

## **PdCu/Al<sub>2</sub>O<sub>3</sub> catalyst for Sonogashira cross-coupling: effect of a Pd/Cu ratio on the catalytic performance**

**Aleksandr V. Rassolov, Galina N. Baeva, Igor S. Mashkovsky and Aleksandr Yu. Stakheev**

### *Catalysts preparation*

For preparation of Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalyst with different Cu/Pd ratios (Cu/Pd ratio = 0.5, 0.67, 1, 1.5, 2, 3, and 4) pre-calcined support ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $S_{sp} = 8 \text{ m}^2/\text{g}$ , «Alfa Aesar») was impregnated with corresponding solutions of 10%Pd(NO<sub>3</sub>)<sub>2</sub>/10%HNO<sub>3</sub> and Cu(NO<sub>3</sub>)<sub>2</sub>•3H<sub>2</sub>O. After impregnation all samples were dried at room temperature, calcined in an air flow (550°C, 4 h) and then reduced in 5 vol. % H<sub>2</sub>/Ar flow (550°C, 1 h). For all synthesized catalysts metal content was 3 wt.% Pd.

Monometallic Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> samples were also prepared using described above technique.

For preparation of physical mixtured catalysts Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> obtained as described above were thoroughly grinded to powder in corresponding amounts to attain Pd<sub>1</sub>-Cu<sub>0.5</sub>, Pd<sub>1</sub>-Cu<sub>1</sub>, and Pd<sub>1</sub>-Cu<sub>2</sub> ratios in a final catalyst.

### *X-ray diffraction (XRD)*

XRD powder diffractograms were registered on a D8 Advance diffractometer (Bruker, Germany; CuK $\alpha$ , Ni filter, LYNXEYE detector, reflection geometry). The identification of peaks was performed with the PDF-2-2014 database. The experimental details were reported elsewhere.<sup>1</sup> The composition of the Pd-Cu nanoparticles was evaluated according to the Vegard's law using the parameters of the Pd-Cu crystal lattice.<sup>2</sup>

### *Transmission electron microscopy (TEM)*

The microstructure of the samples was studied on a Hitachi HT7700 (Japan) instrument at the Center of Collective Use of the Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. The optimization of microscopic measurements was carried out within the framework of described approach.<sup>3</sup> In accordance with standard technique before the measurements, powdered

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<sup>1</sup> A. V. Gavrikov, P. S. Koroteev, Zh. V. Dobrokhotova, A. B. Ilyukhin, N. N. Efimov, D. I. Kirdyankin, M. A. Bykov, M. A. Ryumin and V. M. Novotortsev, *Polyhedron*, 2015, **102**, 4.

<sup>2</sup> A. G. Bagmut, I. G. Shipkova and V. A. Zhuchkov, *J. Surf. Invest.: X-Ray, Synchrotron Neutron Tech.*, 2011, **5**, 460.

<sup>3</sup> V. V. Kachala, L. L. Khemchyan, A. S. Kashin, N. V. Orlov, A. A. Grachev, S. S. Zalesskiy and V. P. Ananikov, *Russ. Chem. Rev.*, 2013, **82**, 648.

samples were supported from a suspension in isopropanol onto copper gauzes (o.d. = 3 mm) covered with a layer of carbon. The images were obtained in the transmitted electron detection mode (bright field imaging) at an accelerating voltage of 100 kV. The average size of metal particles was determined based on the measurement of 180–200 particles in the micrographs of different sections of the samples.

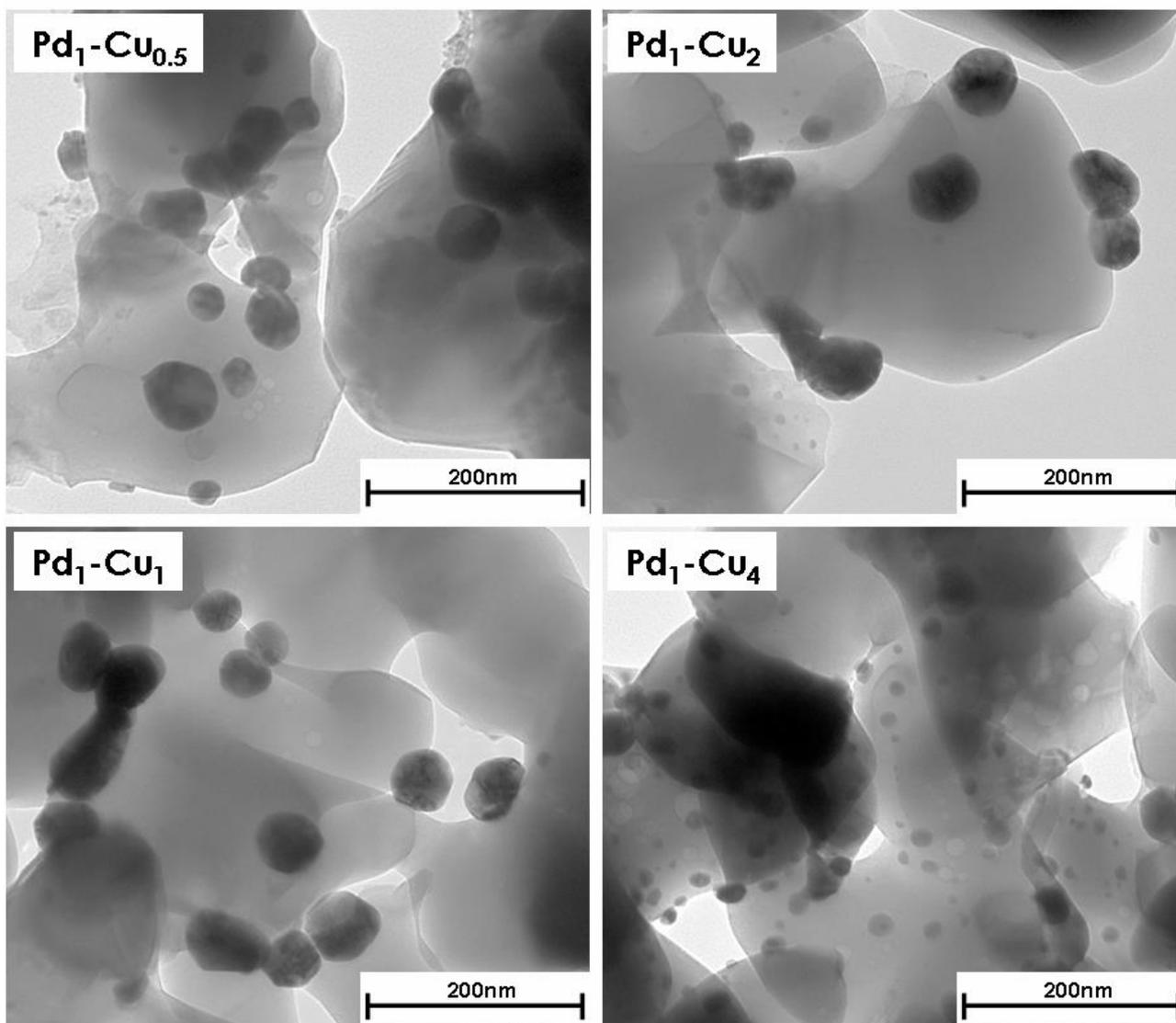
#### *Sonogashira cross-coupling*

Typical procedure for Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalyzed Sonogashira coupling reaction is as follows. Phenyl iodide (1 mmol, 112 µl), catalyst (0.01 mmol, 35.5 mg), pyrrolidine (5 mmol, 410.6 µl,) and DMF (2 ml) were added to flask under aerobic conditions. The resulting mixture was stirred at 80°C for 5 min and then phenylacetylene was added (1.5 mmol, 164.7 µl) and the reaction mixture was stirred at 80°C for a specific time.

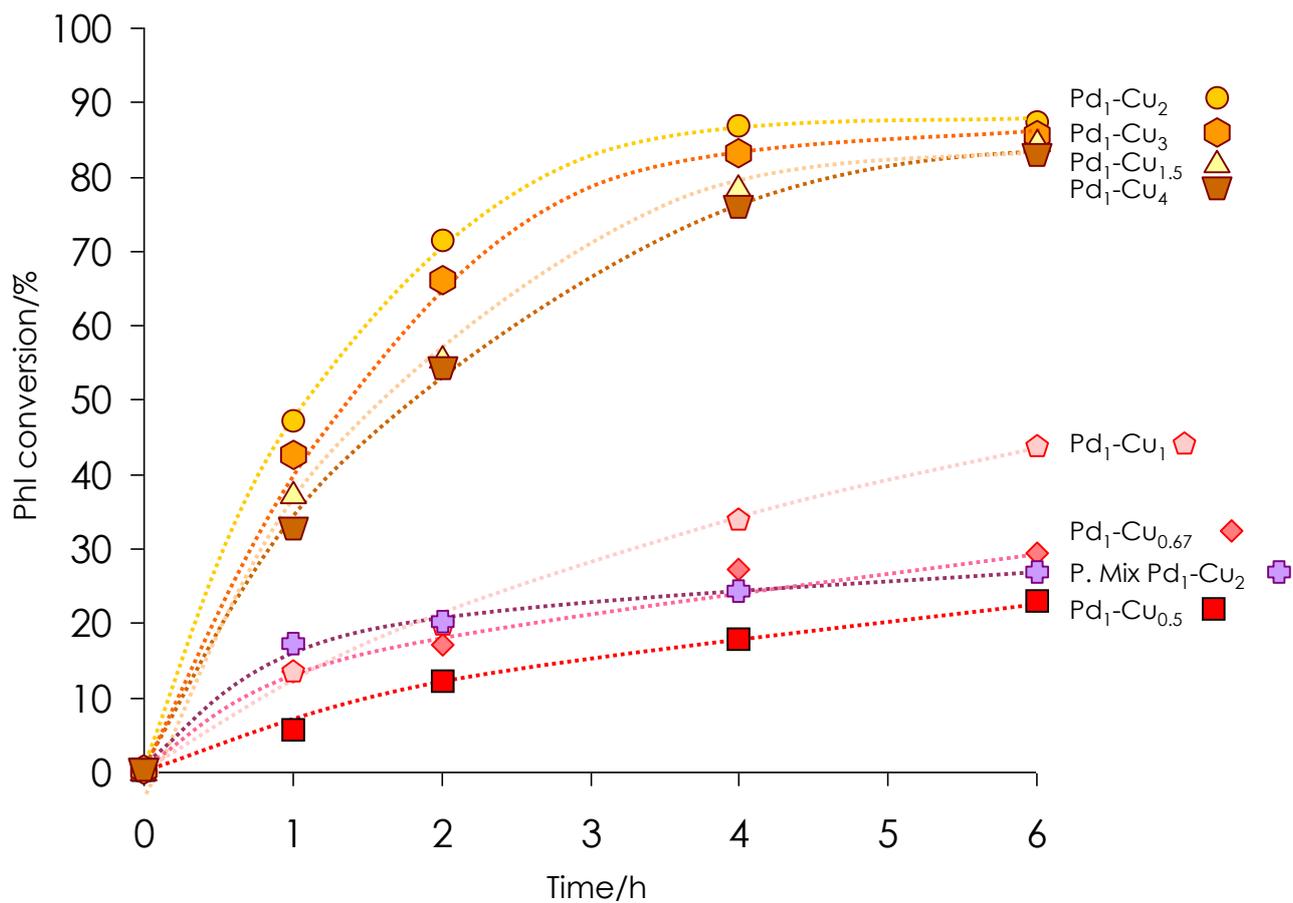
After the completion of the reaction the mixture was cooled to room temperature and solid catalyst was separated by centrifugation. The resulting mixture was decanted, diluted with water (10 ml) and extracted with ethyl acetate (3x10 ml). The combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the desired product was isolated by flash chromatography using hexane/ethyl acetate (35:1).

The reaction products were analyzed on a Crystal 5000 chromatograph (Chromatek, Russia) equipped with a flame-ionization detector and an HP5-MS column (5% phenyldimethylsiloxane; 30 m × 0.25 mm ID with stationary phase film thickness 0.25 µm; with helium as carrier gas).

All reagents and solvent were obtained from commercial suppliers and were used without further purification.



**Figure S1** Representative TEM micrographs of the bimetallic Pd-Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst with various Pd/Cu ratios.



**Figure S2** Dependence of iodobenzene conversion (%) on the reaction time for Pd-Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst with various Pd/Cu ratios.