

Particle growth and redispersion of monodisperse rhodium nanoparticles supported by porous carbon microspherules during catalyzing vapor phase methanol carbonylation

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Abstract

Monodisperse Rh nanoparticles mounted in the porous carbon microspherules were synthesized through the controlled carbonization of poly(vinylidene chloride) beads containing di- μ -chlorotetracarboxydirhodium as Rh precursors. Rh nanoparticles were formed spontaneously and simultaneously with the evolution of carbon structures from the composite polymeric precursors. X-ray photoelectron spectroscopy (XPS) was used to detect the transformation of high valent Rh species to zero-valent Rh atoms. The dispersion state and particle size were characterized by EPMA and TEM in detail. The as-synthesized Rh nanoparticles were in the monodisperse state with the particle size of about 10 nm. Under catalytic vapor phase methanol carbonylation conditions, particle growth and redispersion take place through a mechanism involving the formation and transportation of Rh-containing volatile molecules. This is evidenced by the comparison of the dispersion state and particle size of the supported Rh nanoparticles before and after catalyzing vapor phase methanol carbonylation. It is clearly demonstrated that the Rh nanoparticles move to the support's surface and grow to about 30 nm after 50-h reaction on stream.

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1. Introduction

Nanometer-sized metal particles exhibit physical and chemical properties that are intermediate between metal atoms and bulk metal [1–3]. The high fraction of the metal atoms exposed at the surface, combined with electron quantum-confinement in very small metal particles, bestows them attractive properties for catalysis [4–9]. The well-defined catalytic metal nanoparticles can be obtained by chemical or electrochemical reduction of higher valent species of the metal, thermal, photochemical or sonochemical decomposition of a zero-valent metal complex and vapor deposition [7]. To prevent agglomeration, the presence of protecting agents is indispensable for the formation of well-dispersed nanoparticles. Many solid materials such as carbon materials [10–12], metal oxides [13], polymers [14] and other mesostructured materials [15] have been considered as efficient supports for catalytic metal nanoparticles. Previously, we

have synthesized a type of nanoporous carbon materials derived from poly(vinylidene chloride) and applied them as supports for metal nanocrystal [16]. Such carbon materials performed excellently as supports for Group VIII metals in vapor phase carbonylation reactions [17]. Under reaction conditions, the metal crystallite stability of the supported metal nanoparticles is an important factor affecting their catalytic activity. Deactivation of the supported catalytic metal nanoparticles mainly results from their particle growth and redispersion, which may involve complex physicochemical processes. There may be three mechanism causing the particle growth and redispersion: (1) metal crystallite migration, (2) atomic migration, and (3) vapor transport [18,19].

Vapor phase methanol carbonylation catalyzed by supported metal has been thoroughly studied and its reaction mechanism is well established [20–24]. Carbon materials were proved to be the best supports. Here, it is used as the model reaction to examine the particle growth and redispersion of supported Rh nanoparticles under specific reaction conditions. Metal nanoparticles supported by activated carbons are prepared by the wet impregnation of the supports in the metal precursor solution, followed by reduction of metal precursors to zero-valent metal

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[25–28]. Because of the drawbacks of the wet impregnation and the poor microstructure homogeneity of the supports, it is difficult to prepare monodisperse metal nanoparticles with uniform particle size distribution. Monodisperse Rh nanoparticles are formed spontaneously and simultaneously with the development of carbon porous microspherules from poly(vinylidene chloride) precursors. Di- μ -chlorotetracarboxydirhodium is the precursor of Rh nanoparticles, which has been immobilized in the poly(vinylidene chloride) precursors during the incipient preparation. Dai and co-workers have reported spontaneous formation of Au and Pt nanoparticles on single-walled nanotubes in corresponding metal ion solutions [29]. The spontaneous formation of Au and Pt nanoparticles is due to direct redox reaction between nanotubes and metal ions. In this case, the formation of Rh nanoparticles is attributed to reducing reaction between small six-membered carbon segments with Rh precursors.

2. Experimental

2.1. Synthesis of nanoporous silica–carbon hybrid spherules

Cetyltrimethylammonium chloride (CTAC) of 0.05 mol was dissolved in 150 ml deionized water in a 250 ml glass flask with magnetic stirrer in water bath at 50 °C. Tetraethoxysilane was added drop by drop under vigorous agitation. When the mixture became turbid, cool it to 5 °C in ice-water bath. Then 15 ml purified vinylidene chloride, with the initiator ABVN (azobisisobutyl-

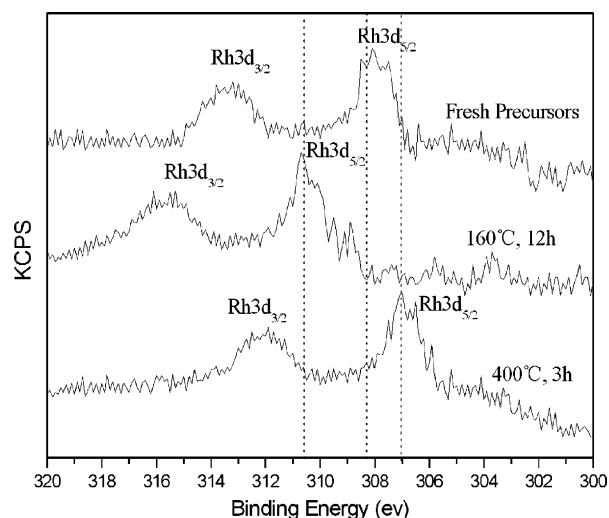


Fig. 1. XPS spectra analysis of rhodium oxidation states in different carbonization periods: before treatment; 160 °C, 12 h in argon stream; 400 °C, 3 h in argon stream.

valeronitrile, 1% mole ratio) and di- μ -chlorotetracarboxydirhodium (1.5 wt%) dissolved, was added dropwise carefully. The mixture was kept at 45 °C for 12 h under agitation of 250–300 rpm. The resulting hybrid polymeric spherules were washed by hot water to remove silica and dried at room temperature. The resulting materials were put into a quartz tube and carbonized at 160 °C for 12 h, and heated to 200 °C gradually in 3 h. From 200 to 400 °C, the treatment tempera-

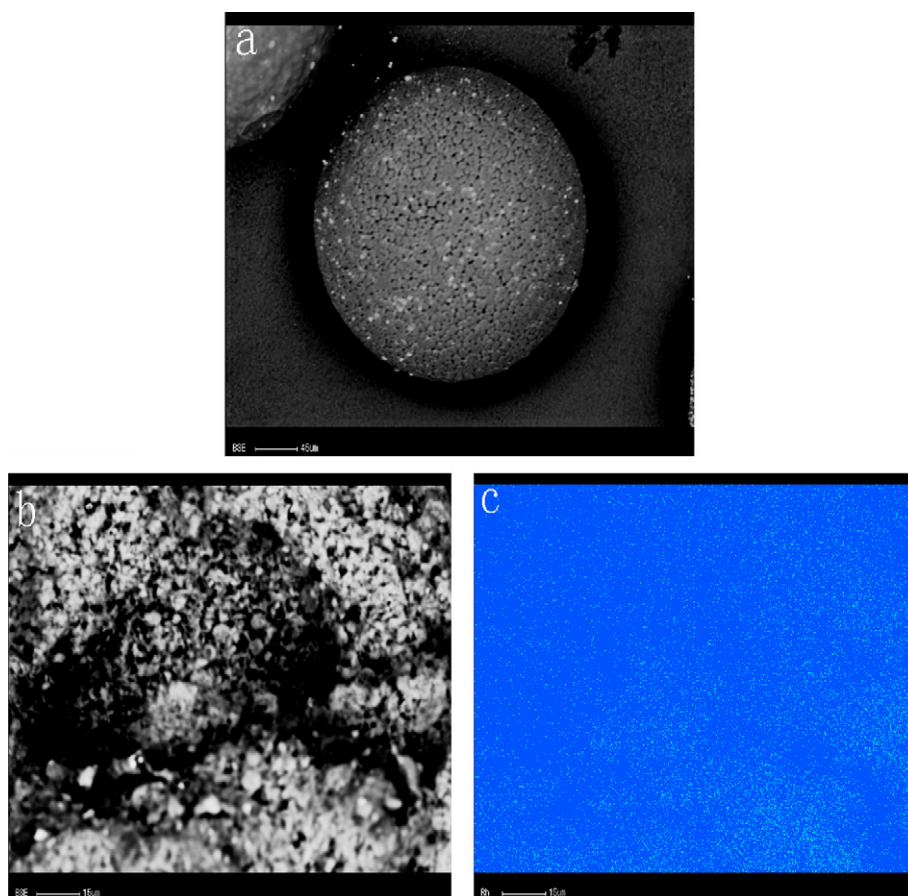


Fig. 2. EMPA images of a single carbon microspherule. (a) The chosen silica–carbon spherule; (b) the morphological structure of a local surface of the spherule depicted in (a); (c) Rh nanoparticles dispersion over the surface depicted in (b).

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