



Is it always necessary to remove a metal nanoparticle stabilizer before catalysis?



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ABSTRACT

The answer is no. It depends on the catalyzed reaction and the active metal. For Ru and Ir nanoparticles stabilized by polyvinylpyrrolidone (PVP), their activities in an indan ring opening are not affected by the residual polymer, while CO chemisorption requires complete polymer removal. The in situ cleaning effect of the reaction atmosphere was found negligible. The findings are supported by TEM, XPS, CHN analysis, indan- and CO-TPD, CO chemisorption analyses and catalytic measurement. The necessity for complete polymer removal must be evaluated on a case-by-case basis; in some cases mild catalyst pretreatment is enough.

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1. Introduction

Numerous methods involving colloidal chemistry techniques are well established for the synthesis of metal nanoclusters using protecting agents [1,2]. One can maximize catalytic activity and selectivity through precisely controlled nanoparticle morphology, as opposed to the traditional impregnation methods resulting in broad particle size distributions.

Among the capping agents, poly(vinylpyrrolidone) (PVP) is the most commonly used organic stabilizer for the preparation of various metal nanoparticles [3]. As shown for Pt and Rh nanoparticles of <7 nm size, PVP molecules act as electron donors that cap the surface atoms of the metallic clusters via C=O, C–N and/or CH₂ functional groups [4]; whereas, for larger particles (Pt > 25 nm), charge transfer occurs from the metal to the side chain of PVP [5]. For Pd nanoparticles, PVP molecules chemisorb via oxygen atoms in the pyrrolidone rings on small nanoparticles but with both O and N atoms on the larger particles [6]. Such interactions which are necessary to provide efficient stabilizing action, become a drawback in terms of further catalytic applications, as the chemisorbed species could block active sites and deteriorate catalytic performance. Therefore, removal of these capping agents is critical for efficient catalysis [7], which is a general consensus.

The excess PVP used during synthesis is usually removed by solvent washing before or after deposition on a catalyst support [8]. However, the removal of chemisorbed organic species from a metal surface is challenging. Thermal treatment is the most common method of PVP removal [7]. Free PVP decomposes at 330 °C; the presence of metal nanoparticles may catalyze the combustion of PVP and bring down the decomposition temperature [9]. Rioux et al. concluded that calcination in dilute oxygen (20% O₂/He) is a more effective method than thermal treatment in inert atmosphere for cleaning Pt surfaces. Ethylene hydrogenation activity was maximized with an in situ oxidation–reduction cycle at 200 °C [9]. The nature of the metal being protected has a strong effect on the decomposition behaviour of PVP, as each metal interacts with PVP in a unique way; for example, the PVP–Rh interaction is stronger than that of Pt nanoparticles [4]. The strength of the interaction also depends on the size of nanoparticles due to the different chemisorption modes of the pyrrolidone rings on metal surfaces.

Other strategies such as chemical [8], UV-ozone [10] and plasma treatments [11] are also used for the removal of organic capping agents. For chemical treatments, there may be specific procedures for the removal of each organic capping agent [12]. Blavo et al. reported that triple washings in ethanol/hexane cycles removed the majority of organic species (PVP) from the surface of Pt nanoparticles [13]. Naresh et al. found that ethanol/hexane washing followed by prolonged treatment with tert-butylamine provides a PVP- and Br-free Pd surface [14]. Furthermore, treatments in strong acid or base solutions have also been investigated for the removal of

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polymers [12] and surfactants [15], respectively. However, chemical treatments may lead to metal loss during repetitive washing. Further removal of chemical additives could also lead to a complicated process, which may not be a preferred industrial practice. Vig reviewed that UV-ozone exposure is an effective method of removing a variety of contaminants from surfaces [16]. This method uses UV light with wavelengths of 184.9 nm and 253.7 nm. The 184.9 nm wavelength is absorbed by oxygen and thus generates ozone; the 253.7 nm wavelength is absorbed by most hydrocarbons and ozone, which is responsible for the oxidation of the carbon-containing compounds into carbon dioxide and water [16]. The UV-ozone technique has been applied in catalysis, allowing the decomposition of organic capping agents from metallic nanoparticles at room temperature. Somorjai's group reported that UV-ozone treatment could successfully eliminate TTAB and PVP from the surface of Pt nanoparticles; the absence of the capping agent was confirmed by XPS and DRIFTS [10]. Organic ligands on the surface of nanoparticles can also be removed by nitrogen, hydrogen, and oxygen plasmas through a combination of sputtering, electron-induced reactions, and etching with free radicals [17]. However, plasma techniques require special equipment [11].

Thus, a stabilizer removal is considered necessary for efficient catalysis, and a variety of techniques have been proposed. The general disadvantages of these procedures are that there is at least one additional step in the catalyst preparation, they require extensive energy and/or materials consumption, and they involve possible structural metal nanoparticle changes due to high temperature or chemical etching. Complete PVP removal without any change in nanoparticle morphology is challenging.

In this study, we report examples in which stabilizer removal is not necessary for efficient catalysis. The two reported cases involve monometallic Ru and Ir nanoparticles stabilized by PVP, deposited on alumina, washed with acetone to remove excess PVP and pretreated at different calcination temperatures before the ring opening reaction of indan (benzocyclopentane) at 350 °C in hydrogen atmosphere. These should be considered exceptions but are of high practical value to show that the necessity of stabilizer removal should be evaluated on a case-by-case basis and, as will be shown below, is dependent on the metal nature.

2. Experimental

Ruthenium (III) nitrosyl nitrate and hydrogen hexachloroiridate(IV) hydrate were reduced in ethylene glycol in the presence of PVP (MW: 40,000) as described earlier [18]. The PVP-to-metal molar ratio was 10/1, which is the minimum amount needed to provide highly monodispersed Ru and Ir nanoparticles without agglomeration according to our experience. The PVP-stabilized Ru and Ir nanoparticles were precipitated with acetone and deposited on γ -Al₂O₃ (150 mesh, 58 Å pore size) by wet impregnation. The products obtained were then washed with acetone three-five times to remove solvents, unreduced metal salts, and excess PVP. Finally, the catalysts were dried in a fume hood. Prior to the catalytic reactions, the catalysts were calcined in a furnace at 200 °C, 250 °C and 300 °C for Ru catalysts and at 200 °C, 300 °C and 400 °C for Ir catalysts. The pre-calcined catalysts were then reduced at 375 °C under H₂ flow for 1 h.

X-ray powder diffraction (XRD) measurements were performed to show the crystallinity of the catalysts. XRD patterns were recorded on a Bruker AXS diffractometer with Cu-K α radiation ($\lambda = 5.4059$ Å) at 40 kV and 44 mA. Continuous X-ray scans were carried out from 2θ of 10° to 110° with a step width of 0.05° and a scan speed of 2°/min. Monometallic Ru and Ir nanoparticles for XRD samples were prepared following the experimental procedures described previously [18,19], but without further

deposition on alumina support. The obtained colloidal solutions were concentrated by rotary evaporation of solvents under vacuum; and drying was carried out in a vacuum oven at 60 °C to preserve the nanoparticle structures.

As-prepared nanoparticles and/or supported catalysts were analyzed by transmission electron microscopy (TEM), neutron activation analysis (NAA), and CO chemisorption as described earlier [18,19]. Before the CO chemisorption, the as-deposited catalysts were calcined in a furnace at 200 °C, 250 °C and 300 °C for Ru catalysts, and 200 °C, 300 °C and 400 °C for Ir catalysts. The pre-calcined catalysts were then reduced at 375 °C under H₂ flow for 1 h.

Exemplary CO-TPD and indan-TPD analyses were performed on the deposited Ir catalysts after 400 °C calcination. The pre-calcined Ir catalyst was packed in a tubular reactor (ring opening setup, as described below) and reduced at 375 °C for 1 h in a hydrogen flow. The reduced sample was cooled down to room temperature. Indan was introduced to the pretreated Ir sample by bubbling H₂ (120 mL/min) through an indan bubbler at room temperature. The indan-Ir/ γ -Al₂O₃ sample was then packed in a quartz reactor and heated up under He flow (10 mL/min) from room temperature to 400 °C. TCD signals of indan desorption were recorded as a function of temperature. The experimental procedures for CO-TPD can be found elsewhere [18]. Ir catalyst for TPD experiments were prepared in ethanol/water system, and followed by acetone precipitation and deposition on alumina support, as described earlier [19].

In order to trace PVP residuals and coke formation during indan ring opening, CHN and XPS analyses were performed on a series of Ru/ γ -Al₂O₃ catalysts under different pretreatment conditions, that is, fresh, calcined at 200 °C in air for 1 h, calcined at 200 °C in air for 1 h followed by hydrogen reduction at 375 °C for 1 h, calcined at 250 °C in air for 1 h, and calcined at 250 °C in air for 1 h followed by hydrogen reduction at 375 °C for 1 h, as well as the spent catalysts after ring opening reactions. The fresh Ru catalyst was prepared by rinsing the as-prepared Ru catalyst with acetone five times to remove ethylene glycol and excess PVP. Analytical conditions for CHN and XPS can be found elsewhere [20,21].

For the catalytic ring opening reaction, the procedure described elsewhere was used [18,19]. In this study, the pre-calcined catalyst loading corresponds to 2.2 mg active Ru or 2.0 mg active Ir. Indan was fed into the catalytic system by bubbling 120 mL/min H₂ through indan at a constant bath temperature of 10 °C, giving a indan flow rate of $(4.7 \pm 0.6) \times 10^{-6}$ mol/min. Before the reaction, the catalysts were pretreated in situ in hydrogen flow for 1 h at 375 °C. The catalytic reactions were performed at an internal temperature of 350 °C and atmospheric pressure. Steady state was established after 80 min time on stream; and the reaction rates are reported for the 80- to 200-min time on stream with negligible deactivation.

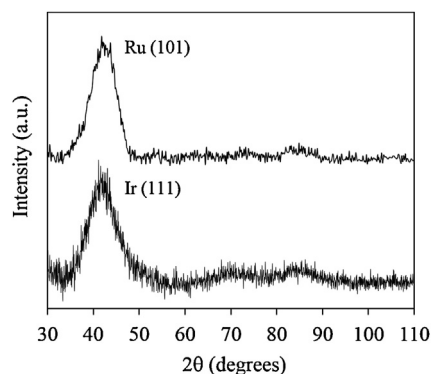


Fig. 1. XRD patterns of as-synthesized PVP-Ru and Ir nanoparticles.

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