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Synthesis of monodispersed palladium nanoparticles to study structure sensitivity of solvent-free selective hydrogenation of 2-methyl-3-butyn-2-ol

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Abstract

A novel method for isolation of monodispersed Pd nanoparticles from a reverse microemulsion was developed using hydrocarbon evaporation and methanol-assisted particle purification from a surfactant. Fcc Pd nanoparticles of 6, 8, 11, and 13 nm in diameter were isolated from water/AOT/isooctane mixture and used to study a size effect during solvent-free hydrogenation of 2-methyl-3-butyn-2-ol to 2-methyl-3-buten-2-ol. The initial TOF calculated per mole of surface palladium atoms was duplicated when particle size was increased from 6 to 13 nm but remained constant when accounted per number of specific Pd atoms on Pd(111) facets. Selectivity to olefinic alcohol was not size-dependent, but an increase in particle size decreased the byproduct ratio of dimers to saturated alcohol. Acetylenic alcohol hydrogenation is shown to be a structure-sensitive but size-independent reaction for Pd particles with size of 6–13 nm. The work shows also that the Pd size controlled the reaction rate and the byproduct distribution.

Keywords: Palladium nanoparticle; Hydrogenation; 2-Methyl-3-butyn-2-ol; Microemulsion; Size effect; Structure sensitivity

1. Introduction

Structure sensitivity is of great interest in heterogeneous catalysis. Metal particle morphology and size influence the turnover frequency (TOF) and selectivity due to well-known electronic and geometric effects [1–6]. The relative ratio of surface atom types (vertex, edge, and facet atoms) changes substantially with varying particle size; large particles have mainly large crystal planes with atoms of high coordination number, whereas metal atoms with low coordination numbers constitute small particles [6,7]. The reactions that require a special type of surface atom or an ensemble of surface atoms are strongly affected by the variation in the particle size, for example, Pd-catalyzed hydrogenations or Suzuki reactions [8,9].

The main requirement in studying the structure sensitivity of catalytic reactions is that the particle size should be varied in the absence of other influences [7]. The use of different metal precursors, catalyst supports, or preparation conditions had led to catalysts that are intrinsically different from each other besides in particle size [2,7,10]. Colloid preparation techniques may provide suitable catalysts for such studies [2]. Among these, the reverse microemulsion (ME) technique is of special interest. Reversed (water-in-oil) MEs are thermodynamically stable, optically isotropic dispersions of water and oil consisting of nanosized domains of water in oil, stabilized by an interfacial film of surface active molecules [11]. The water droplets can be considered spatially confined nanoreactors of 5–100 nm for the formation of monodispersed particles with a standard deviation less than ±10%. In this case, monodispersed nanoparticles with controlled sizes are synthesized [12–17]. Through this approach, catalytic metal nanoparticles of different sizes are prepared in the same manner by simply varying the water-to-surfactant ratio in MEs.

ME-derived nanoparticles are widely used in catalytic reactions, mainly as a nanoparticle-containing MEs per se or deposited onto supports. The use of ME itself [18–25] implies the addition of extra components to the catalytic reaction mixture (hydrocarbon, water, surfactant, excess of a metal re-

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ducing agent). This leads to an increase of the reaction volume, and a catalytic reaction may be affected through "medium" and "solubilization" effects [26,27]. Multicomposition of ME also does not allow conducting solvent-free reactions. Several attempts have been made to purify nanoparticles from the ME components. Hydrocarbon evaporation [11,28] or freeze-drying/sublimation [29] did not allow elimination of surfactant molecules, whereas cross-flow ultrafiltration [30] resulted in concentrated nanoparticle suspension. Nanoparticles also may be deposited onto solid support by mixing the ME with a support. This step is usually followed by calcination [12,16,17,21, 31–41]. However, these heterogeneous catalysts can be hardly applied for size effect studies because of specific particle–support interactions [21] and the sintering of the particles at high temperatures during the calcination step.

Here we propose a simple method of preparing monodispersed metal nanoparticles for size effect studies. It implies purification of nanoparticles synthesized in reverse ME and their dispersion in a pure reactant. The method allows us to obtain monodispersed nanoparticles with controlled sizes and to recover solvent/surfactant from MEs.

Hydrogenation of 2-methyl-3-butyn-2-ol (MBY) to 2-methyl-3-buten-2-ol (MBE) was taken as a model reaction because it is important in the synthesis of vitamins and perfumes. The reaction yields a number of byproducts (see Fig. 1) and thus allows the study of the influence of Pd particle size on both activity and selectivity.

Data on size effects in alkyne hydrogenation are rather controversial, although most studies have shown that an increase in metal dispersion decreases TOF [6]. The size effect in alkyne Pd-catalyzed hydrogenation was first reported by Boitiaux et al. [42]. Lower selectivity and more than a 10-fold decrease in TOF were observed when the metal dispersion increased from 20 to 100%. The low activity of small metal particles (with a dispersion of $>20\%$) is usually explained by the strong complexation of the highly unsaturated electron-rich alkyne to the electron-deficient atoms with low coordination numbers on small particles. Moreover, the β-PdH phase disappears with decreasing metal particle size [43]. Some studies have shown this phase to be responsible for the direct alkyne hydrogenation to alkane [5], whereas others did not find this detrimental effect [6,44]. Pd-catalyzed hydrogenation of acetylenic alcohols

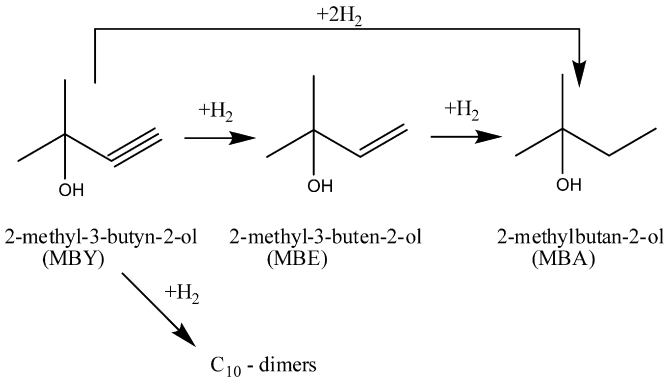

Fig. 1. Reaction pathways for the conversion of 2-methyl-3-butyn-2-ol.

is also known to be a structure-sensitive reaction. However, the size dependence is strongly affected by the catalyst preparation. When Pd nanoparticles were stabilized by poly(vinylpyrrolidone), an increase in the particle size from 5 to 7 nm led to a twofold decrease in TOF and an 8% increase in selectivity during the hydrogenation of 2-butyne-1,4-diol [10]. Pd nanoparticles deposited on activated carbon fiber fabrics exhibited lower TOFs and selectivities at higher dispersions [45,46]. Pd nanoparticles 7.5 nm in size showed sixfold higher activity and 14% higher selectivity in MBY hydrogenation compared with 2.5-nm particles [47,48], but the reactions were carried out with the supported particles, and no tests for the kinetic regime were reported.

No studies on the size effect in hydrogenation of acetylenic alcohols have been reported for particles larger than 7.5 nm. Usually, the structure-sensitive reactions are considered to not reveal size dependence above 5 nm owing to the relatively small variation of the portion of the specific atoms (edge and face) on the nanoparticle surface [7]. Thus, the aim of this work was to elaborate a method for monodispersed Pd nanoparticle preparation and to study size effect in 2-methyl-3-butyn-2-ol hydrogenation using the nonsupported Pd nanoparticles 6–13 nm in size.

2. Experimental

2.1. Materials

Tetraamminepalladium(II) chloride monohydrate (99.99+%; Aldrich), isooctane (2,2,4-trimethylpentane, extra dry, with molecular sieve, water <30 ppm; Acros Organics), fumic hydrochloric acid (purum, p.a.; Fluka), nitric acid (puriss., p.a.; Fluka), hydrazinium hydroxide (for synthesis; Merck), 32% ammonium solution (extra pure; Merck), methanol (for analysis; ReactoLab C.A.), 2-methyl-3-butyn-2-ol (purum, $\geqslant$99%; Fluka), and hydrogen ($\geqslant$99.99% purity; Carbagas, Switzerland) were used as received. AOT (sodium di-2-ethylhexylsulfosuccinate, or docusate sodium salt, purum, $\geqslant$96%; Fluka) was vacuum-dried for 24 h at 333 K directly before use. All glassware was air-dried at 393 K. Demineralized bidistilled water was used throughout this work. Pd black (Aldrich) was reduced at 573 K for 3 h immediately before use.

2.2. Pd nanoparticles: preparation and characterization

A general scheme for preparation of metal nanoparticles for size-effect studies is presented in Fig. 2. Pd nanoparticles were synthesized in reverse ME of water/AOT/isooctane at different water-to-surfactant ratios (3, 4, 5, and 7) as described previously [49]. The aqueous solution of $PdCl_2(NH_3)_4$ (0.05 M) was used as a metal precursor (pH 9, adjusted with ammonia), and the solution of hydrazine hydrate (3 M) as a reducing agent, giving a hydrazine-to-Pd molar ratio of 60 to ensure precursor reduction. The reverse ME containing metal precursor or reducing agent was prepared by injecting the required amounts of the corresponding aqueous solution into an isooctane solution of