Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2016, **26**, 502–504
Mendeleev Communications

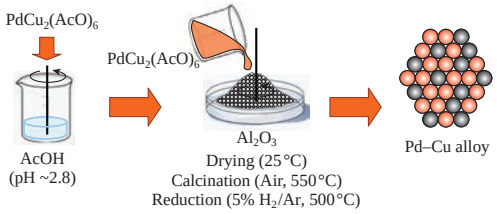
Pd–Cu catalyst prepared from heterobimetallic $PdCu_2(OAc)_6$: an XRD-EXAFS study and activity/selectivity in the liquid-phase hydrogenation of a C≡C bond

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

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: st@ioc.ac.ru*
[b] *National Research Centre 'Kurchatov Institute', 123182 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2016.11.014

The formation of a PdCu alloy with an fcc structure in 1% Pd–1.2% Cu_2/Al_2O_3 (as evidenced by XRD and EXAFS data) significantly improves catalyst selectivity in the semi-hydrogenation of internal and terminal alkynes, which makes 1% Pd–1.2% Cu_2/Al_2O_3 a promising alternative to the commercial Lindlar catalyst.



The selective hydrogenation of a carbon–carbon triple bond is widely used in the industrial synthesis of pharmaceuticals and fine chemicals and in laboratory practice.[1,2] Pd supported catalysts are the best candidates for the hydrogenation of alkynes to alkenes in terms of activity.[3] However, Pd can catalyze the undesirable hydrogenation of an olefinic bond with a loss of selectivity to alkene. An improved selectivity of a Pd catalyst for alkene formation can be achieved using bimetallic compositions (Pd–Ni, Pd–Zn, Pd–Ag, and Pd–Cu).[4–8] However, two major requirements should be met for favorable selectivity of bimetallic catalysts: (1) avoiding or minimizing the formation of monometallic Pd^0 species and (2) ensuring the identical composition of bimetallic Pd–M nanoparticles. These requirements can be fulfilled using a Pd–M precursor containing both metals. The promising example of such a compound is a Pd–M acetate complex, in which Pd and the second metal atom are linked together by acetate bridges thus remaining in tight contact during all stages of catalyst preparation and enabling the formation of uniform bimetallic nanoparticles in a final catalyst.[9–12] Previously, this method has been used for the preparation of $PdCu/Al_2O_3$ and $PdCu_2/Al_2O_3$ catalysts.[13,14] The catalysts have been studied in liquid-phase diphenylacetylene (DPA) hydrogenation, and $PdCu_2/Al_2O_3$ demonstrated the best selectivity. Transmission electron microscopy data[14] showed that the catalysts contained metal particles having average diameters of ~3.5, and PdCu alloy formation was confirmed by the FTIR spectroscopy of adsorbed CO. However, the composition of Pd–Cu species remained unclear. In order to gain better insight into a relationship between the structure of PdCu nanoparticles and their catalytic performance, we studied 1% Pd–0.6% Cu/Al_2O_3 and 1% Pd–1.2% Cu_2/Al_2O_3 catalysts by XRD and EXAFS techniques and investigated the performance of $PdCu_2/Al_2O_3$ in the hydrogenation of various internal and terminal alkynes. A commercial Lindlar catalyst (5% Pd / 4% PbO / $CaCO_3$, Aldrich) and 1% Pd/Al_2O_3 were taken as reference samples.

XRD analysis has shown that both samples contained a PdCu substitution alloy with an fcc structure (Figure 1). According to Vegard's law based on the lattice parameters of bulk metals, the ratios Pd : Cu in the samples can be evaluated as 20 : 80 and 40 : 60 for $PdCu_2/Al_2O_3$ and $PdCu/Al_2O_3$ catalysts, respectively, which are in a reasonable agreement with Pd : Cu ratios in the initial precursors. Probably, the copper fraction is overestimated due to the fact that nanoparticles are generally characterized by lattice parameters smaller as compared to respective bulk phases. One can also see that the alloy peaks are asymmetric to indicate the presence of two types of fcc structures in the samples.

EXAFS data confirm the formation of a PdCu alloy in both samples (Figure 2, Table 1) since two metals are simultaneously present in the local environments of copper and palladium atoms. In the case of a random solid solution, coordination numbers for Pd–Cu and Pd–Pd pairs (palladium coordination environment as determined from Pd K-edge EXAFS) and Cu–Pd and Cu–Cu pairs (copper environment from Cu K-edge EXAFS) should be proportional to the respective fractions of Pd and Cu in the alloy. Indeed, best-fit coordination numbers (see Table 1) are consistent with the nominal Pd : Cu ratios in the catalysts in terms that copper is more abundant in the local environment of both Pd and Cu for the $PdCu_2$ sample. Nevertheless, in all four cases (the environment of Pd and Cu in two catalysts), the fractions of heteropairs are systematically larger than those estimated from

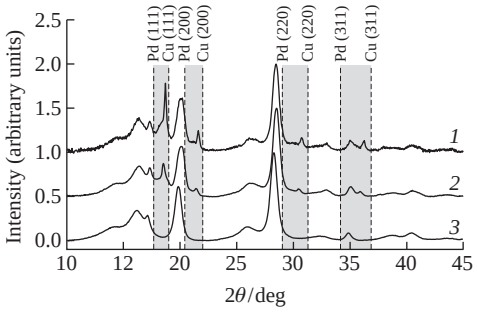


Figure 1 XRD patterns of the samples: (*1*) $PdCu_2/Al_2O_3$, (*2*) $PdCu/Al_2O_3$, and (*3*) γ-Al_2O_3. Regions between the reflexes of fcc-Cu and fcc-Pd metals are highlighted.

Table 1 Parameters obtained during EXAFS fitting.[a]

Sample	Path	R/Å	CN	σ^2/Å^2	S_0^2	ΔE/eV
Pd foil	Pd–Pd	2.750 (5)	12 (fixed)	0.0064 (3)	0.85 (fixed)	3.3 (10)
Cu foil	Cu–Cu	2.530 (4)	12 (fixed)	0.0097 (3)	1.00 (fixed)	3.3 (9)
$PdCu/Al_2O_3$	Pd–Pd	2.698 (15)	3.8 (11)	0.0084 (14)	0.85 (fixed)	–9.6 (22)
	Pd–Cu	2.587 (14)	4.2 (9)			
	Cu–Pd	2.561 (33)	2.6 (10)	0.0068 (45)	1.00 (fixed)	1.5 (27)
	Cu–Cu	2.550 (41)	2.0 (8)			
$PdCu_2/Al_2O_3$	Pd–Pd	2.711 (13)	3.1 (10)	0.0078 (11)	0.85 (fixed)	–8.6 (21)
	Pd–Cu	2.590 (14)	5.6 (10)			
	Cu–Pd	2.553 (26)	2.0 (6)	0.0047 (38)	1.00 (fixed)	2.1 (19)
	Cu–Cu	2.544 (20)	2.6 (7)			

[a] The values in the parentheses are the standard errors in the last digit as estimated by the LARCH software (version 0.9.24).

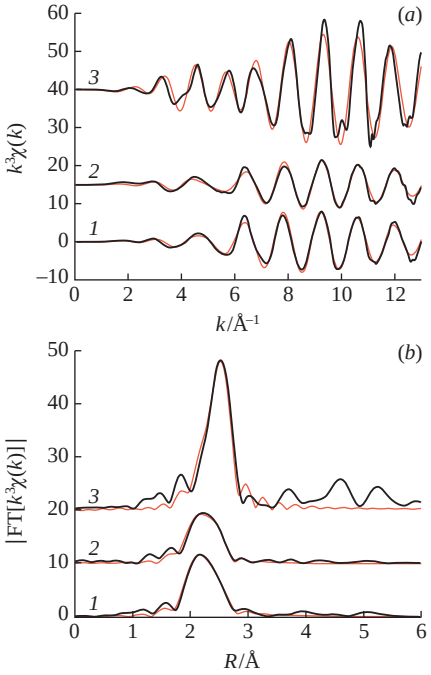


Figure 2 (*a*) EXAFS and (*b*) FT data at the Pd K-edge: (*1*) $PdCu_2/Al_2O_3$, (*2*) $PdCu/Al_2O_3$, and (*3*) Pd foil.

stoichiometry indicating a tendency towards a specific chemical short-range order similar to that in ordered intermetallic compounds. Furthermore, for both catalysts, the total coordination numbers of Pd (8.0 and 8.7 for PdCu and $PdCu_2$, respectively) are substantially larger than that of Cu (4.6 for both catalysts) and closer to 12, which implies that the palladium local environment is more ordered and bulk-like. This may be attributed to some enrichment of the surface and a subsurface layer of Pd–Cu nanoparticles in Cu, which decreases the average coordination number of Cu.[15,16]

Typical dependences of H_2 uptake on the reaction time and the relationship between selectivity to alkene and alkyne conversion are displayed in Figures 3 and 4, respectively, for diphenylacetylene hydrogenation. Experimental results for all substrates are systematized in Table 2.

Analyzing the kinetic profiles of H_2 uptake (Figure 3) and TOF values (Table 2) for mono- and bimetallic catalysts in diphenylacetylene hydrogenation, one can conclude that the reaction rate is lower for $PdCu_2/Al_2O_3$, as compared to that on monometallic Pd/Al_2O_3. This is typical of a Cu-modified Pd catalyst[17] because of the enrichment of the Pd–Cu surface in Cu.

A comparison of TOF_1 (alkyne hydrogenation) and TOF_2 (alkene hydrogenation) for Pd/Al_2O_3 and $PdCu_2/Al_2O_3$ suggests

Table 2 Kinetic parameters of liquid-phase alkyne hydrogenation at P_{H_2} = = 10 bar and T = 25 °C.

Substrate	Catalyst	TOF_1/ s^{-1}	TOF_2/ s^{-1}	TOF_1/TOF_2	Selectivity[a] (%)	
					$X^{\equiv}_{50\%}$	$X^{\equiv}_{95\%}$
Diphenyl-acetylene	$PdCu_2/Al_2O_3$	3.0	0.04	75.2	95.7	92.9
	Lindlar	0.2	0.02	8.5	98.6	94.9
	Pd/Al_2O_3	9.7	2.5	3.9	88.6	82.5
1-Phenyl-prop-1-yne	$PdCu_2/Al_2O_3$	0.3	0.04	8.3	93.6	87.0
	Lindlar	0.1	0.02	6.5	93.3	80.5
	Pd/Al_2O_3	2.3	0.6	4.1	86.8	77.9
1-Phenyl-but-1-yne	$PdCu_2/Al_2O_3$	0.06	0.01	5.9	90.4	82.0
	Lindlar	0.2	0.01	24.8	89.2	81.4
	Pd/Al_2O_3	7.5	0.2	41.8	81.8	67.4
1-(Prop-1-ynyl)-cyclohexanol	$PdCu_2/Al_2O_3$	2.4	0.05	50.6	93.2	90.5
	Lindlar	0.1	0.01	28.5	95.5	93.5
	Pd/Al_2O_3	8.7	0.4	21.0	89.1	85.9
Phenyl-acetylene	$PdCu_2/Al_2O_3$	4.1	0.8	5.2	93.8	90.0
	Lindlar	0.3	0.15	2.1	96.5	90.5
	Pd/Al_2O_3	2.7	1.7	1.6	90.3	78.5

[a] Selectivity was determined at alkyne conversions of 50% ($X^{\equiv}_{50\%}$) and 95% ($X^{\equiv}_{95\%}$).

that Cu modification affects hydrogenation activities in alkyne and alkene hydrogenation in different ways: while TOF_1 decreases by a factor of 3 (from 9.71 to 3.04 s^{-1}), TOF_2 (alkene hydrogenation) decreases by a factor of 60 (from 2.47 to 0.04 s^{-1}). As a result, TOF_1/TOF_2 increases from 3.9 for Pd/Al_2O_3 to 75.2 for $PdCu_2/Al_2O_3$, and the dependence of H_2 uptake on the reaction time for $PdCu_2/Al_2O_3$ exhibits pronounced downward bending after consumption of 1 equiv. of H_2 (Figure 3). Such significant inhibition of the reaction rate of the undesired double bond hydrogenation favors effective kinetic control of the process.

The analysis of reaction products revealed a significant improvement in the selectivity for alkene formation on $PdCu_2/Al_2O_3$ within the whole range of diphenylacetylene conversions (Figure 4). Thus, at a conversion of 95%, selectivity for $PdCu_2/Al_2O_3$ is ~93%, which is close to the selectivity of the commercial Lindlar catalyst (~95%) and significantly higher than that for monometallic Pd/Al_2O_3 (~83%).

As can be seen in Table 2, $PdCu_2/Al_2O_3$ demonstrates similar characteristics in the hydrogenation of asymmetrical alkynes [1-phenylprop-1-yne and 1-(prop-1-ynyl)cyclohexanol]. For these substrates, hydrogenation rates decrease at both stages of the process, but a more pronounced deceleration is observed at the second hydrogenation stage (undesired alkene to alkane conversion). Therefore, TOF_1/TOF_2 ratios are significantly higher for $PdCu_2/Al_2O_3$ than those for monometallic Pd/Al_2O_3, or for Lindlar catalysts, which facilitates the kinetic control of hydrogenation over $PdCu_2/Al_2O_3$.

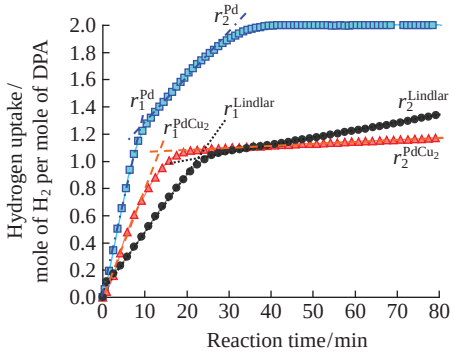


Figure 3 Typical dependence of hydrogen uptake on the reaction time for $PdCu_2/Al_2O_3$, Pd/Al_2O_3 and Lindlar catalysts in the liquid-phase hydrogenation of diphenylacetylene.

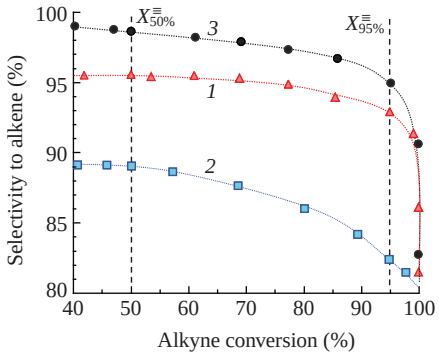


Figure 4 Selectivity for alkene as a function of alkyne conversion on Pd and PdCu supported catalysts in DPA hydrogenation: (*1*) $PdCu_2/Al_2O_3$, (*2*) Pd/Al_2O_3, and (*3*) Lindlar catalyst.

The only exception is revealed in case of 1-phenylbut-1-yne. For this substrate, the TOF_1/TOF_2 ratio for $PdCu_2/Al_2O_3$ becomes lower than those for Pd/Al_2O_3 and the Lindlar catalyst (5.9, 24.7 and 41.8, respectively), and one can observe an opposite trend in variations of TOF_1/TOF_2 ratios for the catalysts under study, as compared to other substrates: Pd/Al_2O_3 > Lindlar catalyst > $PdCu_2/Al_2O_3$.

An analysis of the kinetic data shows that such an unusual trend originates from an exceptionally high reaction rate over Pd/Al_2O_3 at the first hydrogenation stage and its significant reduction for the Lindlar catalyst and $PdCu_2/Al_2O_3$. The reason for such a discrepancy between 1-phenylbut-1-yne and other substrates remains unclear.

An analysis of the catalyst performances in the hydrogenation of asymmetrical internal akynes (at 50 and 95% alkyne conversions) indicates that for all substrates the selectivity of $PdCu_2/Al_2O_3$ in olefin formation is higher than that of monometallic Pd/Al_2O_3. Note that the selectivities of $PdCu_2/Al_2O_3$ are closer or even higher (for 1-phenylprop-1-yne) than the selectivity of the commercial Lindlar catalyst. Taking into account that the favorable selectivity of the Lindlar catalyst is attained by its modification with a significant amount of toxic lead, the high selectivity of $PdCu_2/Al_2O_3$ makes 1% $PdCu_2/Al_2O_3$ a promising alternative to this commercial catalyst.

In the hydrogenation of terminal phenylacetylene, the modification of Pd/Al_2O_3 with Cu accelerates alkyne hydrogenation to an olefin. TOF_1 for the $PdCu_2$ sample increases by a factor of 1.5 in comparison with that on the Pd/Al_2O_3 catalyst (from 2.69 to 4.12 s^{-1}). On the other hand, TOF_2 at the second hydrogenation step becomes lower than that for Pd/Al_2O_3 (0.79 *vs.* 1.69 s^{-1}). As a result, the TOF_1/TOF_2 ratio increases from 1.6 for monometallic to 5.23 for bimetallic catalyst (Table 2) thus improving the kinetic control of hydrogenation.

Styrene selectivity in phenylacetylene hydrogenation over $PdCu_2/Al_2O_3$ is higher than that over monometallic Pd/Al_2O_3. An improvement in the selectivity is particularly pronounced at high phenylacetylene conversions ($X^{\equiv}_{95\%}$): 90% for $PdCu_2/Al_2O_3$ *vs.* 78.5% for Pd/Al_2O_3. It is important that the selectivity for $PdCu_2$ is equal to the selectivity of the Lindlar catalyst (Table 2).

Thus, the formation of Pd–Cu nanoalloy species with an fcc structure was revealed by XRD and EXAFS analysis for both $PdCu/Al_2O_3$ and $PdCu_2/Al_2O_3$. The nanoalloy composition in the catalysts is determined by the Pd/Cu ratio in the initial heterobimetallic complexes used as precursors. Due to the formation of $PdCu_2$ nanoalloy species, the selectivity of $PdCu_2/Al_2O_3$ in the hydrogenation of internal and terminal alkynes was significantly improved, as compared to that of monometallic Pd/Al_2O_3, and found to be identical to the selectivity of the commercial Lindlar catalyst.

This study was supported by the Russian Science Foundation (grant no. 16-13-10530).

We are grateful to Professor M. N. Vargaftik and Dr. I. A. Yakushev (N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences) for supplying us with the $PdCu_2(AcO)_6$ complex for the catalyst preparation. We are also grateful to the International Analytical Center at the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences for performing GC/MS analyses.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.11.014.

References

1 (*a*) H.-U. Blaser, A. Schnyder, H. Steiner, F. Rössler and P. Baumeister, in *Handbook of Heterogeneous Catalysis*, Wiley-VCH, Weinheim, 2008, pp. 3284–3308; (*b*) D. Heller, A. H. De Vries and J. G. De Vries, in *Handbook of Homogeneous Hydrogenation*, eds. J. G. de Vries and C. J. Elsevier, Wiley-VCH, Weinheim, 2007, vol. 3, pp. 1483–1516.

2 (*a*) V. P. Ananikov, L. L. Khemchyan, Yu. V. Ivanova, V. I. Bukhtiyarov, A. M. Sorokin, I. P. Prosvirin, S. Z. Vatsadze, A. V. Medved'ko, V. N. Nuriev, A. D. Dilman, V. V. Levin, I. V. Koptyug, K. V. Kovtunov, V. V. Zhivonitko, V. A. Likholobov, A. V. Romanenko, P. A. Simonov, V. G. Nenajdenko, O. I. Shmatova, V. M. Muzalevskiy, M. S. Nechaev, A. F. Asachenko, O. S. Morozov, P. B. Dzhevakov, S. N. Osipov, D. V. Vorobyeva, M. A. Topchiy, M. A. Zotova, S. A. Ponomarenko, O. V. Borshchev, Yu. N. Luponosov, A. A. Rempel, A. A. Valeeva, A. Yu. Stakheev, O. V. Turova, I. S. Mashkovsky, S. V. Sysolyatin, V. V. Malykhin, G. A. Bukhtiyarova, A. O. Terent'ev and I. B. Krylov, *Russ. Chem. Rev.*, 2014, **83**, 885; (*b*) V. P. Ananikov, E. A. Khokhlova, M. P. Egorov, A. M. Sakharov, S. G. Zlotin, A. V. Kucherov, L. M. Kustov, M. L. Gening and N. E. Nifantiev, *Mendeleev Commun.*, 2015, **25**, 75.

3 A. J. McCue and J. A. Anderson, *Front. Chem. Sci. Eng.*, 2015, **9**, 142.

4 (*a*) S. A. Nikolaev, L. N. Zanaveskin, V. V. Smirnov, V. A. Averyanov and K. L. Zanaveskin, *Russ. Chem. Rev.*, 2009, **78**, 231 (*Usp. Khim.*, 2009, **78**, 248); (*b*) O. G. Ellert, M. V. Tsodikov, S. A. Nikolaev and V. M. Novotortsev, *Russ. Chem. Rev.*, 2014, **83**, 718.

5 X. Cao, A. Mirjalili, J. Wheeler, W. Xie and B. W.-L. Jang, *Front. Chem. Sci. Eng.*, 2015, **9**, 442.

6 G. X. Pei, X. Y. Liu, A. Wang, A. F. Lee, M. A. Isaacs, L. Li, X. Pan, X. Yang, X. Wang, Z. Tai, K. Wilson and T. Zhang, *ACS Catal.*, 2015, **5**, 3717.

7 S. Furukawa, M. Endo and T. Komatsu, *ACS Catal.*, 2014, **4**, 3533.

8 Z. Wang, L. Yang, R. Zhang, L. Li, Z. Cheng and Z. Zhou, *Catal. Today*, 2016, **264**, 37.

9 N. Yu. Kozitsyna, S. E. Nefedov, F. M. Dolgushin, N. V. Cherkashina, M. N. Vargaftik and I. I. Moiseev, *Inorg. Chim. Acta*, 2006, **359**, 2072.

10 I. S. Mashkovsky, G. N. Baeva, A. Yu. Stakheev, M. N. Vargaftik, N. Yu. Kozitsyna and I. I. Moiseev, *Mendeleev Commun.*, 2014, **24**, 355.

11 P. V. Markov, G. O. Bragina, G. N. Baeva, O. P. Tkachenko, I. S. Mashkovskii, I. A. Yakushev, M. N. Vargaftik and A. Yu. Stakheev, *Kinet. Catal.*, 2016, **57**, 617 (*Kinet. Katal.*, 2016, **57**, 621).

12 P. V. Markov, G. O. Bragina, G. N. Baeva, I. S. Mashkovskii, A. V. Rassolov, I. A. Yakushev, M. N. Vargaftik and A. Yu. Stakheev, *Kinet. Catal.*, 2016, **57**, 625 (*Kinet. Katal.*, 2016, **57**, 629).

13 P. V. Markov, G. O. Bragina, G. N. Baeva, O. P. Tkachenko, I. S. Mashkovsky, I. A. Yakushev, N. Yu. Kozitsyna, M. N. Vargaftik and A. Yu. Stakheev, *Kinet. Catal.*, 2015, **56**, 591 (*Kinet. Katal.*, 2015, **56**, 599).

14 I. S. Mashkovsky, P. V. Markov, G. O. Bragina, O. P. Tkachenko, I. A. Yakushev, N. Yu. Kozitsyna, M. N. Vargaftik and A. Yu. Stakheev, *Russ. Chem. Bull, Int. Ed.*, 2016, **65**, 425 (*Izv. Akad. Nauk, Ser. Khim.*, 2016, 425).

15 A. J. McCue and J. A. Anderson, *J. Catal.*, 2015, **329**, 538.

16 F. Cheng, X. He, Z.-X. Chen and Y.-G. Huang, *J. Alloys Compd.*, 2015, **648**, 1090.

17 A. J. McCue, A. M. Shepherd and J. A. Anderson, *Catal. Sci. Technol.*, 2015, **5**, 2880.

Received: 28th July 2016; Com. 16/5011