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Preparation of Highly Dispersed Pd-Supported Catalysts for Hydrogenation Processes by Microemulsion Method

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Abstract

Preparation of nano-dispersed palladium particles on alumina support is described here using reverse microemulsion (water-in-oil) method. This synthesis protocol leads to a narrow Pd particle size distribution with particles of average size, which were significantly smaller compared to those prepared by classical impregnation method. It is shown that the particle size could be effectively controlled both by the microemulsion chemical composition such as concentration of PdCl₂ and the water/surfactant molar ratio and by the catalyst reduction process. Under the optimal reaction conditions, a Pd/Al₂O₃ catalyst with a homogeneous distribution of Pd particles of average size ~2.2 nm was obtained.

Keywords: Pd catalyst, particle size, reverse microemulsion, impregnation, particle size distribution

1. Introduction

Powder Pd-supported catalysts are indispensable in chemical processes to produce fine chemicals and intermediates in the pharmaceutical industry. These Pd-based catalysts are particularly used as universal catalysts for hydrogenation under mild conditions, which avoid the destruction of the reaction components. They are used, e.g. in reductive amination, carbonyl reduction, nitro compound reduction and reduction of imines and Schiff bases.

Pd-supported catalysts are also highly selective hydrogenation or hydrotreating catalysts widely used in important industrial processes, e.g. in selective hydrogenation of acetylene to ethylene of C₂ cracking fraction and selective hydrogenation of triple and diene bonds to

the corresponding olefins in C3 fraction or selective hydrogenation of phenols to ketones, e.g. cyclohexanone from phenol. Palladium is also very active in the hydrogenation of nitro compounds and it is used in the production of aniline by DuPont and the Bayer process.

The activity of supported catalysts containing noble metals is influenced by the type of catalyst support, the type of noble metal, the amount of an active component in the catalyst, the way of catalyst preparation, etc. The preparation of the supported catalysts in most cases requires the highest metal dispersion and thus the largest surface area of an active component. For these reasons, the particle size of Pd in supported catalysts can have a significant effect on catalytic activity and selectivity of these catalysts. For some types of reactions, it is necessary to optimize the size of metal crystallites at a certain critical value. If the average particle size of Pt is higher or lower than its optimal value, the activity of such a catalyst for toluene combustion in the gas phase decreases [1].

The distribution of the active component in the catalyst pellet along with the diameter and shape of the active component particles is closely connected with the method of the preparation [2]. That is why it is important to choose a suitable method for the preparation of the catalyst to provide an optimal dispersion of the active component in the catalyst and also its optimal location in the catalyst. There are various methods for catalyst preparation. The most commonly practiced techniques are incipient wetness impregnation with a metal salt solution, ion exchange with a metal-containing cation or anion and the use of organometallic complexes as precursors [3]. Using incipient wetness impregnation, the nanoparticles in solution can be stabilized by capping agents such as sugars (glucose, starch, carboxymethyl cellulose) to avoid aggregation and widening of the particle size distribution [4]. The use of microemulsion could be another preparation method promising the formation of small metal nanoparticles of a narrow size distribution, located on the external surface of the support. This method is described in this chapter.

The term microemulsion was first defined by Schulman and Friend in the 1940s [5]. Microemulsion (a reverse micellar system) is defined as a thermodynamically stable dispersion of two immiscible liquids stabilized by a surface film of emulsifier. It is a three-component system consisting of organic phases: oil, an aqueous phase and a surfactant. The surfactant is a substance which stabilizes the emulsion by reducing the interfacial tension between the dispersed particles of water in oil to a minimum, thus preventing the formation of large aggregates. For the preparation of heterogeneous catalysts, microemulsions of type W/O (water-in-oil) are important since highly dispersed particles of the metal salts or the metal particles can be prepared.

Synthesis of the metal nanoparticles from the microemulsion was first reported by Boutonnet et al. in 1982 [6], who synthesized the metal nanoparticles of Pt, Pd, Rh and Ir by the reduction of the salt dissolved in the aqueous phase of W/O microemulsion using hydrazine or hydrogen. Nanoparticles were used for the preparation of the supported catalysts. Kishida et al. [7, 8] described a new method of preparation of Rh catalysts with the very narrow metal dispersion. Isolated metal crystallites were first synthesized by hydrazine reduction of a metal precursor in the microemulsion. Subsequently the catalyst support was precipitated by the hydrolysis of metal alkoxide (tetraethyl orthosilicate, aluminium triisopropoxide, zirconium or titanium tetrabutoxide) in the microemulsion and the metal nanoparticles were

immobilized on the catalyst support. However, under such conditions, a part of the active metal particles is closed in pores of the support and therefore is catalytically inactive. By this phenomenon, the authors explained the differences between the values obtained from chemisorption measurements and TEM (transmission electron microscopy). Some of the metal particles buried in the support were not exposed on the surface for CO chemisorption [8]. Nevertheless, the catalysts prepared in this way showed higher activity than similar ones prepared by conventional incipient wetness impregnation method. These authors studied the effect of the surfactant selection and its molar ratio to water in the preparation of catalysts using the microemulsion. The dependence of the effect of the molar ratio of water and surfactant on the resulting particle size went through a minimum, but for each microemulsion system was specific. Kosydar et al. [9] used two microemulsion systems with anionic bis(2-ethylhexyl)sulfosuccinate (AOT) and non-ionic polyoxyethylene(7–8)octylphenyl ether (Triton-X 114) surfactants. Pd nanoparticles with sizes in a narrow range but various average sizes (8–9 and 4 nm) were obtained using hydrazine hydrate or NaH_2PO_2 as a reducing agent. Semagina et al. [10], Heshmatpour et al. [11] and Noh et al. [12] also reported on the application of water/AOT/isooctane microemulsion system for the preparation of Pd nanoparticles. Different nanoparticle size and size distributions were obtained depending on the reducing agent or precursor salt. Using N_2H_4 as a reducing agent, larger nanoparticles and a broader size ranges (6–13 nm) were obtained compared to NaBH_4 (3.9–5 nm). Although reducing agent plays an important role in the size of the metal nanoparticles formed, Chen et al. [13] reported on the formation of similar Pd nanoparticle size when N_2H_4 or NaBH_4 was used as a reducing agent, thus indicating the contribution of other factors. Thus Perez-Coronado et al. [14] synthesized Pd nanoparticles by a water-in-oil (w/o) microemulsion method using the water/AOT/isooctane system. N_2H_4 and NaBH_4 were used as reducing agents and water-to-surfactant ratios between 3 and 7 were considered. Results [14] showed that Pd nanoparticles with higher size were obtained when the water-to-surfactant molar ratio was increased. Lower reaction time and higher evaporation temperature led to the formation of smaller Pd nanoparticles. Higher values of mean size Pd nanoparticles were obtained with N_2H_4 compared to NaBH_4 . Wojcieszak et al. [15] investigated the size of palladium nanoparticles (1.6 wt.%) synthesized by the modified water-in-oil microemulsion method using hydrazine as the reducing agent by varying the nature of the organic surfactant and solvent. The results confirmed the dependence of the particle size on the nature of organic surfactants. Smaller particles were obtained with organic solvents and anionic surfactants. Kim et al. [16] compared the catalytic performance of Pd/ZrO₂ catalysts prepared from microemulsion with the ones prepared by the conventional impregnation method. The catalysts prepared by the microemulsion method exhibited a much higher activity for the hydrogenation of CO, the size distribution of Pd particles of the catalysts was remarkably narrow, and the average particle size was much smaller than that of the catalysts prepared by the impregnation method. It was found that the Pd particle size of the catalyst prepared by the microemulsion method could be controlled by the concentration of palladium salts in water pools. Kim et al. [16] also found that some of Pd particles of the catalyst were partly or wholly buried in zirconia support. Significantly higher activity of Pt catalysts for the combustion of toluene prepared from the microemulsion compared to those prepared by the impregnation with the aqueous solution of H_2PtCl_6 was observed by Rymeš et al. [1] as well. Pt particle size was up to ten times smaller. Poceroba

et al. [17] prepared 2.5 wt.% Pd/Al₂O₃ exhaust gas catalysts by incipient wetness impregnation technique and from microemulsion as well. Contrary to other authors, the catalysts prepared by incipient wetness impregnation technique consisted of smaller crystallite size than 2 nm and Pd was found to be well dispersed in comparison to microemulsion when the particle size was in the 20–40 nm range and the distribution of noble metal was irregular.

Eriksson et al. [18] published an extensive review focused on the preparation of catalysts from microemulsion and their applications in heterogeneous catalysis. This review covered most of the applications concerning heterogeneous catalysts, not only Pd supported but other noble metals were mentioned as well. It was concluded that the majority of the catalysts obtained from microemulsion showed high catalytic activity and the main advantages of using microemulsion technique were related to the possibility of controlling properties such as particle size, morphology and size distribution.

The aim of the study described here was to prepare highly dispersed Pd hydrogenation catalyst by the microemulsion method since the microemulsion method is more suitable for metal catalysts preparation [7, 8, 16] in comparison with conventional incipient wetness impregnation method. In this research, the focus was on optimizing the microemulsion preparation conditions, investigating the influence of reduction conditions, evaluating the physical properties and comparing them with the properties of the catalysts prepared by incipient wetness impregnation method. Details of these procedures and results are presented in the following pages. It is noted that the results presented in the figures and tables are original and not published anywhere before.

2. Experimental

2.1. Catalyst preparation

The reverse micellar system W/O was prepared from a commercial surfactant IGEPAL CO-520 dissolved in cyclohexane. The reason for choosing non-ionogenic surfactant was to reduce the influence of impurities such as Na⁺, K⁺ and SO₄²⁻ (which are contained in ionogenic surfactants) on the properties of the resulting catalyst. The concentration of the surfactant in cyclohexane was 0.5 mol/dm³. The aqueous solution of palladium chloride (0.85 g of PdCl₂ solution of concentration 1.0 mol/dm³) was added to the microemulsion prepared in such amounts that the catalyst (B [ME]) with demanded amount 3 wt.% of Pd was obtained. The exact amount of commercial support (2.49 g of γ-Al₂O₃, S_{BET} = 313 m²/g) calcined at 623 K was inserted in the microemulsion. The commercial surfactant IGEPAL CO-520 in the amount of 4.23 and 15.0 g of cyclohexane was used. This suspension was stirred under reflux and tempered at 298 K for 24 h. Precipitates were decanted, filtered, washed with ethanol and then dried at 393 K overnight. The samples were calcined in air at 623 K for 2 h. The catalyst prepared by this method will be denoted by [ME].

Catalysts I [IMP] and J [IMP] were prepared by incipient wetness impregnation. Impregnation of the commercial support (2.25 g of γ-Al₂O₃, S_{BET} = 313 m²/g) with aqueous solution of palladium chloride (0.99 g of PdCl₂ solution of concentration 1.5 mol/dm³) stabilized with hydrochloric

acid in such amount to obtain the catalyst (J [IMP]) with 3 wt.% of Pd. 20.0 g H₂O was used. The mixture was stirred for 24 h at room temperature. After filtration, the catalyst was first dried at 393 K for 2 h, then calcined in air at 623 K for 2 h.

The active component of the catalyst in the form of palladium oxide prepared by both methods was subsequently reduced to metallic palladium.

2.2. Catalyst reduction

Reduction of Pd precursors was carried out either in gas phase using hydrogen or in liquid phase using hydrazine monohydrate. The catalysts reduced in the gas phase by a mixture of hydrogen and helium (10:90) were placed in a quartz tube. Reduction was performed at 723 K with a heating rate 15 K/min for 2 h and was followed by desorption of hydrogen in inert gas at the same temperature for 1 h.

Reduction in the liquid phase was done using hydrazine monohydrate in the stoichiometric excess of 3:1 at 363 K for 2 h. After reduction, the sample had to be washed with ethanol to remove excess reducing agent and was dried at 393 K in an inert atmosphere.

2.3. Characterization of the catalysts

2.3.1. Surface area

BET surface areas of the catalysts were determined using Pulse Chemisorb 2700, Micromeritics, USA.

2.3.2. Size and distribution of palladium particles

Morphology, particle size and particle size distribution of metal were determined by transmission electron microscopy (HRTEM) on JEOL JEM 3010 operating at 300 kV and equipped with an energy-dispersive spectroscopy (EDS) detector (INCA/Oxford) and CCD Gatan (Digital Micrograph software). The transmission electron analysis was carried out on samples that were subsequently dispersed in propan-2-ol, followed by the application of a drop of a diluted suspension on Cu grid.

Pd particle size was determined using CO chemisorption as well. For the measurements, a custom-made apparatus was used [19]. The catalyst was dried prior to measurement in the air at 393 K for 2 h. The sample treatment was performed first in the inert and then in the reducing atmosphere. The treatment in the reducing H₂ atmosphere was carried out for the reduction of PdO contained in the catalyst. Since hydrogen is not only very strongly absorbed on the surface of Pd, but also dissolved in the subsurface layers of the metal it is necessary to include hydrogen desorption step at 523 K after reduction of the catalyst. Hydrogen desorption provided decomposition of the resulting β -hydride of Pd, which is very easily formed even at room temperature and, according to literature, is unstable at high temperatures and low pressure [20]. CO chemisorption measurements were carried out with CO (5 vol.% in He) at 298 K using pulse technique. To calculate average Pd particle size (d_{AV}) and specific surface area of Pd (S_{Pd}) from chemisorption data, the following parameters were used: constant depending

on the shape of metal particles and contact with the support ($k = 6$); surface density of metal atoms ($C_{\text{Pd}} = 1.26 \times 10^{19}$ atom/m²) and stoichiometry of adsorption Pd:CO ($S_{\text{AV}} = 2$) [21].

2.3.3. Reducibility of active centres of catalyst

Temperature-programmed reduction (TPR) was used to describe the reducibility of different active centres and their concentrations. The samples were first dried in air at 393 K for 2 h to constant weight. TPR analysis of the samples was performed using a commercial device Autochem II 2920 Micromeritics, USA, with H₂/Ar mixture 5/95. During the analysis, the temperature was increased linearly with time to a temperature of 923 K with a heating rate of 5 K/min.

2.3.4. Metal content determination

The metal content was determined directly by X-ray fluorescence (XRF) analysis and indirectly by atomic absorption spectrometry (AAS). The indirect determination of Pd content in the catalyst consisted of a liquid sample analysis, which was prepared by multiple leaching of a defined amount of Pd catalyst using aqua regia. Quantitative transfer of Pd in the solution was indicated by the support discoloration and the last extract from the catalyst was colourless as well. Quantitative dissolution of Pd gave PdCl₄²⁻ solution which was analysed by atomic absorption spectroscopy.

3. Results and discussion

3.1. Effect of preparation conditions of microemulsions on the physical properties of catalysts

When the effect of preparation conditions of microemulsions was monitored, attention was paid to two parameters namely the concentration of metal salts in the aqueous solution and the molar ratio of water and surfactant.

3.1.1. Effect of PdCl₂ concentration

According to literature [7, 8, 16], the concentration of metal component precursor in the form of soluble salts in the aqueous solution has a significant impact on the final size of metal particles. Therefore, the effect of PdCl₂ concentration in the aqueous solution was studied. Palladium catalysts were prepared from PdCl₂ solutions of different concentrations in the range from 0.25 to 1.5 mol/dm³. Other preparation conditions of microemulsions such as surfactant type, its concentration in the solvent and the molar ratio of water to surfactant remained constant. The molar ratio of water to surfactant was 4 to evaluate the influence of PdCl₂ concentration on Pd crystallite size in the final catalyst.

The observed Pd crystallite size dependence on the concentration of PdCl₂ goes through a minimum as is shown in **Table 1**. When using 1 M solution of PdCl₂ for the preparation of the

| Catalyst | $c(\text{PdCl}_2)$ [mol/dm ³] | w_{Pd} [%] | $d_{\text{AV}}(\text{Pd})^a$ [nm] | S_{Pd} [m ² /g _{Pd}] |
|----------|---|---------------------|-----------------------------------|--|
| A [ME] | 1.50 | 2.9 | 3.0 | 131.4 |
| B [ME] | 1.00 | 2.9 | 2.2 | 180.9 |
| C [ME] | 0.50 | 2.5 | 2.3 | 172.8 |
| D [ME] | 0.25 | 2.1 | 2.6 | 152.2 |

^aDetermined from chemisorption measurements.

Table 1. Effect of PdCl₂ concentration on Pd crystallite size in the resulting catalyst.

microemulsion, the resulting average Pd particle size determined by CO chemisorption was 2.2 nm. When the effect of PdCl₂ concentration on the final particle size of Pd in the prepared catalyst was evaluated, an efficiency of Pd loading on the support was studied as well. When using both 1 and 0.5 M solutions, highly dispersed catalysts with Pd particle size of approximately 2.3 nm were obtained. However, when using PdCl₂ solution of 1 M concentration, the catalyst with desired Pd content of 3 wt.% was obtained, while at the concentration of 0.5 M, the Pd content was only 2.5 wt.%.

3.1.2. Effect of molar ratio of water to surfactant

Another parameter influencing the final metal particles is the molar ratio of water and surfactants, the so-called R factor. The amount of surfactant in the microemulsion affects the size and shape of water drops dispersed in an oil phase. Too high a value of R factor can lead to the formation of unstable microemulsion and its breaking. To evaluate the influence of the R factor values, PdCl₂ concentration of 1 mol/dm³ was used based on the results shown in **Table 1**.

The values reported in **Table 2** show that the molar ratio of water and the surfactant does not affect the final Pd content loading on the support since the Pd content was close to the desired value of 3 wt.% for all catalysts.

When increasing the surfactant content in microemulsion, Pd dispersion increased. When R factor was equal to 8, the final Pd particle size determined from chemisorption data was 2.3 nm.

| Catalyst | R factor | w_{Pd} [%] | $d_{\text{AV}}(\text{Pd})^a$ [nm] | S_{Pd} [m ² /g _{Pd}] |
|----------|----------|---------------------|-----------------------------------|--|
| E [ME] | 4 | 2.9 | 2.2 | 180.9 |
| F [ME] | 8 | 2.9 | 2.3 | 172.4 |
| G [ME] | 12 | 2.9 | 2.8 | 142.7 |
| H [ME] | 16 | 2.8 | 4.1 | 96.9 |

^aDetermined from chemisorption measurements.

Table 2. Effect of molar ratio of water to surfactant on Pd crystallite size in the resulting catalyst.

On further lowering the R factor, the particle size remained almost unchanged. Therefore, for the further preparation of catalyst, the value of $R = 4$ was used. This result is in compliance with the conclusions mentioned by Perez-Coronado [14] and Kim et al. [16], who minimized the Pd particle size in a similar system (Pd/ZrO₂) using R factor equal to 4.4.

3.2. Controlled sintering of metal component

The process of calcination is necessary for removing the surfactant after catalyst preparation using the microemulsion technique. Calcination is also responsible for the decomposition of metal precursors to the formation of oxides; therefore, calcination is carried out in air atmosphere at high temperatures. Calcination at various high temperatures can affect the resulting metal particle size in the prepared catalyst because of the sintering of the particles. Recently it has been reported by Forman et al. [22] that silica-encapsulated Pd nanoparticles prepared from microemulsion showed more sintering-resistant behaviour compared to the particles prepared by the impregnation method.

Pd catalyst prepared from microemulsion and subsequently calcined at 723 K showed high dispersion with a narrow size distribution of Pd crystallites since almost 80% of Pd particles were in the range 1–3 nm based on HRTEM measurements (**Figures 1 and 2**).

P0 [ME] catalyst was divided into five parts (**Table 3**), which were treated in the range from 773 to 1223 K in an inert atmosphere for 2 h. In this temperature range, no irreversible changes of the catalyst support were observed. BET surface areas of 3% Pd/Al₂O₃ catalysts calcined at 723 and 1223 K were 274 and 264 m²/g, respectively.

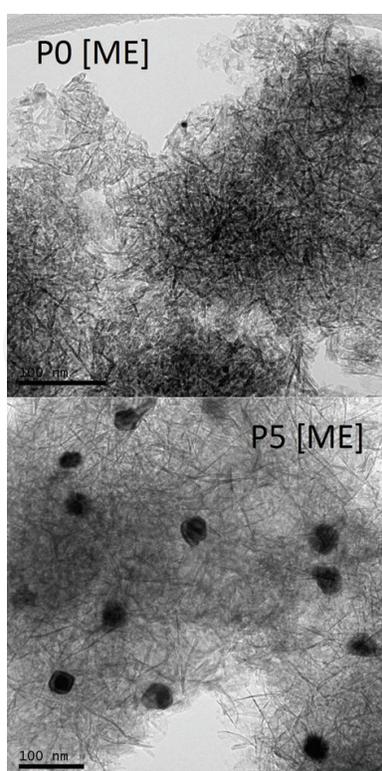


Figure 1. HRTEM micrographs of highly dispersed catalysts P0 [ME] and P5 [ME] (bar length = 100 nm).

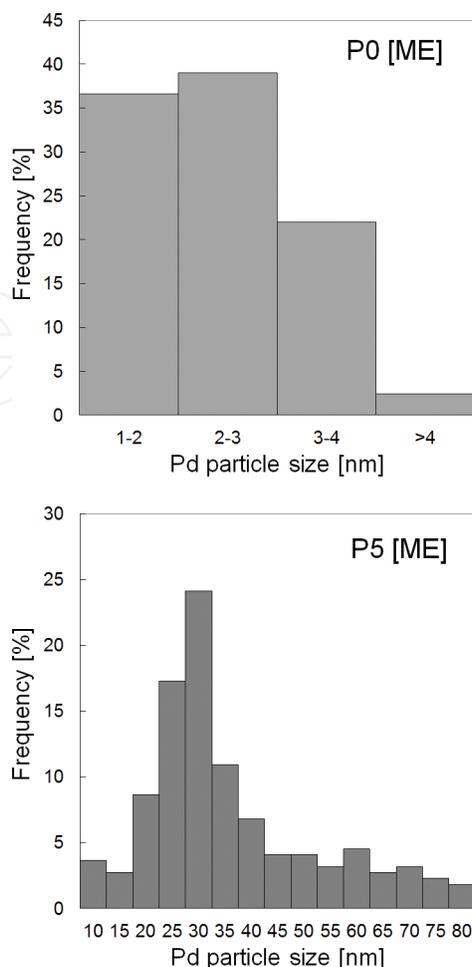


Figure 2. Histograms of Pd particle sizes determined by HRTEM in catalysts (P0 [ME] and P5 [ME]) prepared by the microemulsion technique.

Results obtained from both chemisorption measurements (**Table 3**) and HRTEM analyses (**Figure 2**) for very small metal particles (in units of nm) showed high degree of sintering at a temperature of 923 K. However, when using temperatures higher than 1023 K, further significant decrease of Pd specific surface area (S_{Pd}) did not occur. S_{Pd} values of the catalysts treated at temperatures 1023, 1123 and 1223 K were almost constant (**Table 3**).

| Catalyst | $T_{\text{calcination}}$ [K] | d_{AV} (Pd) ^a [nm] | S_{Pd} [m ² /g _{Pd}] |
|----------|------------------------------|---------------------------------|---|
| P0 [ME] | 723 | 2.2 | 169.6 |
| P1 [ME] | 773 | 5.7 | 70.1 |
| P2 [ME] | 923 | 16.3 | 25.6 |
| P3 [ME] | 1023 | 27.6 | 14.4 |
| P4 [ME] | 1123 | 31.3 | 12.7 |
| P5 [ME] | 1223 | 32.0 | 12.4 |

^aDetermined from chemisorption measurements.

Table 3. Effect of calcination temperature on Pd crystallite size in the resulting catalyst.

Pd catalyst prepared from microemulsion and subsequently calcined at 723 K showed high dispersion with a narrow size distribution of Pd crystallites since almost 80% of Pd particles were in the range 1–3 nm based on HRTEM measurements (**Figures 1 and 2**).

The results obtained from HRTEM analyses confirmed that Pd particle size after reaching a certain size did not increase. The largest Pd crystallites found in the HRTEM micrographs had the size of approximately 80 nm. At the Pd content of 3 wt.%, these crystallites were large enough to be separated from each other on the support. The further sintering of Pd particles could occur only with difficulty.

Catalysts treated at higher temperatures compared to P0 [ME] catalyst showed a wider size distribution (**Figure 2**). For example, the catalyst sintered at 1223 K contained 70% of Pd particles in the range 15–40 nm. The average particle size determined by CO chemisorption was 32 nm. Controlled sintering at high temperatures does not lead to a catalyst with a narrow particle size distribution. Sintering is very fast probably due to the high metal content in the catalyst. To prepare a series of the catalysts with different Pd dispersion, but with the narrow particle size distribution, it is necessary to choose a different method than controlled sintering, e.g. to control the particle size with microemulsion preparation conditions. It would be necessary to optimize several parameters so that the catalysts prepared under different conditions showed, besides the Pd dispersion, the same parameters such as content of metal and impurities.

3.3. Effect of catalysts' reduction on Pd particle size

Reduction of metal precursors of the catalysts can be performed in several ways. The most common is reduction in the gas phase using hydrogen or its mixture with an inert gas as a reducing agent. Another way is reduction in the liquid phase using hydrazine or formaldehyde.

To determine the temperature needed to reduce PdO, produced during calcination of the metal precursors in air atmosphere at high temperatures, TPR was used. On the TPR record of the catalyst, two reduction maxima were observed in the temperature range from 578 to 663 K. Therefore for the reduction of Pd/Al₂O₃ catalyst in the gas phase, the temperature of 723 K was chosen. At the temperature of approximately 363 K, a negative peak was clearly visible. It represented a decomposition of β -hydride of Pd described in literature [20] which is formed due to contact of Pd with hydrogen.

The dispersion of Pd in the catalysts reduced in the gas and the liquid phase was determined from the CO chemisorption measurements of Pd specific surface area. It was found that the catalyst reduced in the liquid phase showed lower S_{Pd} value determined by CO chemisorption. It was assumed that this difference can be caused by the blocking of active sites for CO adsorption by unreacted hydrazine. This was denied by experiment (*b* in **Table 4**) using the higher drying temperature for desorption of impurities in an inert atmosphere (623 K). S_{Pd} value of that catalyst was close to the previous experiment (*a* in **Table 4**). Since hydrazine reduction was performed at 363 K, no sintering of Pd crystallites can occur. Also, desorption at 623 K should not cause the sintering of Pd crystallites because reduction in the gas phase was carried out at 723 K and this phenomenon was not observed. The lower values of S_{Pd} can be

| Reducing agent | S_{Pd} [m^2/g_{Pd}] | d_{AV} (Pd) ^c [nm] |
|--|---------------------------|---------------------------------|
| H ₂ (g) | 169.6 | 2.2 |
| N ₂ H ₄ (l) ^a | 65.8 | — |
| N ₂ H ₄ (l) ^b | 70.6 | 5.8 |

^aDrying of the catalyst sample at 393 K after reduction in the liquid phase.

^bDrying of the catalyst sample at 623 K after reduction in the liquid phase.

^cDetermined by HRTEM.

Table 4. Effect of reducing agent on Pd specific surface area and on Pd crystallite size.

explained by recrystallization of Pd particles, their diffusion on the support and a formation of larger clusters. The formation of larger Pd crystallites during reduction in the liquid phase was confirmed by d_{AV} (Pd) determination from HRTEM measurements (**Table 4**).

This observation is inconsistent with the commonly known theory, according to which the reduction performed in the liquid phase should be the more efficient way to keep high dispersion of the metal on the support.

3.4. Preparation of catalysts by incipient wetness impregnation

Method of incipient wetness impregnation of the support with aqueous solutions of salts and acids is a basic procedure for the preparation of heterogeneous catalysts. This procedure was used to compare such prepared catalyst with that prepared from the microemulsion. The amount of impregnation solution was chosen to keep the same Pd content and concentration in the resulting suspension with the support as in the preparation of A [ME] catalyst using the microemulsion. The other preparation conditions namely impregnation time, calcination temperature and reduction in the gas phase have been retained as well. The Pd particle size in the resulting catalyst was determined by CO chemisorption.

The determined Pd content in such prepared catalyst (I [IMP]) was only 1.5 wt.% (**Table 5**). Therefore, for further comparison, the catalyst with two-times higher Pd content (J [IMP]) in the impregnation solution was prepared. Increasing Pd content on the support led to the increase of Pd crystallite size and the decrease in the specific surface area of Pd in the catalyst. J [IMP] catalyst of comparable Pd content, prepared by incipient wetness impregnation, contained Pd particles of average size 5.6 nm. Obtained results therefore indicate that the microemulsion preparation technique leads to higher dispersion of Pd than wet impregnation method.

| Catalyst | w_{Pd} [%] | S_{Pd} [m^2/g_{Pd}] | d_{AV} (Pd) ^a [nm] |
|----------|--------------|---------------------------|---------------------------------|
| I [IMP] | 1.5 | 79.2 | 4.7 |
| J [IMP] | 2.7 | 66.8 | 5.6 |

^aDetermined by HRTEM.

Table 5. Properties of catalysts prepared by incipient wetness impregnation of support.

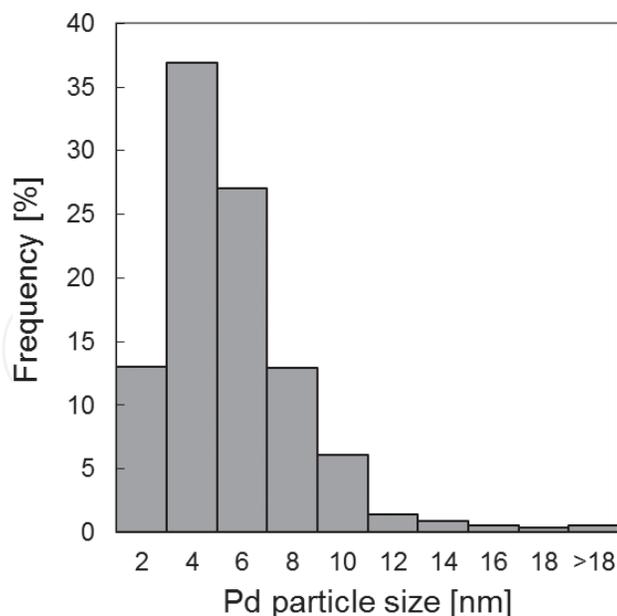


Figure 3. Histogram of Pd particle sizes determined by HRTEM in I [IMP] catalyst.

Based on HRTEM measurements it was found that the Pd particle size distribution of I [IMP] catalyst was broader in comparison with P0 [ME] catalyst (**Figures 2 and 3**). The highest frequency of particles was in the range 2–6 nm. However, I [IMP] catalyst contained particles larger than 10 nm unlike P0 [ME] catalyst.

4. Conclusions

Experimental results presented here show that the Pd/Al₂O₃ catalysts prepared from the microemulsions contained much smaller Pd particles and had narrower distribution of Pd particle size than the catalysts prepared by classical incipient wetness impregnation of the supports with water solutions of palladium chloride.

Study of the effect of the preparation conditions of the microemulsions was focused on the concentration of PdCl₂ in an aqueous solution and the molar ratio of water and surfactant. It was found that the optimal PdCl₂ concentration was equal to 1 mol/dm³. Using this concentration, catalysts with the highest Pd content and high Pd dispersion were obtained. The average particle size in such catalysts was 2.2 nm. Another condition of the microemulsion preparation technique influencing the final size of metal particles was the molar ratio of water and surfactant. It was found that with decreasing ratio of water and surfactant, Pd dispersion on the support increased. The optimal value of R factor equal to 4 for the microemulsion system with used surfactants was found. Thus, the prepared catalyst showed a narrow particle size distribution, containing 80% Pd crystallites in the range 1–3 nm.

Using controlled sintering at high temperatures the catalyst with the narrow particle size distribution could not be obtained. Pd particle sintering proceeded very fast at temperatures

above 773 K. Catalysts calcined at higher temperatures in the range from 1023 to 1223 K showed almost the constant value of the d_{AV} (Pd) \sim 30 nm. Pd particle size after reaching a certain value did not further increase. The largest particles were up to 80 nm.

Furthermore, it was found that the method of reduction has a significant effect on the resulting Pd dispersion. The average particle size of palladium in catalysts reduced in the gas phase using hydrogen was lower than the one reduced in the liquid phase using hydrazine monohydrate. These results were confirmed by HRTEM measurements.

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