

# Preparation of an organophilic palladium montmorillonite catalyst in a micellar system

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The cation-exchange reaction between sodium montmorillonite and tetradecyltrimethylammonium bromide serving as a stabilizing agent in a palladium hydrosol led to the formation of alkylammonium montmorillonite with simultaneous immobilization of the palladium nanoparticles in the organoclay host; the Pd-organoclay proved to be catalytically active in olefin hydrogenation in the liquid phase.

The incorporation of Pd<sup>2+</sup> ions, Pd(II) complexes or metallic Pd particles between the silicate layers of montmorillonite permits liquid-phase hydrogenation reactions with improved catalytic activity and specificity as compared with those involving supported Pd catalysts prepared by conventional impregnation routes, or with Pd(II) catalysts used in homogeneous solution. Pd(II) acetate and Pd(II) chloride have earlier been anchored to internal surface sites of montmorillonite *via* bipyridyl, diphenylphosphine and other linkages to produce interlamellar functionalized montmorillonite Pd(II) catalysts.<sup>1,2</sup> Reaction of ion-exchanging Na<sup>+</sup>-montmorillonite with [Pd(NCMe)<sub>4</sub>]<sup>2+</sup> and subsequent reduction of the Pd<sup>2+</sup> in methanol afforded highly-dispersed metallic Pd particles in the clay galleries.<sup>3</sup> Ethanol is both a solvent and a reducing agent for Pd(II) acetate.<sup>4</sup> The preferential adsorption of ethanol from dilute hydrocarbon solutions in the interlamellar spaces of alkylammonium montmorillonite<sup>5,6</sup> and alumina-pillared montmorillonite<sup>7</sup> provided a suitable environment for *in situ* reduction of the Pd(II) acetate precursor in the interlamellar spaces of the clay host. The present work describes a new pathway for the production of organophilic Pd-montmorillonite (Pd-M) with a good control over the size of the Pd nanoparticles and the Pd content of the clay. The method involves the synthesis of a monodispersed Pd hydrosol with subsequent deposition of the Pd particles onto the clay lamellae.

The preparation of the Pd hydrosol and a systematic study relating to the control over the Pd particle size were performed under the following experimental conditions. 25–200 μL of Pd(II) acetylacetonate [Pd(acac)<sub>2</sub>] solution (0.5–3 w/v% in CHCl<sub>3</sub>) were added to 10 mL of tetradecyltrimethylammonium bromide (C<sub>14</sub>TAB) surfactant solution [5–50 times the critical micelle concentration (cmc = 3.9 mM at 298 K in water)]. An excess of NH<sub>2</sub>NH<sub>2</sub> solution (55 w/w% in water) was then introduced into the micellar system, which was left under vigorous stirring overnight to produce ultrafine Pd particles stabilized by the cationic surfactant.

The preparation of Pd-M and a systematic study concerning the control over the Pd content of the Pd-organoclay included the following experimental conditions. 50–200 mL of Pd hydrosol (stabilized with C<sub>14</sub>TAB, 5–50 times the cmc) were added to 100–500 mL Na<sup>+</sup>-montmorillonite suspension (0.1–2 w/w% in water) and the system was mixed vigorously overnight. The surfactant molecules rendered the clay surface hydrophobic, in parallel with the adsorption of the Pd particles on the silicate surface. The Pd-M material was purified by several centrifugation/redispersion cycles in ethanol and finally dried in the oven.

The proposed mechanism for the successive formation of the Pd hydrosol and the Pd-organoclay is outlined in Fig. 1. Whereas water is a poor solvent, CHCl<sub>3</sub> is a good solvent for Pd(acac)<sub>2</sub>. The apparent solubility of CHCl<sub>3</sub> in water increases considerably if a sufficient quantity of C<sub>14</sub>TAB surfactant is present in the aqueous phase (*c* > cmc). This solubilization effect allows the preparation of an aqueous colloidal solution of Pd(acac)<sub>2</sub> previously dissolved in CHCl<sub>3</sub>. The UV-VIS spectra (UVIKON 930 spectrophotometer) of Pd(acac)<sub>2</sub> indicated a shift in the absorbance maximum in the micellar solution (340 nm) as compared with that in pure CHCl<sub>3</sub> solvent (327 nm). This observation may be attributed to the change in the microenvironment of Pd(acac)<sub>2</sub> upon solubilization, or to the formation of an adduct between the surfactant and the palladium salt.<sup>8</sup> In either case, the addition of an aqueous NH<sub>2</sub>NH<sub>2</sub> solution to the Pd(acac)<sub>2</sub>-CHCl<sub>3</sub>-C<sub>14</sub>TAB-water micellar system resulted in the formation of nanoscale Pd particles, partly sterically and partly electrostatically stabilized by the cationic surfactant molecules adsorbed on the surface of the particles (Fig. 1). The size distribution of the Pd particles in the hydrosol was determined by using a Philips C-10 transmission electron microscope (TEM) at 100 kV, assisted by the UTHSCSA Image Tool program. The present preparation method yielded spherical, monodispersed particles with a good control of size in the range 1.5–6 nm. We found that the particle size in the Pd hydrosol decreases with a decrease of the Pd(acac)<sub>2</sub> concentration and, in particular, with an increase of the C<sub>14</sub>TAB concentration.

The formation of Pd-M was readily achieved by mixing the hydrosol with a dilute montmorillonite suspension. Reaction of the ion-exchanging Na<sup>+</sup>-montmorillonite with the stabilizing (and in part with free) cationic surfactant molecules resulted in the formation of organophilic alkylammonium montmorillonite with the simultaneous release and subsequent deposition of the Pd nanoparticles onto the surface of the silicate layers (Fig. 1).

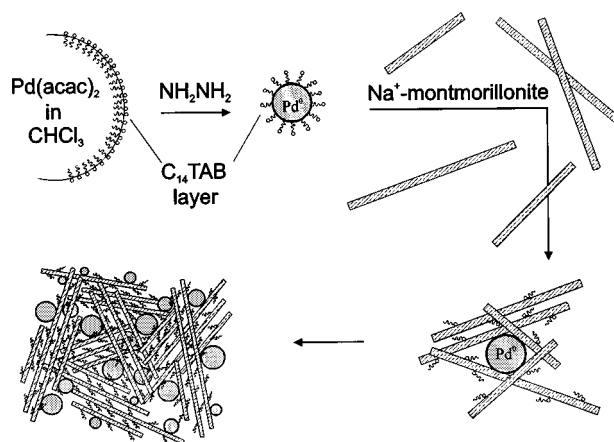


Fig. 1 Schematic illustration of the proposed mechanism for the successive formation of Pd hydrosol and Pd-organoclay in a micellar system.

**Table 1** Characterization of organophilic Pd-montmorillonite catalysts

| Catalyst code number | d(TEM)/nm | Pd (w/w%) (UV-VIS) | Pd (w/w%) (ICP-AES) | $10^{-3}r_1^a$ (styrene) | $10^{-3}r_1^a$ (hex-1-ene) | $10^{-3}r_1^a$ (cyclohexene) |
|----------------------|-----------|--------------------|---------------------|--------------------------|----------------------------|------------------------------|
| Pd-M1                | 2.42      | 0.09               | 0.11                | 275.1                    | 101.8                      | 9.5                          |
| Pd-M2                | 3.25      | 1.15               | 1.32                | 34.8                     | 26.5                       | 5.8                          |
| Pd-M3                | 5.21      | 1.68               | 1.90                | 1.8                      | 1.1                        | 0.8                          |

<sup>a</sup> Initial rate of hydrogenation,  $r_1$  [mL H<sub>2</sub> (g Pd min)<sup>-1</sup>], in toluene.

TEM images indicated that the particles are more or less uniformly distributed on the external surface sites. The Pd contents of the Pd-M samples were determined indirectly by measuring the absorbance of the supernatant at 600 nm<sup>9</sup> during adsorptive removal of the Pd colloids by montmorillonite. Further, the Pd content was measured directly by inductively coupled plasma atomic emission spectroscopy at 229.7 nm<sup>7</sup> (ICP-AES, Jobin Yvon 24). It was established that the Pd content of the organoclay increases with decreasing solid to liquid ratio and, in particular, with decreasing surfactant concentration. X-Ray diffraction measurements on dry Pd-M samples were made with a Philips 1820 diffractometer (40 kV, 35 mA, Cu-K $\alpha$  radiation) in the diffraction angle range  $2\theta = 1-10^\circ$ . Each material gave a broad  $d_{001}$  reflection, with an interlayer spacing substantially smaller than the mean diameter of the Pd particles as determined by TEM. This finding is consistent with a disordered deposition of layer packets encapsulating the Pd particles (Fig. 1). A regular pattern of intercalation of the Pd species between the layers is unlikely.

Pd-M can be dispersed in organic solvents (ethanol, benzene, acetone, etc.) that are generally used in contact catalytic hydrogenation reactions in the liquid phase. Three Pd-M samples were selected for catalytic test reactions (Table 1). Toluene was used as the reaction medium: this solvent readily wets and swells the organoclay and provides access to the Pd particles for the reactant molecules. The rates of styrene, hex-1-ene and cyclohexene hydrogenation were recorded by using an automated vibration reactor at atmospheric pressure at 303 K. Typically, the reaction vessel contained 1 mL of toluene, 0.1 mL of substrate and a calculated amount of catalyst loaded with 25  $\mu$ g of Pd. A Hewlett Packard GC-MS apparatus (HP 5890; HP 5970) was used for product analysis. Close correlations were found between the catalytic activity and the position of the C=C double bond of the substrate, and the catalytic activity and the degree of dispersion of the Pd particles (Table 1). For a given substrate, the initial rate of hydrogenation,  $r_1$ , increases appreciably with decreasing particle size. For a given Pd-M catalyst,  $r_1$  increases in the sequence styrene > hex-1-ene > cyclohexene. The C=C bond in conjugation with the aromatic ring displays the highest affinity toward the uptake of hydrogen, and the reactivity is higher for the terminal olefin than for the internal one. GC-MS analysis at intermediate stages indicated

that the consecutive (isomerization plus hydrogenation) reactions hex-1-ene  $\rightarrow$  (*trans*- and *cis*-hex-2-ene)  $\rightarrow$  *n*-hexane are superimposed on the hydrogenation reaction hex-1-ene  $\rightarrow$  *n*-hexane. While the simultaneous hydrogenation and isomerization of hex-1-ene were found to be fast processes, as was the hydrogenation of styrene, the rate of conversion to *n*-hexane was moderated by the appearance of the hex-2-ene isomers and the kinetic curve resembled that of cyclohexene (internal olefin).

It is anticipated that the basic principles of the present preparation method can be applied to other systems where the metallic particles are stabilized by ionic surfactants and the solid support is an oppositely charged ion exchanger. For example, if transition metal particles (M) stabilized by anionic surfactants are mixed with positively charged layered double hydroxides (LDH), organophilic M-LDH will be formed, which can be used in contact catalytic reactions in organic solvents. Experimental work on this system is currently being undertaken.

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## Notes and references

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