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SUPPORTED PALLADIUM NANOPARTICLES
PREPARED BY COLLOIDAL SYNTHESIS:
CHARACTERIZATION AND CATALYTIC ACTIVITY

Ph. D. Thesis

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Supervisor: László Guzzi



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1. INTRODUCTION

Nowadays we can witness an ever increasing progress of materials science. In the field of space technology, electronics and semiconductor industry there is a growing need for novel materials, which possess unique mechanical, electronic, optical and chemical properties. Thus, investigation of nanosize materials is of great importance, as particles built up from only a few hundreds of atoms have characteristics different from the bulk.

Nanosize materials, primarily metal particles dispersed on a support, have been applied for a long time in the field of heterogeneous catalysis. Due to their high surface excess energy, metal particles several nanometers in diameter are very sensitive to changes in their environment, and in the absence of sufficient stabilization thermodynamical driving forces cause aggregation. As a result of their special electronic and morphological properties, these small particles show unique catalytic activity. The knowledge obtained about the catalytic behaviour of nanosize metals is by no means complete, and so there is a need for further investigations. This research requires synthesis methods by which the planned catalyst structure and morphology can be realized.

Aiming the preparation of monodisperse metal particles, colloid chemical synthesis methods are likely to offer intriguing possibilities. In order to produce particles a few nanometer in diameter, the rate of nucleation and particle growth must be well balanced or particle growth should be geometrically restricted. Reduction of metal precursor ions in the liquid phase results in the formation of nanoparticles, which are able to maintain their integrity only in the presence of stabilizers.

The support surface itself may also act as a stabilizer. In this case the reduction of metal ions takes place in the solid/liquid interfacial layer of the support

suspended in a binary liquid system. Under optimal circumstances the concentration of one solvent component, that of ethanol, is greatly increased in the interfacial layer of the support, while it becomes almost negligible in the bulk solution. The precursor ions diffusing into the interfacial layer are reduced by ethanol. Thus, by the above method that we call “controlled colloidal synthesis” (CCS), supported metal catalysts can be prepared in a single synthetic step. Aggregation of metal nanoparticles formed by liquid phase reduction can also be prevented by the use of polymers. Doing so, the reduction step results in a sol which can subsequently be deposited on a support. However, supported metal catalysts prepared by this so-called “sol method” usually contain a significant amount of organic contaminant.

In the present work the above colloid chemical preparation methods are evaluated through the investigation of supported Pd nanoparticles prepared by these liquid phase reduction techniques. Advantages and disadvantages of these colloid chemical methods as compared to the more traditional impregnation technique are also discussed.

The aim of this work can be summarized as follows:

- To prepare supported Pd catalysts both by particle growth in the solid/liquid interfacial layer of the support and by adsorption of sols, and to investigate the structure of the catalysts;
- To determine the conditions by which monodisperse metal nanoparticles can be produced, and to study the possibility of size control;
- To investigate the catalytic performance of samples prepared by the different methods, and to reveal the possible effect of contamination on catalytic activity.

2. EXPERIMENTAL

The samples were synthesized using PdCl_2 or $\text{Pd}(\text{OAc})_2$ as metal precursor and Aerosil, nonporous SiO_2 as support.

Pd^{2+} ions were reduced by ethanol in the solid/liquid interfacial layer of the support. In ethanol/toluene/Aerosil or ethanol/water/Aerosil suspensions composition of the binary liquid mixture has been changed due to adsorption on the support. This change in the concentration was measured by refractometer or gas chromatograph. Based on these results, the adsorption excess isotherms of ethanol were determined, and the optimal compositions of the systems were chosen. Parameters of the reduction process were altered to obtain SiO_2 supported Pd nanoparticles of different size.

Pd sols were prepared by ethanol reduction of Pd^{2+} ions and were stabilized by poly(diallyldimethylammonium chloride) (PDDA). By addition of different amounts of ethanol and PDDA to the PdCl_2 solution, nanoparticles of different size were obtained. Supported catalysts were prepared by the adsorption of the sols onto Aerosil.

Reference samples were prepared by impregnation of Aerosil with Pd^{2+} ions followed by oxidation and reduction at different temperatures.

Particle size and Pd dispersion were determined by means of transmission electron microscopy (TEM) and CO-chemisorption measurements. The presence of crystalline Pd phases was revealed by X-ray powder diffraction (XRD), the oxidation state of Pd and the surface composition of the catalysts were determined by X-ray photoelectron spectroscopy (XPS). Temperature programmed reduction (TPR) was applied to test the presence of Pd species other than Pd^0 and to set the reduction temperature of Pd precursors. X-ray fluorescence (XRF) was used to measure the metal content of the samples. Prompt-gamma activation analysis

served to determine the chloride content. Temperature programmed oxidation (TPO) gave information on the amount and the nature of organic contamination originating from the preparation conditions. The nature of carbonaceous deposits formed during the reduction of PdO/SiO₂ by gas phase ethanol was also investigated. The structures of the supported catalysts were further characterised by rheological measurements applying a rotational viscosimeter. The morphology of Pd was investigated by infrared spectroscopic (FTIR) measurements of adsorbed CO.

Catalytic activity was tested in the gas phase benzene hydrogenation reaction in a plug-flow reactor coupled with a gas chromatograph for analysis. Reaction rates were measured at 393 K in "as received" state and after oxidation and reduction treatments at different temperatures.

3. NEW SCIENTIFIC RESULTS

1. Possibilities of size control

- 1.1. In ethanol/toluene liquid mixture after the initial nucleation Pd²⁺ ions being reduced do not form new nuclei but are deposited on the surface of the nuclei already formed. The experimental data coincide with the theoretical curve describing the dependence of the diameter of spherical particles on the amount of Pd, supporting the above-mentioned conclusion.
- 1.2. In ethanol/water liquid mixture nucleation and particle growth can hardly be separated in time, and increase of the Pd particle size leads to a more heterogeneous size distribution. The Pd particle size could be controlled by variation of the reduction temperature and the initial Pd²⁺ ion concentration.
- 1.3. Using the sol deposition method, the presence of PDDA stabilizer prevents the aggregation of Pd particles formed in liquid phase. Decrease of Pd particle

size down to 3 nm was accomplished by increasing the ethanol and PDDA concentrations. Adsorption of the sols onto the support results in stable, evenly distributed Pd particles.

1.4. Pd/SiO₂ catalysts prepared by colloid chemical methods maintain their original particle size and size distribution during calcination and/or reduction up to 573-673 K.

2. Carbonaceous contamination of the catalysts

2.1. TPO investigations of carbonaceous deposits showed that toluene and Pd-acetate do not play a significant role as sources of contamination. During TPO measurements CO₂ appeared as a rather sharp peak generally between 560-643 K. The sharp peak indicates the removal of deposits located near the metal particles that convert to CO₂ in a catalytic reaction with oxygen activated on Pd. The TPO spectrum of sample prepared from Pd sol containing a higher amount of polymer has a different character – in this case the metal surface is likely partly covered.

2.2. According to TPO and TPD measurements, ethanol and acetaldehyde remaining from the liquid phase reduction desorb from the support surface at low temperatures. Other organic fragments observed in the higher temperature range of the TPO spectrum are assigned to byproducts formed during the reduction and subsequent drying, as well as during the TPO run.

2.3. In TPO spectra taken after gas phase ethanol reduction of PdO/SiO₂ immediate CO₂ formation was observed, and a broader peak around 500 K was also seen. The first peak is attributed to the oxidation of CO formed by the decomposition of ethanol on Pd surface. The other, broad peak is related to the oxidation of the organic residues located on the metal particles and near to metal particles.

- 2.4. Experiments modelling the drying process of samples prepared by CCS revealed that the presence of air at 353 K promotes desorption and oxidation of CO and other reduction byproducts. This “self-cleaning” behaviour is of great importance from a catalytic point of view.
- 2.5. Calcination at 573 K – according to XPS and XRD measurements – causes the removal of carbonaceous deposits and partial or total oxidation of Pd, as well. However, dispersion data based on CO-chemisorption and TEM measurements in “as received” state agree well, and after oxidation/reduction treatment do not change significantly (except for the sample prepared by sol method in the presence of a higher amount of polymer), suggesting that carbonaceous deposits are located mainly on the support surface.

3. Catalytic activity in benzene hydrogenation

- 3.1. TOF values calculated by dispersion based on CO-chemisorption or TEM measurements increased after calcination and reduction. This result is explained by Pd surface restructuring during Pd/PdO/Pd phase conversion. The reduction carried out in hydrogen at 353 K produces a disordered Pd surface with numerous defect sites, which may increase the amount of weakly bound hydrogen and simultaneously promotes benzene conversion.
- 3.2. Investigations of adsorbed CO by IR spectroscopy revealed that PdO reduction results in the formation of an open, disordered Pd surface (in the case of the monodisperse samples investigated, the intensity of peak at 1980-1990 cm^{-1} , assigned to CO bound to Pd(100) surface, increased).
- 3.3. Changing the temperature of reduction following the oxidation steps causes reversible changes in the reaction rates measured. Reduction at higher temperature “smooths” the Pd surface, which leads to a decrease in activity.

The rather disordered and more active Pd surface can be formed again by the repeated oxidation followed by low temperature reduction.

4. APPLICATION OF RESULTS

The results obtained are mainly of scientific importance. Improvement of the particle growth method to produce monodisperse and smaller supported metal particles is indeed hopeful; for example, application of nonporous SiO₂ may open new possibilities.

Metal particles in sol stabilized by PDDA are proper precursors of supported catalysts, since positive charge of the PDDA together with the increase of pH allow the deposition of higher amounts of the polymer, furthermore, the removal of stabilizer does not cause Pd sintering.

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