Electronic supplementary materials *Mendeleev Commun.*, 2016, **26**, 502–504

Pd–Cu catalyst prepared from heterobimetallic $PdCu_2(OAc)_6$: an XRD-EXAFS study and activity/selectivity in the liquid-phase hydrogenation of a C≡C bond

Pavel V. Markov, Galina O. Bragina, Aleksandr V. Rassolov, Galina N. Baeva, Igor S. Mashkovsky, Vadim Yu. Murzin, Yan V. Zubavichus and Aleksandr Yu. Stakheev

Catalyst preparation

The 1%Pd-0,6%Cu/Al_2O_3 and 1%Pd-1,2%Cu_2/Al_2O_3 samples were prepared by incipient wetness impregnation of Al_2O_3, (Sasol, S_{sp}=150 m^2/g) with acetic acid solution of $PdCu(AcO)_4$ and $PdCu_2(AcO)_6$ complexes (pH = 2.6-2.8), respectively, followed by drying overnight at room temperature, calcination (air, 550°C, 4 h) and reduction (5%H_2/Ar, 500°C, 1 h) before catalytic measurements.

Catalytic tests

Catalytic measurements were carried out in a stainless-steel autoclave-type reactor at 10 atm H_2, 25°C in *n*-hexane (98%, «Merck») as a solvent.

Dependence of Pd-Cu_2/Al_2O_3 catalytic characteristics on alkyne structure was studied in hydrogenation of the following internal and terminal alkynes: diphenylacetylene, 1-phenyl-1-propyne, 1-phenyl-1-butyne, 1-propynyl-1-cyclohexanol, phenylacetylene. All substrates were produced by «Aldrich». Alkyne/Pd molar ratio was c.a. 4000.

The GC/MS analysis of the reaction products was performed on a “Maestro-2” gas chromatograph (“Interlab”, Russia) equipped with a capillary column HP5-MS (5% phenyldimethylsiloxane, 30 m × 0.25 mm ID with film thickness 0.25 μm).

The reaction rates were measured by the rate of H_2 uptake on the first (hydrogenation of triple bond to double) and the second (alkene intermediate hydrogenation) reaction steps (r_1 and r_2, respectively).

Specific catalytic activity was evaluated by the turnover frequencies on the first (TOF_1) and the second (TOF_2) steps of the reaction calculated as the ratio of consumed H_2 molecules on the first and the second hydrogenation step, respectively, to the overall Pd atoms in the catalyst

per second. In addition to that, reaction kinetics was characterized by TOF_1/TOF_2 ratio according to[1].

Selectivity of the catalysts (S) was calculated as a molar ratio of the hydrogenation products (n_{CnH2n} and $n_{CnH2n+2}$) in the reaction mixture determined by GC/MS analysis data as:

$$S = n_{CnH2n} / (n_{CnH2n} + n_{CnH2n+2}).$$

Catalyst characterization

XRD: X–ray absorption spectroscopy and X-ray diffraction analysis were performed using techniques described elsewhere.[2] Wavelength was fixed at λ = 0.68886 Å. Phase identification was made using the PDF–2 database.[3]

EXAFS: The EXAFS spectra at Cu and Pd K–edges were measured in the fluorescence mode by means of ionization chamber filled with air and a silicon (single crystal) avalanche photodiode detector. Si (111) and Si (220) channel–cut monochromators were used for Cu and Pd, respectively. In each case corresponding metal foil was used as a standard. The EXAFS spectra were analyzed and fitted using LARCH software (version 0.9.24).[4] The effective scattering amplitudes, phase shifts and inelastic loss functions for Cu-Cu, Cu-Pd, Pd-Cu and Pd-Pd FEFF paths were calculated using FEFF6 code.[5,6] The data were weighted by k^3 and fitted in the 2.0-13.0 $Å^{-1}$ region of photoelectron wavevectors.[7]

[1] M. P. R. Spee, J. Boersma, M. D. Meijer, M. Q. Slagt, G. van Koten, J. W. Geus, *J.Org. Chem.*, 2001, **66**, 1647
[2] A. A. Chernyshov, A. A. Veligzhanin, Ya. V. Zubavichus, *Phys. Res. A: Nucl. Instrum. Methods*, 2009, **603**, 95.
[3] PDF-2 Data Base (Sets 1-47), 1997, JCPDS - International Centre for Diffraction Data.
[4] M. Newville, *J. Phys.: Conf. Ser.*, 2013, **430**, 012007−1-7
[5] J. J. Rehr, S. I. Zabinsky, A. Ankudinov, R. C. Albers, *Physica B*, 1995, **208**/**209**, 23.
[6] S. I. Zabinsky, J. J. Rehr, A. Ankudinov, *Phys. Rev. B*, 1995, **52**, 2995
[7] S. D. Kelly, S. R. Bare, N. Greenlay, G. Azevedo, M. Balasubramanian, D. Barton, S. Chattopadhyay, S. Fakra, B. Johannessen, M. Newville, J. Pena, G. S. Pokrovski, O. Proux, K. Priolkar, B. Ravel, S. M. Webb, *J. Phys.: Conf. Ser*., 2009, **190**, 012032−1-4