetylene (4 ml, 750 mM, 3.0 mmol), iodobenzene (0.40 g, 2.0 mmol) and TBAA (4 ml, 750 mM, 3.0 mmol) were placed on side **B** of the membrane reactor. Pd cluster suspension (3 ml, 10 mM, 1.0 mol%) prepared in DMF was added on side **A**. The total volume of DMF on each side was 50 ml. The reactor was heated at 70 ºC and the samples from both the sides were analyzed using GC.

XPS study of the γ-alumina membrane used for the Pd clusters retention. The elemental composition of the γ-alumina layer on and below the surface after membrane reactor experiments was determined by XPS. After determining the elements present in the system, the C $1s$, N $1s$, Na $1s$, Al $2p$, O $1s$, Fe $2p$, Pd $3d$ and I $3d$ peaks were measured. Measurements were done at several selected spots on the membrane surface. To obtain the elemental composition of the γ-alumina membrane at a depth of about 40 nm below the surface, the surface layer was removed by sputtering an area of 3×3 mm with 2 keV Ar^+ ions (estimated sputter rate 5.1 nm/min), and spectra were recorded. Hydrogen cannot be detected by XPS. The main elements found are Al, O, C and N. These can be attributed to the mesoporous $\gamma\text{-}Al_2O_3$ phase, and the reactants and solvent used in the reaction. Carbon is also a naturally present element in all samples. The trace elements Na, Pd and I can all be attributed to the reactants, base, solvent and/or catalyst that were used in the Heck reaction.
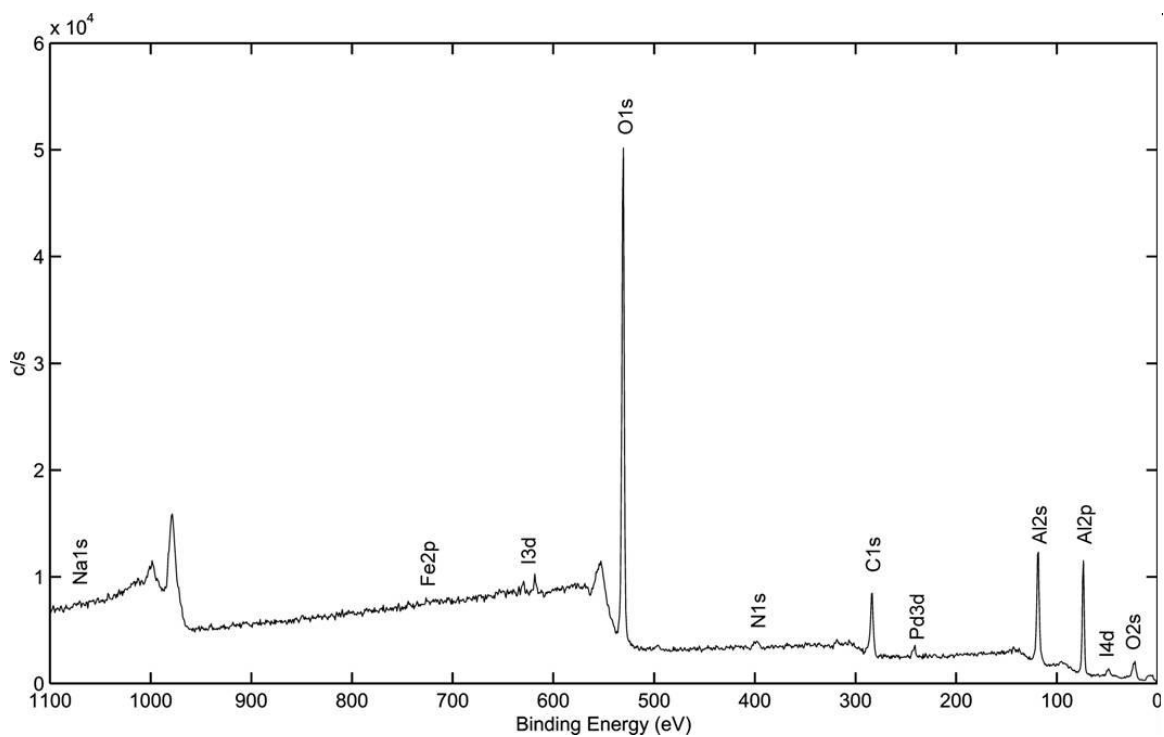
Table S1. Atomic concentration of elements found using XPS.

Element	Atomic concentration (at %)	
	Surface	Sub-surface
C	23.74	19.15
N	2.61	2.08
O	49.93	51.42
Na	0.15	0.04
A	23.29	27.10
Fe	0.18	0.00
Pd	0.02	0.05
I	0.08	0.16