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Additional Information

Synthesis of Polymer Protected Pd-Ag/ZnO Catalysts for Phenylacetylene Semyhydrogenation

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Abstract

A simple and environmentally friendly method, based on sequential adsorption of polyacrylamide (PAM) and transition metal ions (Pd^{2+} , Ag^+) on zinc oxide precipitated from water solution, was used to synthesize supported mono- and bimetallic catalysts with various Pd:Ag ratios. The catalyst characterization results indicated that PAM and metal ions are completely adsorbed by zinc oxide, forming polymer-stabilized Pd and Ag nanoparticles of 1-3 nm in size, evenly distributed on the support surface. The catalysts were studied in the hydrogenation of phenylacetylene under mild conditions (0.1 MPa, 40°C). Although Ag-free 1%Pd-PAM/ZnO catalyst presents an interesting catalytic performance (in terms of activity and selectivity), the optimal catalyst was 1%Pd-Ag(3:1)-PAM/ZnO, presenting a selectivity to styrene of 88% at 85.4% conversion of phenylacetylene. For comparison, similar Pd-Ag (3:1) bimetallic catalysts modified with polysaccharides such as pectin (Pec), chitosan (Chit) and 2-hydroxyethylcellulose (HEC) were studied in the hydrogenation process. The catalysts demonstrated nearly the same selectivity to styrene. The activity of the catalysts decreases in the following order: 1%Pd-Ag(3:1)-HEC/ZnO > 1%Pd-Ag(3:1)-PAM/ZnO > 1%Pd-Ag(3:1)-Pec/ZnO > 1%Pd-Ag(3:1)-Chit/ZnO.

Keywords: Hydrogenation, phenylacetylene, palladium catalysts, palladium-silver catalysts, polyacrylamide, polysaccharides.

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1 Introduction

Liquid-phase hydrogenations of C–C triple bonds, and especially the selective hydrogenation of alkynes to alkenes, is still a challenging task from both fundamental and industrial point of view [1-8]. However, in many cases, harsh conditions (high temperatures and pressures) are required. An alternative is the use of palladium catalysts, which can be very effective in hydrogenation of both triple and double carbon-carbon bonds [2-16].

To increase the selectivity in semi-hydrogenation of acetylenic compounds, bimetallic catalysts are often used [6-11]. This is the case of Lindlar's catalysts [9], in which the promoter (Pb) in a CaCO₃-supported Pd catalyst facilitate a control of reaction rates during hydrogenation steps. However, Pb must be replaced by other promoters [10, 11]. Thus, the first step for application of bimetallic catalysts in semihydrogenation reactions is to find optimal metal ratios, which can facilitate higher conversion limiting the consecutive reactions.

Bimetallic nanoparticles combine the properties of both composite metals, and, in some cases, demonstrate improved catalytic properties due to a synergistic effect [8-16]. Supported Pd-Ag catalysts increasingly attract attention, and are used in the hydrogenation of acetylene compounds because of their high selectivity to olefin compounds [17-20]. However, the effect of the ratio of Pd to Ag in the active phase of olefin yield has not been studied, and this can be modified depending on the incorporation of promoters in bimetallic crystals.

On the other hand, stabilizing metal ions with water-soluble polymers has previously been shown to be an effective approach to improve the characteristics of supported catalysts used for hydrogenation of acetylene compounds [21, 22]. Among the polymers used for preparation of supported metal catalysts, renewable and biodegradable natural polysaccharides have recently attracted increasing attention due to their enhanced biosafety, availability, and ability to stabilize metal nanoparticles [23, 24].

In this paper, the liquid-phase hydrogenation of the model substrate, phenylacetylene, was studied, using synthesized Pd-Ag catalysts supported on ZnO modified with polyacrylamide (PAM). Similar Pd-Ag catalysts modified with polysaccharides (pectin, chitosan and 2-hydroxyethylcellulose) were also prepared and studied in hydrogenation process for comparison. The objectives were to characterize the catalysts using different methods, and to determine the optimal metal combination and nature of polymer for the purpose of increasing catalytic activity and selectivity to styrene.

2 Experimental

2.1 Chemicals and Materials

Phenylacetylene of pure grade was purified by distillation, and monitored by chromatography. Ethanol (reagent grade, Sigma-Aldrich), palladium chloride (PdCl₂, 59-60% Pd, Sigma-Aldrich), silver nitrate (AgNO₃, 99.0%, Sigma-Aldrich), potassium chloride (KCl, reagent grade), polyacrylamide (PAM, Mw 500,000), pectin (Pec, degree of esterification 64.3%), 2-hydroxyethylcellulose (HEC, Mv ~ 90,000, Sigma Aldrich), chitosan (Chit, from shrimp shells, degree of deacetylation 75%, Sigma-Aldrich) were

used without additional purification. Zinc oxide (chemically pure) was used as an inorganic support.

2.2. Synthesis of catalysts

A 5 mL solution of 1.9×10^{-2} M PAM (0.0067 g in 5 mL of water) was added dropwise to a suspension of zinc oxide (1 g) in water (15 mL) at room temperature with continuous stirring for 2 h. Then, 5 mL of a 1.9×10^{-2} M transition metal salt solution (K_2PdCl_4 and/or $AgNO_3$) was added for 3 h. The concentration of palladium and silver salt solutions were taken from a calculation for the preparation of catalysts with 1% active phase content. The PAM amount for the preparation of the catalyst was calculated in terms of one transition metal atom per monomer unit. The resulting catalyst was kept in the mother liquor for 12-15 h. Thereafter, it was washed with water until a negative reaction for chloride ions occurred, and then dried in air. The completeness of palladium and silver immobilization was controlled by photoelectric colorimetry and direct potentiometry, respectively.

The concentrations of K_2PdCl_4 and $AgNO_3$ solutions were varied within the range of $4.7 \cdot 10^{-3}$ - $1.4 \cdot 10^{-2}$ M in the case of the synthesis of bimetallic 1% Pd-Ag-PAM/ZnO catalysts with Pd:Ag ratios of 3:1, 1:1 and 1:3. Metal ions were immobilized by successively adding 5 mL of $AgNO_3$ and 5 mL of K_2PdCl_4 solutions to PAM-ZnO suspension.

To evaluate the effect of nature of polymers on catalytic properties, similar bimetallic Pd-Ag (3:1) catalysts modified with polysaccharides such as pectin, chitosan and 2-hydroxyethylcellulose were also prepared using the same procedure.

2.3. Characterization of catalysts

The palladium and silver content in the catalysts was preliminarily evaluated based on the change in metal ion concentration in mother liquor before and after immobilization of Ag^+ and/or $PdCl_4^{2-}$ on a polymer-modified zinc oxide. The palladium content in mother liquors was determined from photoelectric colorimetry data, which were obtained on a SF-2000 UV/Vis spectrophotometer (OKB Spectr, Russia), based on calibration curves constructed at the wavelength $\lambda = 425$ nm. The silver content in mother liquors was determined by direct potentiometry on the ANION 4100 ionometer (Infraspak-Analyte, Russia), with an ion-selective electrode ELIS-131Ag.

The elemental analysis of the samples of catalysts was carried out on an X ArtM energy dispersive X-ray fluorescence spectrometer (Komita, Russia).

A Vario Micro cube elemental analyzer (Elementar Analysensysteme GmbH, Germany) was used in the organic microanalysis of the samples. The carbon content of the samples (CHNS/O) was determined by a method of combustion at $1150^\circ C$, in the presence of pure oxygen with the subsequent reduction of oxides and separation on a chromatographic column with a thermal conductivity detector.

The analysis of the catalysts by X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis Ultra DLD photoelectron spectrometer (Kratos Analytical LTD, United Kingdom). The area of analysis for each sample was $220 \times 220 \mu m^2$, and the depth of an analyzed layer was 1-2 nm. The radiation source was a monochromated Al $K\alpha$ line (1486.6 eV). The energy resolution of the instrument was 0.5 eV (for the Ag 3d 5/2 line of silver). For minimization of charging processes on the sample surface, the powder was pressed in indium foil, and the spectra were measured under identical conditions with the use of a neutralizer, and calibrated based on the C1s line of aliphatic compounds (284.8 eV).

TG/DTA measurements were performed on an STA 409C Luxx instrument coupled with a QMS 403C Aeolos quadrupole mass spectrometer, and on a METZSCHSTA 409 PC/PG instrument, in argon and within a temperature range 30-400 °C (heating rate 10 °C min⁻¹).

Fourier transform infrared (FTIR) spectra of catalysts samples were obtained using a Nicolet iS5 (Thermo Scientific, USA) in the 4000-400 cm⁻¹ region. Pellets for infrared analysis were obtained by grinding a mixture of a 1 mg sample with 100 mg dry KBr, followed by pressing the mixture into a mold.

The electron-microscopic studies were performed on a JEM-2100 transmission electron microscope (Jeol, Japan) with an accelerating voltage of 100 kV.

2.4. Hydrogenation of Phenylacetylene

Hydrogenation was performed in a thermostatically controlled long-necked glass flask reactor in an ethanol solution (25 mL) at one atmosphere in ambient hydrogen and at a temperature of 40°C, with intensive stirring (600-700 rockings per minute). The catalyst (0.05 g) was treated preliminarily with hydrogen directly in the reactor for 30 min, with intensive stirring. Then, 2.23 mmol (0.09 mol/L) of a substrate was introduced. The substrate amount was taken based on the uptake of 100 mL of hydrogen. The catalytic activity of these catalysts was estimated by measuring the H₂-uptake against time on stream (TOS) under the same reaction conditions.

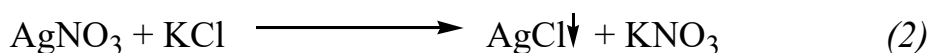
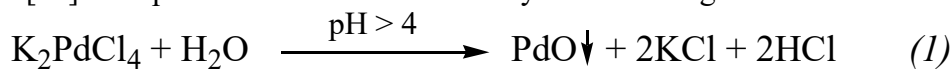
To determine the selectivity to the main reaction products, samples of the reaction mixture were taken at fixed times with a syringe, and analyzed by gas chromatography. The analysis was carried out on a Khromos GK1000 chromatograph (Khromos, Russia) with a flame ionization detector in the isothermal regime using a BP21 (FFAP) capillary column with a polar phase (PEG modified with nitroterephthalate) 50 m in length and 0.32 mm in inside diameter. The column temperature was 90°C, and the injector temperature was 200°C; helium served as the carrier gas; the injected sample volume was 0.2 µL. The selectivity to styrene was evaluated as the fraction of the target product in the reaction products at a specified degree of conversion.

3 Results and Discussion

3.1 Characterization of catalysts

According to the photoelectric colorimetry and direct potentiometry data, 98-99% of the amount of metals introduced was precipitated on PAM modified ZnO. Thus, the content of the active phase (Pd and/or Ag) in the synthesized catalysts was close to the calculated data, and amounted to 1 wt.% of the sum of all components (Table 1).

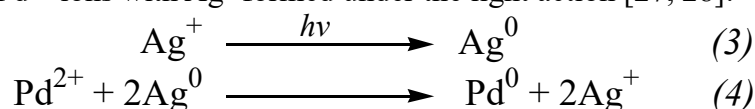
The quantitative immobilization of palladium and silver ions on ZnO is probably due to the basic character of the oxide and the presence of chloride ions in the reaction medium [25]. The processes can be described by the following reactions:



In this way, X-ray fluorescence elemental analysis results of 1%Pd-Ag(3:1)-PAM/ZnO catalyst confirmed the data obtained. The carbon content determined by organic microanalysis was consistent with the calculated values and indicative of the immobilization of polymer on zinc oxide (Table 2).

The presence of the above-mentioned elements on the surface of catalysts is also detected by XPS study of the catalysts. The lines of zinc, oxygen, carbon, palladium, silver and chlorine were observed in the survey XPS spectrum of the 1%Pd-Ag(3:1)-PAM/ZnO catalyst (Fig. 1) and summarized in Table 3.

According to XPS data, palladium in the 1%Pd-Ag(3:1)-PAM/ZnO catalyst is predominantly in the oxidized state, with Pd 3d(5/2) peak at ~ 336.9 eV (~ 92 at.%). A small shoulder at ~ 335.6 eV is observed, indicating the presence of the zero valence palladium (Fig. 2a) [17, 26]. Small amount of Pd⁰ was probably caused by the interaction of Pd²⁺ ions with Ag⁰ formed under the light action [27, 28]:



Silver has a binding energy of ~ 367.1 eV, assigned to Ag 3d(5/2), indicates its oxidized state (Fig. 2b) [17].

As indicated in the experimental part, the catalyst before catalytic reaction was reduced by hydrogen in the reactor for 30 min. The XPS analysis of that catalyst indicated that most of the palladium was in the zero state, with a binding energy of ~ 335 eV related to Pd 3d(5/2) peak [17, 26] (Fig. 2c). The symmetric peak of Ag 3d(5/2) at ~368.1 eV may be assigned to the silver in metallic state [17] (Fig. 2d). Accordingly, small shifting of binding energies of Pd and Ag lines can be explained by the interaction of palladium with the polymer-modified support [17, 29].

The TG/DTA study of the 1% Pd-Ag (3:1)-PAM/ZnO catalyst confirmed the weight loss (ca. 0.76 wt.%) at the temperature of 253°C, which is attributed to destruction of polyacrylamide. The value of mass loss determined is close to the calculated data for the PAM content in the catalyst (0.66 wt.%).

The interactions between the components of the catalysts were studied by IR spectroscopy. PAM shows characteristics bands at 347, 1642, 1622 cm⁻¹, in addition to those in the 1200-400 cm⁻¹ range [30] (Fig. 3, spectra 5 to 7). The shifting of absorption bands of -C=O and -NH groups in the IR spectra of catalysts, compared to the same bands in PAM, metal-PAM, or PAM/ZnO (Fig. 3, spectra 1 to 4), confirm formation of chemisorbed polymer-metal complexes on the surface of zinc oxide.

The study of mono- and bimetallic catalysts by transmission electron microscopy (TEM) showed the formation of palladium and silver nanoparticles of 1-3 nm evenly distributed on the surface of PAM-modified zinc oxide (Fig. 4) [21, 22].

Thus, PAM and noble metal ions were shown to be quantitatively deposited on zinc oxide. In this case, uniformly distributed nanoparticles in the form of polymer-metal complexes are fixed on the support. Of particular interest is the fact that a partial reduction of palladium is observed during the synthesis of Pd,Ag-containing catalysts.

3.2. Phenylacetylene Hydrogenation

The catalytic performance of Pd,Ag-containing catalysts was evaluated in the selective hydrogenation of phenylacetylene. The hydrogenation experiments were carried out in ethanol at 0.1 MPa H₂ and 40°C. Figure 6a shows the variation of H₂-uptake with time on stream during the hydrogenation of phenylacetylene over Pd,Ag-containing catalysts. For comparison the corresponding metallic compounds Pd- and Ag-containing catalysts have been also tested. The 1%Pd-PAM/ZnO catalyst demonstrated the higher catalytic activity, reaching the semi-hydrogenation point (50 mL) after 7 min (Fig. 5a, curve 1). The catalytic activity of the bimetallic catalysts was significantly lower, and reached semi-hydrogenation point after 17, 30 and 45 min for 1%Pd-Ag(3:1)-PAM/ZnO, 1%Pd-

Ag(1:1)-PAM/ZnO and 1%Pd-Ag(1:3)-PAM/ZnO, respectively (Fig 5a, curves 2, 3 and 4). On the other hand, the lowest catalytic activity was shown by the monometallic silver catalyst. The hydrogen uptake reached 20 mL over a 75-minute period (Fig 5a, curve 5). The phenylacetylene hydrogenation rate, calculated from the hydrogen uptake data, is presented in Fig. 5b. The maximum hydrogenation rate for 1%Pd-PAM/ZnO and 1%Pd-Ag(3:1)-PAM/ZnO catalysts was observed after the semi-hydrogenation point. While the reaction rate for the monometallic Ag and the rest of bimetallic Pd-Ag catalysts (i.e. those with Pd:Ag ratios 1:1 and 1:3) was remained unchanged during the most time of the process.

During phenylacetylene hydrogenation, styrene (main reaction product, directly formed from phenylacetylene) and ethylbenzene (as minority and formed by both direct transformation of phenylacetylene and the consecutive reaction from styrene) were the reaction products. This is in agreement with previous results in which it has been proposed that phenylacetylene hydrogenation to styrene and ethylbenzene proceeds by a two-pathway mechanism [26]. One pathway involves the direct hydrogenation of the triple bond to a single bond, and the other involves a two-step hydrogenation including the formation of a single or multiple adsorbed species. The change in the composition of the reaction mixture in the presence of the 1%Pd-PAM/ZnO and 1%Pd-Ag(3:1)-PAM/ZnO catalysts is shown in Fig. 6. According to the chromatographic analysis, styrene is accumulated in the initial period of reaction, and then reduced to ethylbenzene. The maximum yield of styrene was observed after 6 minute (67%) on 1%Pd-PAM/ZnO catalyst. Conversion of phenylacetylene reached only 72% (Fig. 6a). On the other hand, the yield of the mstyrene on the 1%Pd-Ag(3:1)-PAM/ZnO catalyst reached 80% at conversion of the substrate of 90.5% (Fig. 6b). It should be noted that styrene yield on the monometallic palladium catalyst was only 54% at nearly the same (84%) phenylacetylene conversion (Fig. 6). This suggests that bimetallic catalyst possesses better selectivity to styrene to compare with 1%Pd-PAM/ZnO.

Dependence of selectivity on conversion for 1%Pd-PAM/ZnO and 1%Pd-Ag(3:1)-PAM/ZnO catalysts is shown in Fig. 7a. Phenylacetylene is hydrogenated selectively to styrene (> 90%) on the palladium catalyst only during first six minutes, and then after phenylacetylene conversion of 72% the selectivity significantly decreased. However, the hydrogenation of the double bond of the styrene was suppressed by the incorporation of Ag in Pd-containing catalyst. Selectivity to styrene for 1%Pd-Ag(3:1)-PAM/ZnO was 88% at higher phenylacetylene conversion (90.5%). The selectivity on the rest catalysts was also higher than 90%, but their activity was significantly lower to compare with 1%Pd-Ag(3:1)-PAM/ZnO (Fig. 7b).

The catalytic performance in terms of reaction rates for phenylacetylene hydrogenation and the selectivity to styrene are listed in Table 4. The hydrogenation rate on the 1%Ag-PAM/ZnO was low and did not exceed $0.2 \cdot 10^{-6}$ mol/s, and the selectivity to styrene reached 95.6% at a conversion of 41%. Introduction of palladium into the catalyst lead to a more than fourfold increase of the activity. The higher the content of Pd in the catalyst, the higher is the reaction rate. While the selectivity of the process almost remained unchanged with the rise of the share of palladium in the bimetallic catalysts (Fig.7b, and Table 4). The 1%Pd-PAM/ZnO catalyst showed the highest reaction rate ($W = 8.6 \cdot 10^{-6}$ mol/s), but the selectivity was the lowest and did not exceed 64.2% (Table 4).

Although the hydrogenation can be carried out by two different pathways [26], in our case, the reaction mainly carried out by a two-step hydrogenation reaction, in which the consecutive hydrogenation strongly depend on the catalyst composition. Accordingly, a reaction network as indicated in Figure 8 can be proposed in which the

k_1/k_2 y k_2/k_3 ratios strongly depend on the catalyst composition.

The initial selectivity to styrene and ethylbenzene was of 95 and 5% (Fig. 6b), respectively, suggest that $k_2 \ll k_1$ (k_1/k_2 of ca. 0.1) in Ag-free and Ag-promoted palladium catalysts. In this way, it is well know that k_1/k_2 increases when increasing reaction temperature [31], but it can be relatively low a low reaction temperature.

On the other hand, the differences between unpromoted and Ag-promoted Pd catalysts are related to the consecutive reactions, i.e. the rate of styrene hydrogenation to ethylbenzene (Fig. 8, step 3). The bimetallic Pd-Ag catalysts were shown to be more selective in comparison with the monometallic 1% Pd-PAM/ZnO, suggesting that k_2/k_3 is increased with the incorporation of Ag in the catalysts. On the other hand, the increase in the amount of palladium in the silver catalyst lead to an increase in the catalytic activity.

Thus, k_2 should increases when increasing the Pd-content in catalyst. Accordingly, the best catalytic activity with the higher selectivity to styrene seems to be achieved by optimizing both the Pd-content and the Ag/Pd ratio. In our case, the excellent catalytic performance is observed on catalyst 1%Pd-Ag(3:1)-PAM/ZnO catalyst.

These results suggest that the modification of Pd with Ag is an effective approach to facilitate the higher selectivity to semi-hydrogenation of phenylacetylene to styrene. A similar mechanism for the use of promoter in Pd-based catalysts has been also proposed in Pd/Ni supported on nitrogen-doped activated carbon [12], but the higher selectivity to styrene required huger Ni-contents (ca. Pd/Ni ratio of 1 to 2), presenting selectivity to styrene of 84% at 91% phenylacetylene conversion. In addition, this is also improved by using a new catalyst preparation procedure, using polymer protected Pd-Ag/ZnO catalysts.

The low hydrogenation of styrene can be explained by considering modification of catalysts by incorporating promoters, which can interact with palladium particles, blocking active sites on the surface of the catalyst [4] and/or weaken the palladium affinity to an alkene by increasing electron density on the palladium and facilitating alkene desorption from the surface [7]. In addition, we must also consider that the high selectivity can be also due to a change in the electronic state of palladium particles in the presence of silver. In this way, the shift of the electron density from silver to palladium leads to a decrease of the styrene adsorption strength on the palladium surface, making it easier to desorb the target product (styrene) from the active centers of the catalyst to the reaction medium [32, 33].

Thus, a partial isolation of Pd atoms by Ag atoms and/or the incorporation of Ag in small Pd clusters seems to favor the formation of active centers on the surface that are selective for the controlled hydrogenation of phenylacetylene to styrene.

Varying the nature of a polymer-modifier can also be used to form active centers with improved catalytic properties. To confirm this the catalytic properties of 1%Pd-Ag(3:1)-PAM/ZnO catalyst were compared to those for similar bimetallic catalysts modified with pectin, chitosan and 2-hydroxyethylcellulose (Table 4). All catalysts showed nearly the same selectivity to styrene. Nevertheless, the activity of the catalysts decreases in the following order: 1%Pd-Ag(3:1)-HEC/ZnO > 1%Pd-Ag(3:1)-PAM/ZnO > 1%Pd-Ag(3:1)-Pec/ZnO > 1%Pd-Ag(3:1)-Chit/ZnO. In addition, phenylacetylene hydrogenation over the most active 1%Pd-Ag(3:1)-HEC/ZnO resulted in highest styrene yield (Table 4).

4 Conclusion

In summary, this paper describes a simple and environmentally friendly method for synthesis of supported polymer-modified catalysts by sequential adsorption of polymers and metal ions (Pd^{2+} and/or Ag^+) from water solution on zinc oxide. All catalysts were synthesized in ambient conditions.

The catalysts obtained were characterized by several physico-chemical techniques, such as TEM, XPS, IR, TGA and elemental analysis. The characterization results confirm that both polymer and noble metal ions are completely fixed on zinc oxide support. The active phase (i.e. Pd and Ag elements) is immobilized due to the binding of metal ions to PAM, which was previously chemisorbed on ZnO. The formation of uniformly distributed polymer-stabilized nanoparticles on the surface of the support with crystal sizes of 1-3 nm.

Unpromoted and Ag-promoted Pd-PAM/ZnO catalysts are active and selective in the hydrogenation of phenylacetylene under mild conditions (H_2 pressure 0.1 MPa, 40°C). However, the optimal was the bimetallic 1% Pd-Ag-PAM/ZnO catalyst with the ratio of Pd:Ag = 3:1. The selectivity to styrene on this catalyst was 88% at 90.5% substrate conversion, indicating changes in the reaction rate of consecutive reactions with respect to direct hydrogenation reactions. Comparison of catalytic properties of 1%Pd-Ag(3:1)-PAM/ZnO with similar polysaccharide-modified catalysts indicated the prospect for application of non-toxic renewable natural polymers in development of such type of materials for catalysis.

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Conflict of interest The authors declare that there is no conflict of interest regarding the publication of this paper.

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Caption to figures

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Title: Synthesis of Polymer Protected Pd-Ag/ZnO Catalysts for Phenylacetylene Semyhydrogenation

Fig. 1 Survey XPS spectrum of 1% Pd-Ag(3:1)-PAM/ZnO

Fig. 2 The Pd3d (a, c) and Ag3d (b, d) XPS spectra of the 1%Pd-Ag(3:1)-PAM/ZnO catalyst before (a, b) and after (c, d) treatment with H₂

Fig. 3 IR spectra of catalyst samples: 1) PAM; 2) Pd²⁺-PAM; 3) Ag⁺-PAM; 4) PAM/ZnO; 5) Pd-PAM/ZnO; 6) Ag-PAM/ZnO; 7) Pd-Ag-PAM/ZnO

Fig. 4 TEM microphotograph of 1%Pd-PAM/ZnO (a) and 1%Pd-Ag(3:1)-PAM/ZnO catalysts

Fig. 5 Variation of the hydrogen uptake (a) and rate of the reaction (b) with time on stream during the hydrogenation of phenylacetylene at 40°C in the presence of: 1) 1%Pd-PAM/ZnO; 2) 1%Pd-Ag(3:1)-PAM/ZnO; 3) 1%Pd-Ag(1:1)-PAM/ZnO; 4) 1%Pd-Ag(1:3)-PAM/ZnO; and 5) 1%Ag-PAM/ZnO. Reaction conditions in text.

Fig. 6 Changes in the composition of the reaction mixture during the hydrogenation of phenylacetylene at 40°C in the presence of 1%Pd-PAM/ZnO (a) and 1%Pd-Ag(3:1)-PAM/ZnO (b)

Fig. 7 Influence of Pd/Ag ratio on both the selectivity to styrene and the catalytic activity during phenylacetylene hydrogenation on Pd,Ag-containing catalysts: dependence of selectivity to styrene with the substrate conversion for 1%Pd-PAM/ZnO and 1%Pd-Ag (3:1)-PAM/ZnO catalysts (a); variation of selectivity to styrene and reaction rate with palladium content (b)

Fig. 8 Reaction pathways in the hydrogenation of phenylacetylene over Pd- and/or Ag-containing catalysts

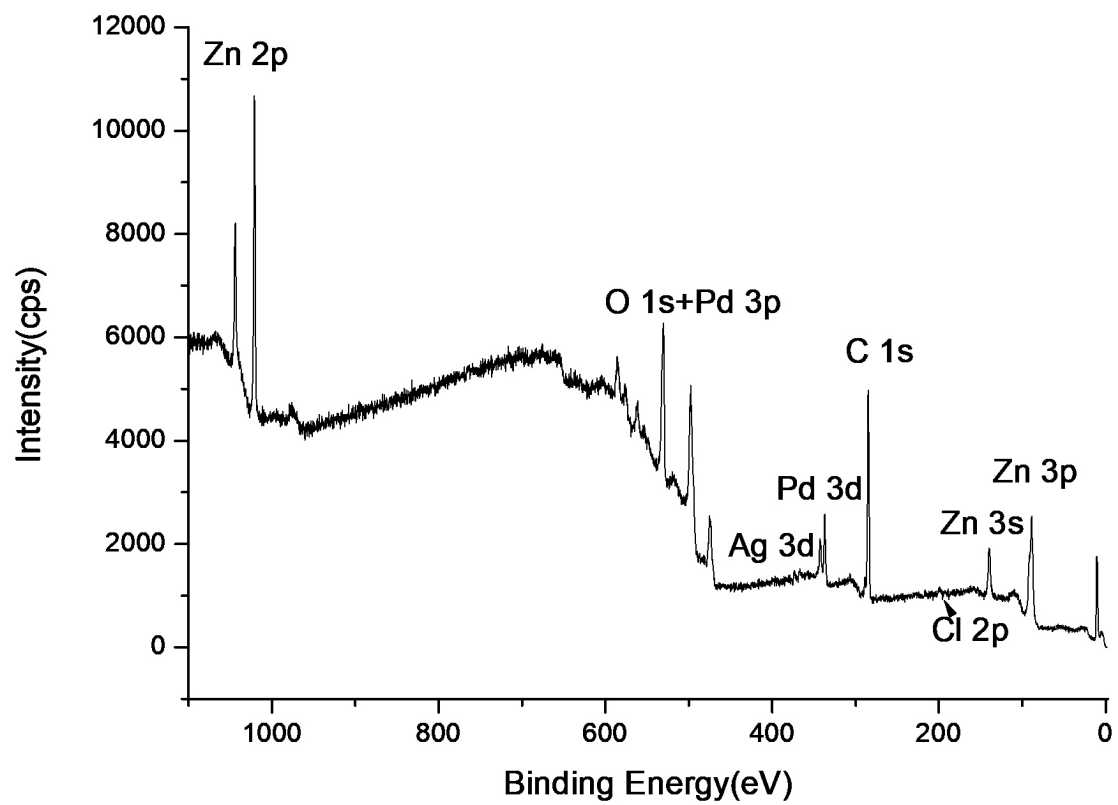


Fig.1

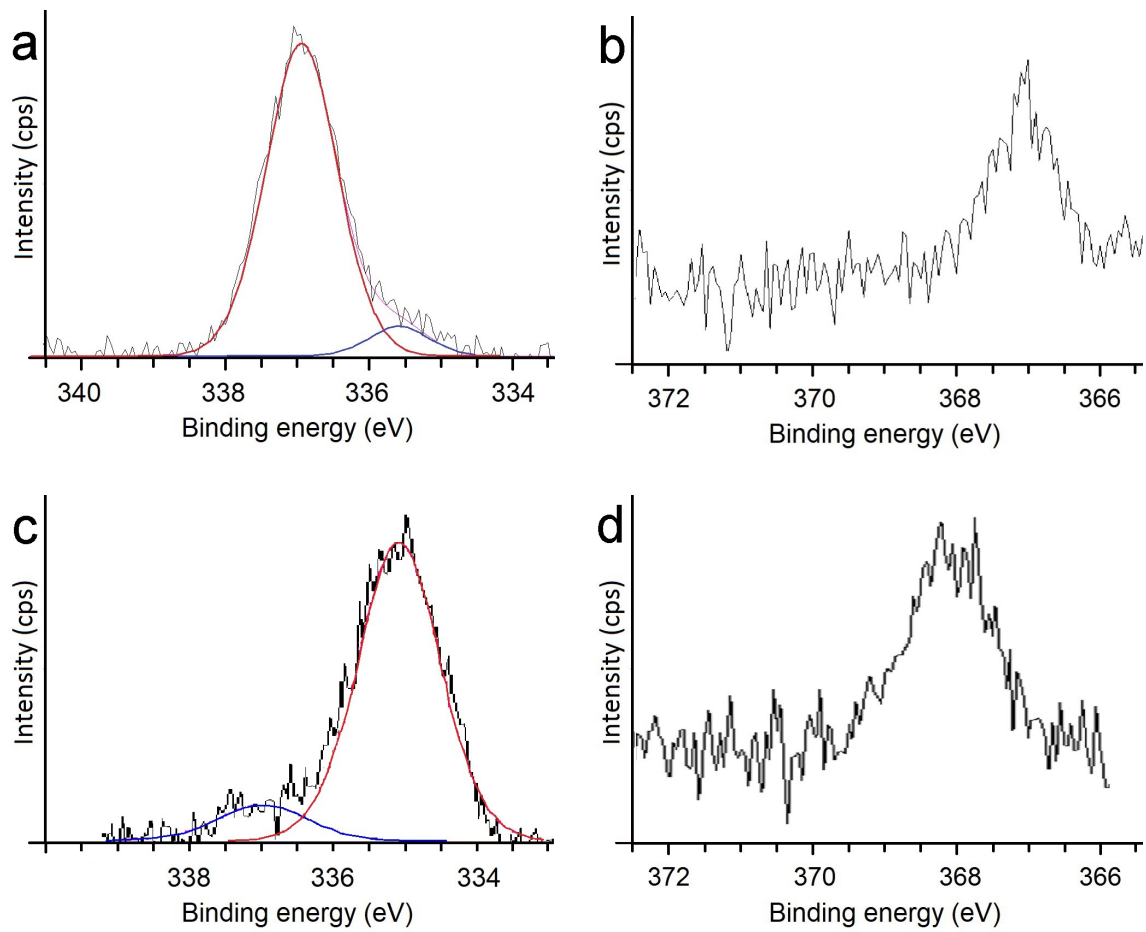


Fig. 2

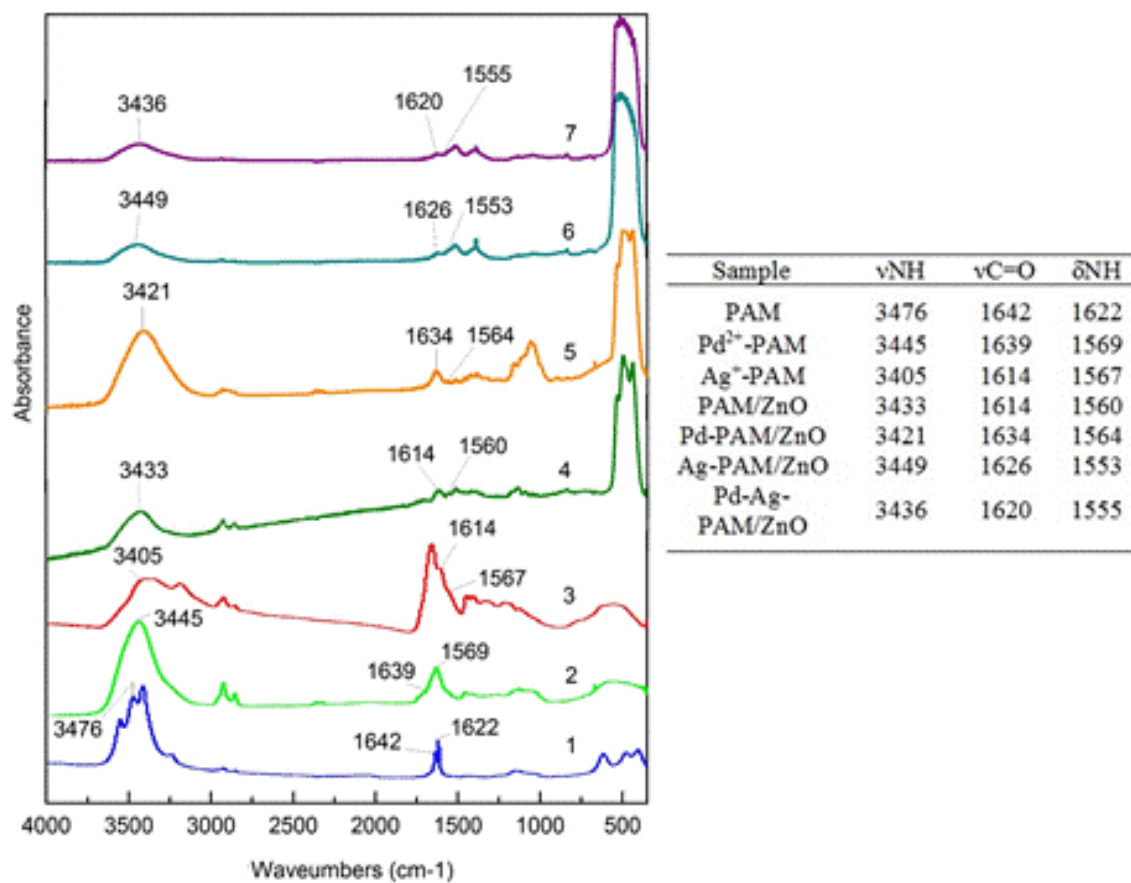


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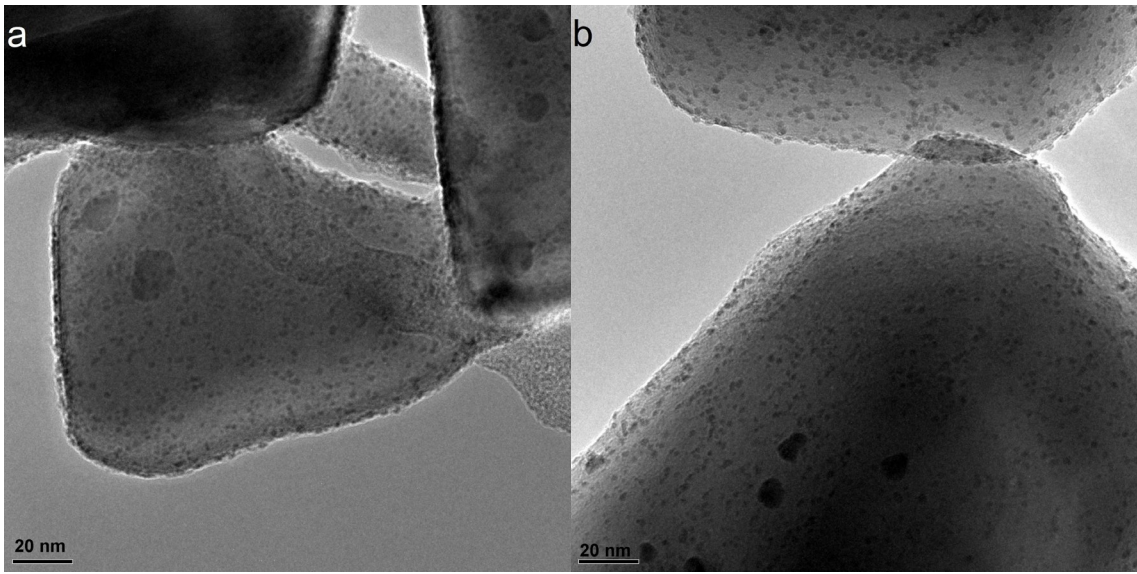


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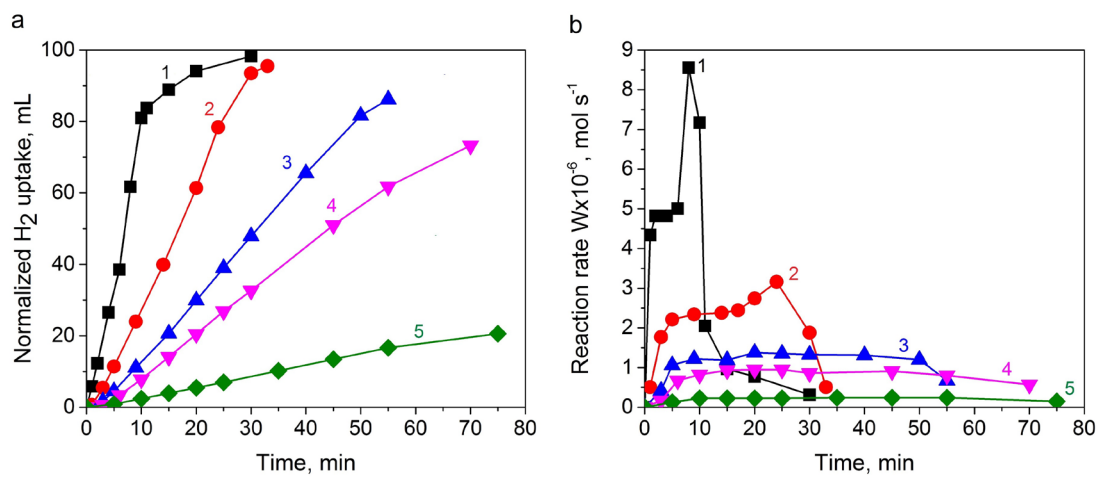


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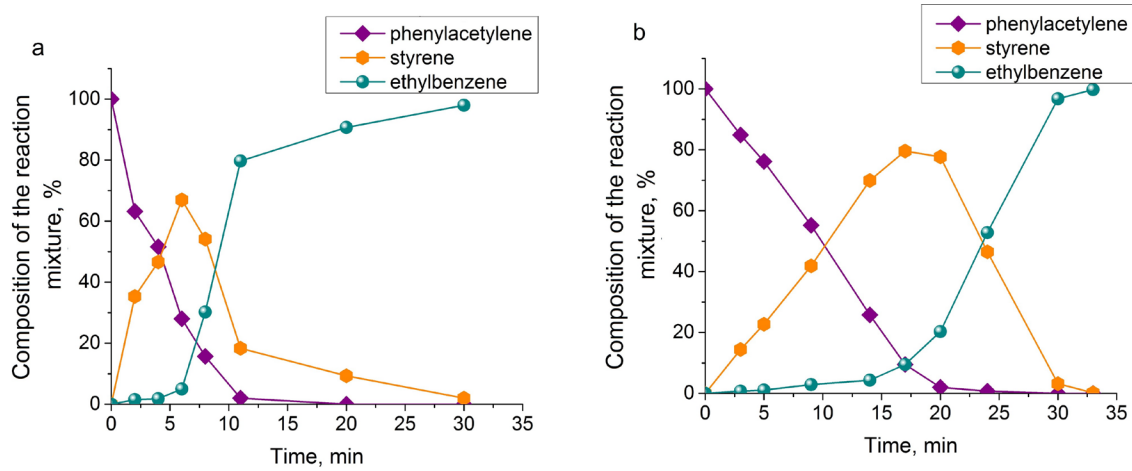


Fig. 6

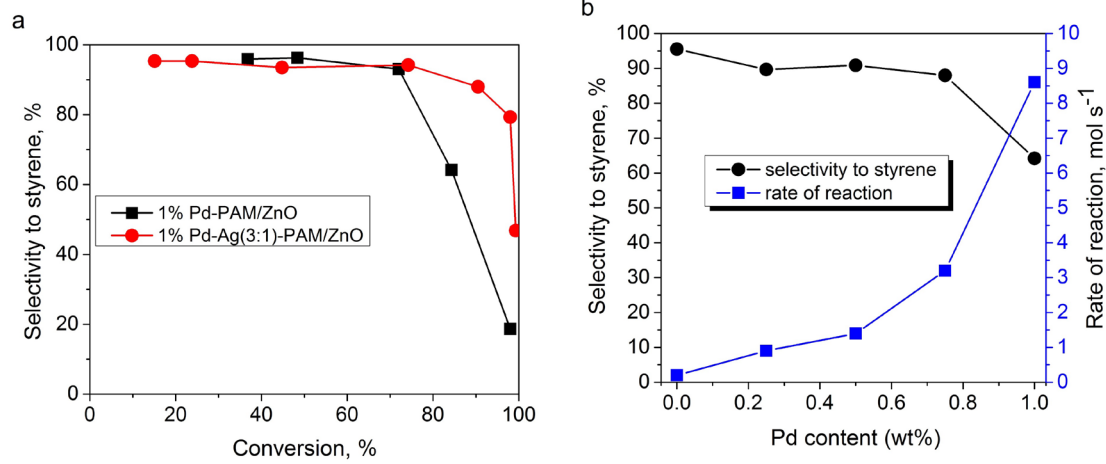


Fig. 7

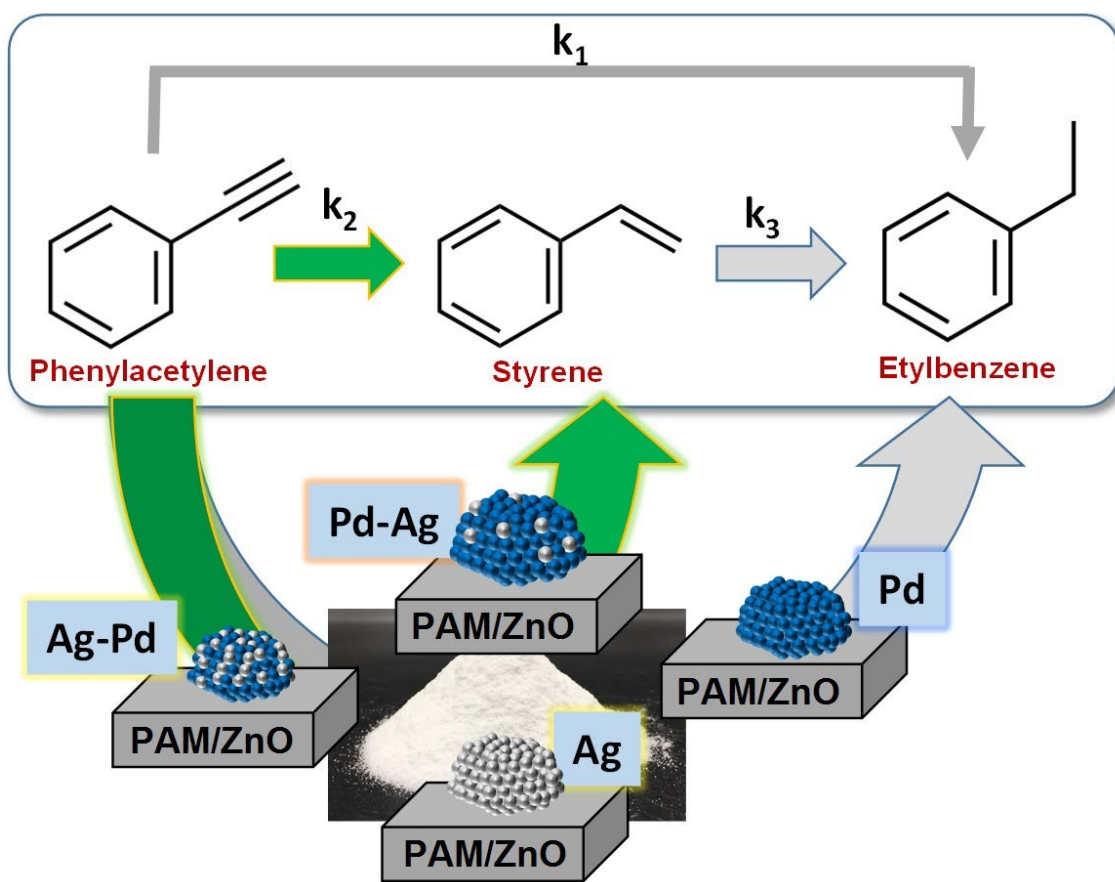


Fig. 8