Hydrogenation of nitro-compounds over rhodium catalysts supported on poly[acrylic acid]/Al$_2$O$_3$ composites

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ABSTRACT

In this report, poly[acrylic acid] gels containing Al$_2$O$_3$ were prepared by simultaneous free-radical polymerization and sol–gel chemistry using different amounts of 3-(trimethoxysilyl)propyl methacrylate (TMPM) as a compatibilizer. The hybrid materials were used as supports for a rhodium catalyst in the chemoselective hydrogenation of 3-substituted aromatic nitro-compounds. The supported rhodium catalyst was prepared by an ion-exchange process. *In situ* H$_2$ flux was used to produce active species of the catalysts. The resulting materials were characterized by infrared spectroscopy, thermogravimetric analysis, solid-state ^{29}Si and ^{13}C NMR, X-ray diffraction, transmission/scanning electron microscopy, and X-ray photoelectron spectroscopy. All materials exhibited simultaneous interpenetrating hybrid network structures (SIHNs). The morphologies and physicochemical properties depended on the amount of TMPM used. The catalysts were found to be effective for the reduction of nitrobenzene in ethanol at room temperature and a hydrogen pressure of 20 atm. The most active and selective catalyst was used in the hydrogenation of different 3-substituted aromatic nitro-compounds. The hydrogenation reactions displayed high conversion levels and promoted exclusive –NO$_2$ group reduction, resulting in the sole formation of the corresponding amino-compound, with the exception of 1,3-dinitrobenzene, in which over-hydrogenation was detected. The presence of electron-donating/electron-withdrawing substituents at the 3-position resulted in different rates of –NO$_2$ group hydrogenation. This effect was quantified in terms of the Hammett relationship, in which the catalyst displayed a linear correlation between the substituent constant (σ_i) and the hydrogenation rate, with the exception of –OH, –NH$_2$, and –OCH$_3$ groups. One explanation for this behavior is a proposed support-substrate hydrogen bond interaction during the catalytic reaction.

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1. Introduction

Metal nanoparticles continue to attract interest in different research areas due to their different physical and chemical properties when compared to bulk metals [1,2]. The surface reactivity of metal nanoparticles results in their potential for application in a variety of fields, such as medicine [3], electronics and optics [4] and catalysis [5]. Particle growth or aggregation leads to a loss of the nano-scale size and the related important properties [2,5].

Essential methods have been developed in response to this challenge, for example: application of polymeric stabilizing agents [3,6,7], electrochemical deposition [4], template growth techniques [8], and functionalized support methods [9–13]. Hybrid polymeric-inorganic materials are a good alternative to pure nanoparticles because these materials can exhibit greater stabilities when compared to their pure counterparts [14,15]. Of particular interest for our work are simultaneous interpenetrating hybrid networks (SIHN). In this case, the material is produced by a sol–gel process in combination with free-radical polymerization of the organic phase [16–18]. This approach allows *in-situ* formation of the inorganic network and thus the homogeneous incorporation of polymers that normally would be immiscible. The use of organic-inorganic coupling agents makes it possible to enhance the compatibility of the two components. The coupling agents generally have hydrolysable groups that participate in the sol–gel chemistry and organic-functionalized ends for incorporation into the organic polymer

[19–21]. Optimizing the mixing of the networks in SIHN materials results in the most homogeneous functional materials. Such systems could result in supported metal nanoparticles that would be completely insoluble in aqueous or organic solvents for use as heterogeneous catalysts.

The focus of this study was on rhodium metal nanoparticles because they are especially active in a supported form for a variety of catalytic applications, including CO hydrogenation [22], hydrogen production [23,24] and chemoselective hydrogenations [9,11,12,25]. Generating such nano-sized particles on a hybrid material is of scientific interest, especially if it results in particles or dispersions with novel properties. In previous reports involving colloidal Rh particles, polymers were used as stabilizers. A variety of well-known polymers are commonly used as protecting agents, such as poly[vinylpyrrolidone] (PVP) [6,26], poly[vinyl alcohol] (PVA) [6] and poly[acrylic acid] (PAA) [6,11]. However, their efficiency and behaviors as protecting agents in mixed-media colloids are hitherto unknown. Therefore, it is important to study how hybrid materials perform as protecting agents for rhodium nanoparticle support.

Aromatic amines are important starting materials and intermediates for the manufacture of a great variety of chemicals. They are generally synthesized by the chemical reduction of nitroarenes [27,28]. Although a variety of methods have been well documented for this purpose, some of these protocols have drawbacks, such as long reaction times, the use of toxic and expensive catalysts, the requirement of carcinogenic solvents, and limited reusability of catalysts [29,30]. The selective reduction of nitro-groups in organic compounds containing other reducible functional groups is a very challenging task in organic synthesis. In addition, the reduction of aromatic nitro-compounds is often associated with the formation of side products, including hydroxylamines, hydrazines, and azoarenes, because the reaction can stop at an intermediate stage [29,30]. Therefore, easily separable, chemoselective, and effective catalysts for the reduction of organic compounds are highly desirable.

In the present work, the hydrogenation of nitrobenzene (NB) using SIHN prepared from PAA/Al$_2$O$_3$ with different amounts of 3-(trimethoxysilyl)propyl methacrylate (TMPM) as a coupling agent was investigated. Furthermore, the catalytic reduction of a series of 3-substituted aromatic nitro-compounds was investigated and the catalytic data were subjected to Hammett treatment.

2. Experimental

2.1. Materials

TMPM (98%), ammonium persulfate (APS; >98%), anhydrous 2-butanol (>99.5%), acrylic acid (AA; anhydrous, containing 180–200 ppm of the monomethyl ether of hydroquinone as an inhibitor, 99%), rhodium(III) chloride hydrate (RhCl$_3$·xH$_2$O; 99.98% trace metal basis), 1-chloro-3-nitrobenzene (NB-Cl; 98%), 1,3-dinitrobenzene (NB-NO$_2$; 97%), nitrobenzene (NB), and 1-cyano-3-nitrobenzene (NB-CN) were obtained from Sigma–Aldrich® and Fluka®. Aluminum tri-sec-butoxide (TSBAl; 97%), acetylacetone (acac), absolute ethanol, 1-methyl-3-nitrobenzene (NB-CH$_3$),1-methoxy-3-nitrobenzene (NB-OCH$_3$) and 3-nitrophenol (NB-OH) were supplied by Merck®. AA was distilled in the presence of terbutylcatechol at reduced pressure prior to use. All other chemicals were used without further purification. All air-sensitive reactions were performed in a polymerization flask using an inert N$_2$ atmosphere. H$_2$ (99.99%) was supplied by AGA® – Chile.

2.2. SIHN synthesis

TSBAl (0.03 mol) was dissolved in anhydrous 2-butanol and heated at 353 K. Subsequently, 0.04 mol of acac, 0.02 mol of AA, and 0.002 mol of APS were added to the reaction mixture. TMPM was added in different mole ratios of TMPM/(TMPM + TSBAl): 0, 0.5, 0.25 and 0.125. The reaction was carried out at 353 K under an N$_2$ atmosphere with continuous stirring. Once the gel point was reached, the solution was cooled to room temperature and deionized water (10 mL) was added to the gel and mixed mechanically. The mixture was left for 8 h at room temperature and later dried in a vacuum oven at 353 K until a fine white powder was obtained. All composites were washed 3 times with deionized water with magnetic stirring for 4 h and dried at 373 K. All materials obtained were labeled as PAA/Al$_2$O$_3$−TMPM(x), where x corresponds to the TMPM/(TMPM + TSBAl) mole ratio.

2.3. Synthesis of catalysts

The catalysts (1.0 g) were prepared at 0.5 wt% Rh using PAA/Al$_2$O$_3$-TMPM(x) as the support. The methodology is analogous to that reported by Torres et al. [31]. The appropriate amount of support (dry hybrid material) was placed in a round-bottom flask containing 50 mL of water. Prior to the introduction of the metal precursor, a stoichiometric quantity of NaOH 0.5 mol L^{-1} (OH$^-$/Rh mole ratio = 3) was also added to the support suspension to obtain a final pH 11. A solution containing the required amount of RhCl$_3$xH$_2$O was added to obtain the desired metal loading, and the system was placed in a thermoregulated bath for 12 h at 318 K with magnetic stirring at 300 rpm. After the sorption of the Rh solution, the temperature was raised to reflux with constant stirring until the color changed from orange to black. The obtained solid was filtered and washed with deionized water until a constant conductivity was obtained. Finally, the catalysts were dried in a vacuum oven at 373 K for 1 h and stored in a desiccator under an N$_2$ atmosphere prior to the catalytic tests. These were labeled as 0.5%Rh-PAA/Al$_2$O$_3$-TMPM(x).

2.4. Characterization

The metal content was quantitatively monitored in triplicate by digesting 0.05 g of loaded composite in 10 mL of concentrated nitric/hydrochloric (1:3) acid solution using microwave-assisted digestion. After the reduction process, the metal loading was measured by inductively coupled plasma mass spectrometry (ICP-MS) on a PerkinElmer Elas 6000S instrument. The structural characteristics of the composites and catalysts were determined by XRD (RigakuD/max-2500 diffractometer with Cu K$_\alpha$ radiation at 40 kV and 100 mA). Spectroscopic analyses were performed using FT-IR spectroscopy (Nicolet 400D in KBr matrix in the range of 4000–400/cm) and solid-state ^{13}C and ^{29}Si CP-MAS NMR spectra were recorded at 100.6 MHz and 79.49 MHz, respectively, using a Bruker AV 400 WB spectrometer. Thermogravimetric analysis was performed with a thermal analyzer (TGA (Netzsch STA 409 PC/PG [STA])) over a temperature range of 300–873 K and a heating rate of 10 K min^{-1} in an N$_2$ atmosphere. N$_2$-BET surface areas and pore volumes were determined on a Micromeritics ASAP 2010 apparatus at 77 K. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The pore size distributions were obtained from the adsorption and desorption branch of the nitrogen isotherms by the Barrett–Joyner–Halenda (BJH) method. Morphological and chemical analyses were performed via SEM-EDS (JEOL JSM-6380), the samples were scanned by a secondary electron scanner, and surface content was analyzed by energy-dispersive X-ray spectroscopy (EDS) using the standards for quantification: C (CaCO$_3$), Si and O (SiO$_2$), Al (Al$_2$O$_3$), S (FeS$_2$).