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Chemo-Bio Catalyzed Synthesis of *R*-1-Phenylethyl Acetate over Bimetallic PdZn Catalysts, Lipase, and Ru/Al_2O_3. Part I[1]

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Abstract—The effect of calcination and reduction temperature on the physical properties of $PdZn/Al_2O_3$ catalysts, prepared by co-precipitation deposition technique and characterized by XPS, XRD, and TEM methods are reported. The temperatures were varied in a range of 300–500°C. The catalyst calcined at 300°C and reduced at 400°C exhibited the metal particle size of 2–6 nm and contained the highest surface concentrations of Pd and Zn according to XPS measurements. The size and the fraction of large particles (above 10 nm) increased with increasing the calcinations and reduction temperatures.

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Combining various catalytic reactions in one-pot brings very clear advantages in lowering environmental burdens through waste minimization and thus increasing overall process efficiency. Such a cascade process of one-pot synthesis of *R*-1-phenylethylacetate (*R*-1-PEAc) starting from acetophenone was the main focus in the current work. In this system, several reactions are combined such as hydrogenation of acetophenone, acylation of the formed *R*-1-phenlyethanol (*R*-1-PE) and racemization of *S*-1-phenylethanol (*S*-1-PE).

Supported Pd catalysts have been very selective in hydrogenation of acetophenone to 1-phenylethanol [1], without hydrogenation of the phenyl ring, as is the case with e.g., Ru [2].

On the other hand, monometallic Pd catalysts are also catalyzing dehydration of 1-phenylethanol thus forming vinylbenzene, which is hydrogenated very rapidly to ethylbenzene. To overcome this challenge, one way is to dilute the effect of Pd by preparing a bimetallic PdZn catalyst, which has been reported to be more selective in acetophenone hydrogenation compared to the monometallic Pd catalyst [3]. The properties of bimetallic PdZn catalysts differ from those of monometallic supported Pd catalysts. It is known that at 280°C ZnO is reduced and, also, PdZn alloys are formed during the interaction between the reduced Zn and metallic Pd [4, 5]. The alloy formation is dependent on the catalyst reduction temperature as well as on the Pd/Zn ratio. The mechanism for the formation of a PdZn alloy was investigated in great detail in both reducing and oxidizing procedures [5] by using a combination of different catalyst characterization methods (XRD, XPS, TPR, TEM).

Racemization of the unreacting enantiomer is very important in connection to the type of one-pot synthesis reactions. Ru/Al_2O_3 was found active in the racemization of *R*-1-PE, at 80°C, resulting in 31% enantiomeric excess [6]. The active species for racemization was stated to be Ru^{3+} [7]. The next step towards a real one-pot synthesis is to optimize the properties of the hydrogenation catalyst and to use Ru/Al_2O_3 as co-catalyst during the one-pot synthesis of *R*-1-PEAc.

The aim in the current work was to synthesize and characterize a bimetallic $PdZn/Al_2O_3$ catalyst, which was calcined and reduced at different temperatures in a range of 300–500°C. Furthermore, the synthesis and properties of Ru/Al_2O_3 are reported here. This catalyst was used in the racemization of *S*-1-PE. The kinetics of one-pot synthesis of *R*-1-PEAc over $PdZn/Al_2O_3$ as a hydrogenation catalyst for acetophenone, lipase using for kinetic resolution of *R*-1-PE and application of Ru/Al_2O_3 as a racemization catalyst are reported in Part II [8].

[1] The article is published in the original.

Table 1. Metal particle sizes determined from TEM measurements and the metal contents according to FESEM-EDX

Catalyst	Particle size, nm	The size range of the Pd particles above 10 nm	Pd, wt %	Zn, wt %
PdZn-300-400	3.8 ± 1.9	15–20	2.1 ± 0.7	5.6 ± 2.8
PdZn-500-400	3.5 ± 1.9	15–40	2.2 ± 0.7	5.9 ± 1.8
PdZn-500-500	2.4 ± 0.9	10–54	2.8 ± 0.7	6.6 ± 2.4

EXPERIMENTAL

Both (2 wt % Pd + 5 wt % Zn)/Al_2O_3 and 4 wt % Ru/Al_2O_3 catalysts were prepared by means of co-precipitation using alumina (UOP, USA) as a support, which has the BET specific area of 306 m^2/g_{cat} [9]. The number of Brønsted and Lewis acid sites in alumina determined by pyridine adsorption was 7×10^{-15} and 156×10^{-15} mol/g_{cat}, respectively [9].

The racemization catalyst—Ru/Al_2O_3 —with the metal loading of 4 wt % (confirmed by EDX analysis), was prepared according to the method described in [10] as follows. An aqueous solution of $RuCl_3$ with the concentration of 8.3 mmol/l was mixed with 2 g of the support (alumina). After adsorption of Ru the solution was filtered and washed with deionized water.

Thereafter, the catalyst was suspended in a basic water solution (pH 13.2) by adding 0.1 M NaOH into the solution. After stirring for 24 h, the catalyst was washed with water and dried and used without any other calcination and reduction steps.

The (2 wt % Pd + 5 wt % Zn)/Al_2O_3 catalyst (the metal contents given as nominal metal loadings) was prepared by deposition-coprecipitation technique [11] using $Pd(NO_3)_2 \cdot 2H_2O$ as a Pd precursor. Palladium nitrate was dissolved in deionized water and acidified with 1% nitric acid. A solution of $Zn(NO_3)_2 \cdot 6H_2O$ was combined with the Pd solution and alumina was added to it. Thereafter, Na_2CO_3 was drop wise added into the solution until pH 9 was reached. The slurry was stirred for 24 h, at 80°C, affording a yellow-brown mixture, which was filtered and washed with deionized water, dried in vacuum, at room temperature, followed by drying at 60°C in air for 24 h. As a result a brown catalyst powder was achieved.

The synthesized PdZn/Al_2O_3 catalyst was divided into 2 portions and then calcined and reduced. Calcination was performed in a muffle oven using the temperature rise velocity 5°C/min until 300°C (or 500°C). The catalysts were additionally divided into two portions and reduced under hydrogen flow as follows: 5°C/min until 400°C (or 500°C) for 3 h and cooled under nitrogen flow.

The resulting catalysts were coded as PdZn-300-400, PdZn-500-400, and PdZn-400-500, where the first number indicates the calcination temperature and the latter one stands for the reduction temperature.

Transmission electron microscopy (TEM) measurements were performed with a LEO 912 Omega operating at the voltage of 120 kV. The samples were analyzed in a suspension of ethanol and more than 100 particles were taken for each sample for calculating the average diameter of particles. FESEM-EDX analysis was performed with a Zeiss ULTRA plus.

Temperature programmed reduction (TPR) of the Ru/Al_2O_3 catalyst was performed with an AutoChem Micromeritics using the following temperature ramp: 10°C/min up to 400°C.

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Ultra electron spectroscop equipped with a delay line detector. A monochromated AlK_α source was operated at 150 W and the analysis area of 0.3×0.7 mm^2 was obtained by using hybrid lens system with magnetic lens. Spectra were processed with the Kratos software.

The samples were analyzed with X-ray diffraction (XRD) for identification of crystalline phases. The XRD analyses were performed with a Bruker d8Advance instrument in θ–θ-mode, and with an optical configuration consisting of a primary Göbel mirror and a Väntec-1 detector. Continuous scans were applied on the sample that was mounted on a rotating low-background Si single-crystal sample holder. By adding repeated scans, the total data collection time for each sample lasted for at least 5 h. The PDF-2 databank [12] together with Bruker software was used to analyze the diffraction patterns.

RESULTS AND DISCUSSION

The metal particle size distributions of the three hydrogenation catalysts (PdZn-300-400, PdZn-400-500, and PdZn-500-400) are shown in Fig. 1 and the mean metal particle sizes are given in Table 1. All the catalyst contained relatively small Pd particles in a range of 2–6 nm and the average metal particles sizes varied between 2.4 to 3.8 nm (Table 1). The proportion and the size of large Pd particles (above 10 nm) increased, however, with increasing calcination and reduction temperatures. One example of a TEM images is given in Fig. 2 for the catalyst calcined at 300°C and reduced at 400°C.

Ru was reduced at 137°C according to the TPR measurement and, thus, during acetophenone hydrogenation it was in oxide state. The oxide form was desired since racemization was reported to occur on Ru^{n+} [7]. The metal particle size of Ru in 4 wt %

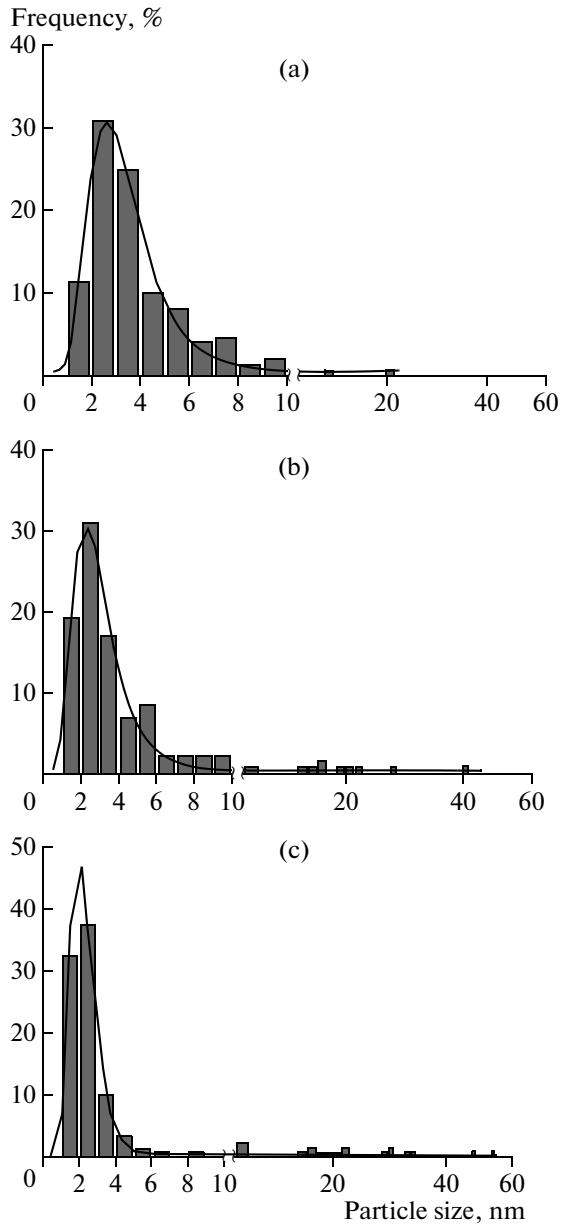

Fig. 1. The particle size distribution images for PdZn-300-400 (a), PdZn-500-400 (b), and PdZn-500-500 (c).

Ru/Al_2O_3 was 1.3 nm according to TEM measurements.

XRD pattern of the $PdZn/Al_2O_3$ catalyst calcined at 300°C and reduced at 400°C is shown in Fig. 3. All the three studied catalysts contained the alloyed phases PdZn(111) at 41.4° and PdZn(200) at 44.4° which correspond to the alloy formation [13], whereas no clear Pd(0) peak was detected at 40.1° [11].

XPS spectrum of the $PdZn/Al_2O_3$ catalyst calcined at 300°C and reduced at 400°C is shown in Fig. 4. The binding energies for the sample PdZn-300-400 were 1021.8 eV (Zn $2p_{3/2}$) and 334.7 eV (Pd $3d_{5/2}$) and 335.8 eV observed for Pd $3d_{5/2}$ (Table 2). It is lower

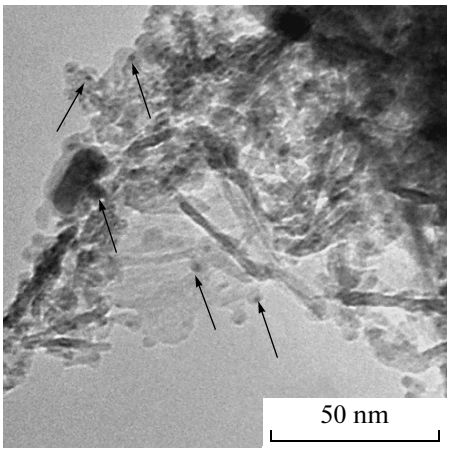

Fig. 2. TEM image for $PdZn/Al_2O_3$ calcined at 300°C (3 h, air) and reduced at 400°C (3 h, H_2).

than those reported for PdZn alloys in the literature [14], where the binding energies for PdZn alloy Pd $3d_{5/2}$ were given 335.6 and 336.2 eV, respectively. Pd exists, thus, mainly in the metallic state in the reduced and spent catalysts (Table 2) [11]. Furthermore, the binding energies of Zn $2p_{3/2}$ agree very well with the values reported in literature [11].

The alloy formation occurred as follows: the hydrogen was spilt from the metallic palladium to the zinc oxide, which was thereafter partially reduced to $Zn(OH)_x$. At increasing the catalyst reduction temperature the alloy formation was enhanced at 300°C, and 500°C was preferable for the alloy form. Small amounts of palladium, however, remained in negatively charge metallic palladium. During the reduction also the shape of palladium particles changed from half ball to coalesced metal particles. The alloy exhibited suppressed hydrogen adsorption capacity compared to the monometallic catalyst.

The atomic ratio Pd/Zn is decreasing in the following order: PdZn-500 > PdZn-300 > PdZn-500-500 > PdZn-300-400 indicating that the concentration of Pd on the surface is reducing whilst zinc concentration is increasing. This also means that the Pd surface concentration was 30% higher in the sample calcined at 500°C (Table 2, entry 4) compared to the one, which was both calcined at 500°C and reduced at 400°C (Table 2, entry 6). Reduction under hydrogen flow promoted falling Pd/Zn atomic ratio to 0.191–0.192 (Table 2, entries 3 and 6). The atomic ratio (Pd + Zn)/Al decreased in the row PdZn-300 > PdZn-500 > PdZn-300-400 > PdZn-500-400 > PdZn-500-500 indicating that the surface concentrations of active species decreased with increasing catalyst calcination and reduction temperatures.

So, three $PdZn/Al_2O_3$ catalysts were synthesized for the purpose of utilizing them in acetophenone hydrogenation combined with acylation of the formed *R*-1-PE over an enzymatic catalyst and racemization

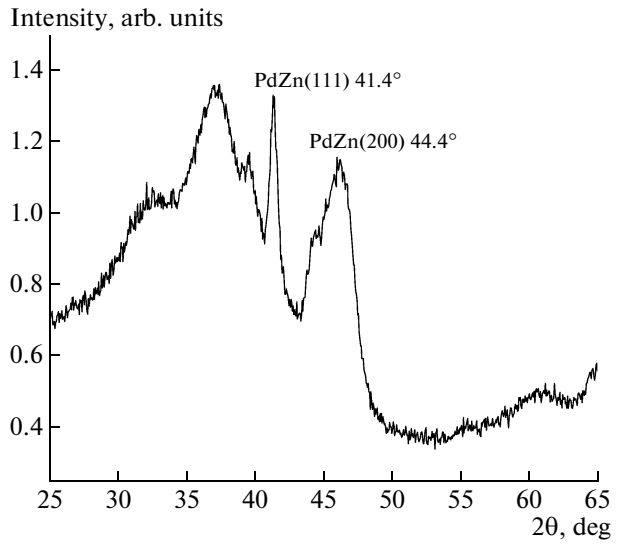

Fig. 3. XRD patterns for $PdZn/Al_2O_3$ calcined at 300°C (3 h, air) and reduced at 400°C (3 h, H_2).

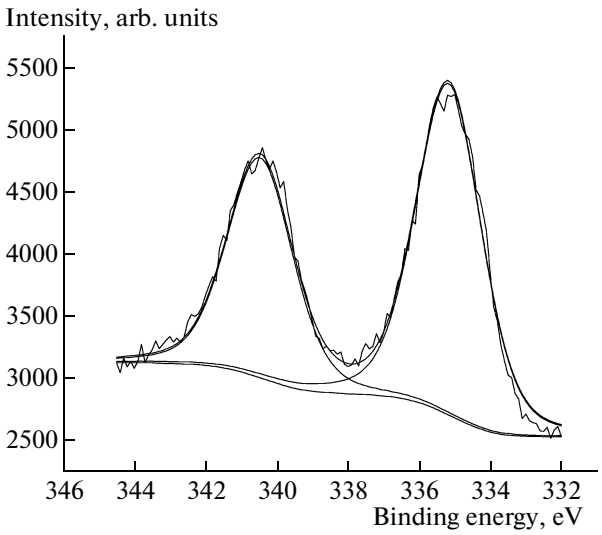

Fig. 4. XPS data for Pd 3p spectrum of $PdZn/Al_2O_3$ calcined at 300°C (3 h, air) and reduced at 400°C (3 h, H_2).

of *S*-1-PE on Ru/Al_2O_3. The former PdZn catalysts were treated in different ways regarding calcination and reduction temperatures. Although the metal particle size varied in the range of 2–6 nm, the size and the proportion of large metal particles increased with increasing calcinations and reduction temperature. Alloy formation was confirmed by XPS measurements revealing the presence of PdZn(111) and PdZn(200) phases. Ruthenium in the racemization catalyst was in the oxidic form.

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Table 2. Comparison of XPS spectra in Pd 3*d* region for $PdZn/Al_2O_3$ catalysts

Entry	Sample	Atomic ratio		Binding energy, eV	
		Pd/Zn	(Pd + Zn)/Al	Pd $3d_{5/2}$	Zn $2p_{3/2}$
1	PdZn-300	0.240	0.094	336.4	1021.8
2	5 wt % Pd/ZnO, H_2, 300°C [11]	0.242	–	335.2	1022.2
3	PdZn-300-400	0.191	0.079	334.7[b] (40%) 335.8[c] (60%)	1021.8
4	PdZn-500	0.275	0.084	336.5 (77.5%) 338.1 (12.5%)	1022.0
5	5 wt % Pd/ZnO, H_2, 500°C	0.207	–	335.7	1022.2
6	PdZn-500-400	0.192	0.072	334.7 (46%) 335.7 (54%)	1021.8
7	PdZn-500-500	0.202	0.067	334.9 (54%) 336.0 (46%)	1021.8
8[a]	5 wt % Pd/ZnO, H_2, 147°C	–	–	334.85	1022.0
9[a]	5 wt % Pd/ZnO, H_2, 147°C	–	–	335.85	1022.0

[a] In [11] Al 2*p* at 74.3 eV was applied as internal standard.
[b] Corresponds to Pd(0).
[c] Corresponds to PdZn or PdO charging.

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